PRESSURE DEPENDENCE OF RAMAN PHONONS IN METALS

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Phonon spectra in metals have been studied by Raman spectroscopy up to 50 GPa. Investigated metals are Mg, Zn, Gd, Sn *and metallic high pressure phases of* Si *and* Ge. *The pressure response of observed phonon modes includes normal behaviour (positive pressure shift), as well as anomalies like soft mode behaviour and splitting of degenerate modes. Available theoretical predictions are compared with the present experimental results.*

Introduction. Phonons in metals are usually investigated by inelastic neutron scattering. This method is not convenient for investigations at higher pressures due to the need of rather large single crystals. Another method to study phonon spectra in metals is Raman scattering, as was shown for the first time by Feldman et al. [1]. In metallic systems the penetration depth of light extends up to a few hundred angstroms only. As a result, the intensities of Raman lines from metals are generally small, making the experiments difficult. Multichannel detectors have significantly improved measurement sensitivity [2]. The validity of this method for high

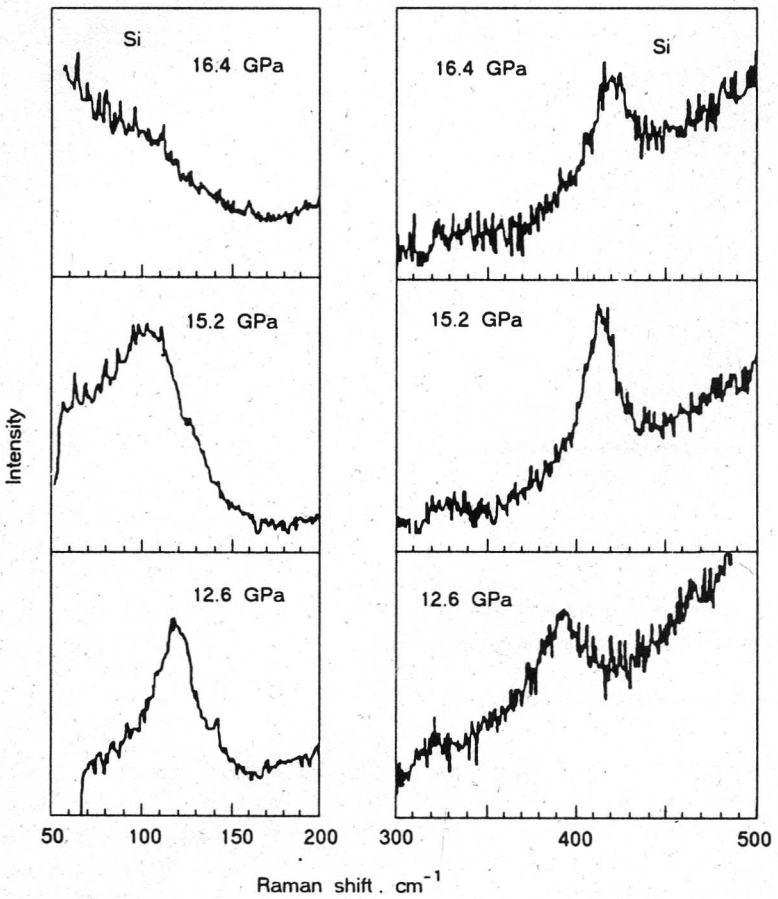

Fig. 1. Raman spectra of Si in the β-tin phase: left hand, LO mode; right hand, TO mode

pressure studies using a diamond anvil cell will be demonstrated in the present paper, which reports recent results on Zn, Mg, Gd and Sn, as well as on metallic high pressures phases of Si and Ge.

Experimental. Polycrystalline or powdered samples were loaded into a gasketed diamond anvil cell of the Syassen-Holzapfel type [3], together with ruby splinters for pressure determination [4] and a 4:1 methanol:ethanol mixture as pressure transmitting medium. Raman spectra were excited by the 488 or 514 nm line of an Ar^+ laser or by the 647 nm line of a Kr^+ laser. Backscattered light was analyzed using a triple spectrograph (Spex, model 1877) equipped with a liquid nitrogen cooled CCD multichannel detector (Photometrics Ltd.).

Results and discussion. The β-tin structure with two atoms per primitive unit cell exhibits three optical branches at the Γ-point of the Brillouin zone. The optical branches consist of one LO mode (Γ_3 in the irreducible representation) and a doubly degenerate TO mode (Γ_5) at higher frequencies [5,6].

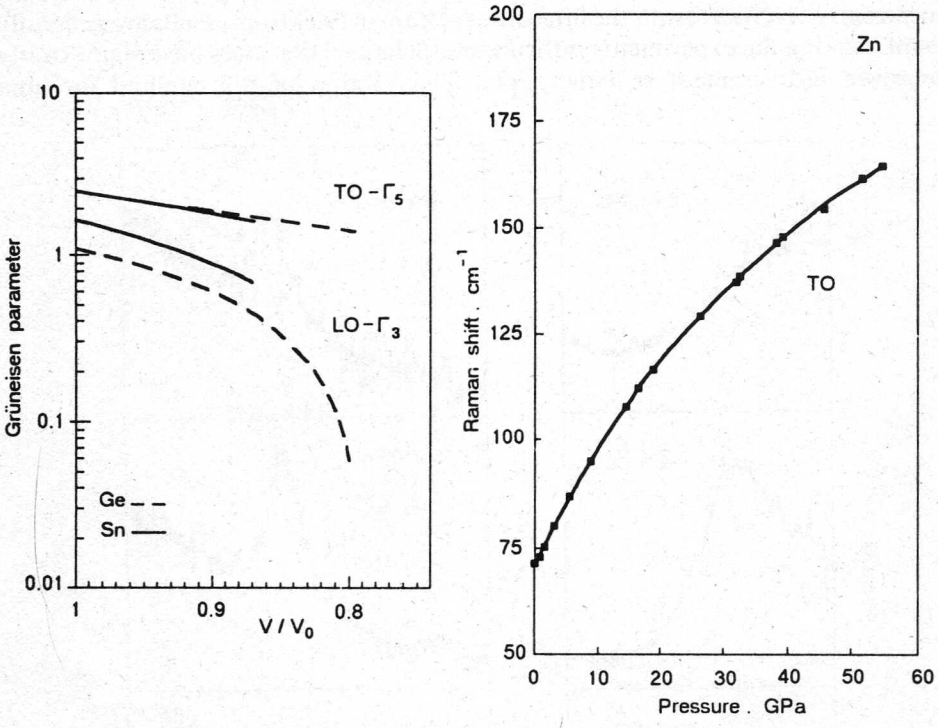

Fig. 2. Mode Grüneisen parameters of Sn and Ge in the β-tin phase. The reference volume V_0 of Ge corresponds to the volume at 10 GPa in the β-tin structure

Fig. 3. Pressure dependence of the TO mode in Zn

In Fig. 1 Raman spectra of Si in the β-tin phase are shown at various pressures [7]. The TO mode shifts to higher frequencies with increasing pressure, whereas the LO mode decreases in frequency and becomes very broad. In the spectrum at 16.4 GPa the intensity of the LO mode has nearly vanished. The LO mode corresponds to displacements of the tetragonal sublattices in c-direction, and the freezing-in of this mode is associated with the transition into the primitive hexagonal (ph) structure [8], which occurs at 13–16 GPa [9,10].

Similar results were obtained also for Ge in the β-tin phase [7], which is stable up to 75 GPa, where a transition into ph occurs [11]. As in the case of Si, the TO mode shifts to higher frequencies with increasing pressure. In contrast, the LO mode frequency initially increases slightly with pressure and reaches a maximum around 50 GPa. At higher pressures, on approaching the transition into the ph structure, a negative pressure shift, as observed for Si, is expected. This behaviour can be seen more clearly from the volume dependence of the mode Grüneisen parameter [12], which decreases from 1 at 10 GPa to nearly 0 at 50 GPa (see Fig. 2). For comparison the corresponding mode Grüneisen parameters of β-Sn [12] are also shown in Fig. 2. For β-Sn softening of the LO mode (negative Grüneisen parameter) is not observed: Sn transforms from β-tin to bct at 9.5 GPa [18], and for this transition softening of some zone boundary modes (TO,TA) is

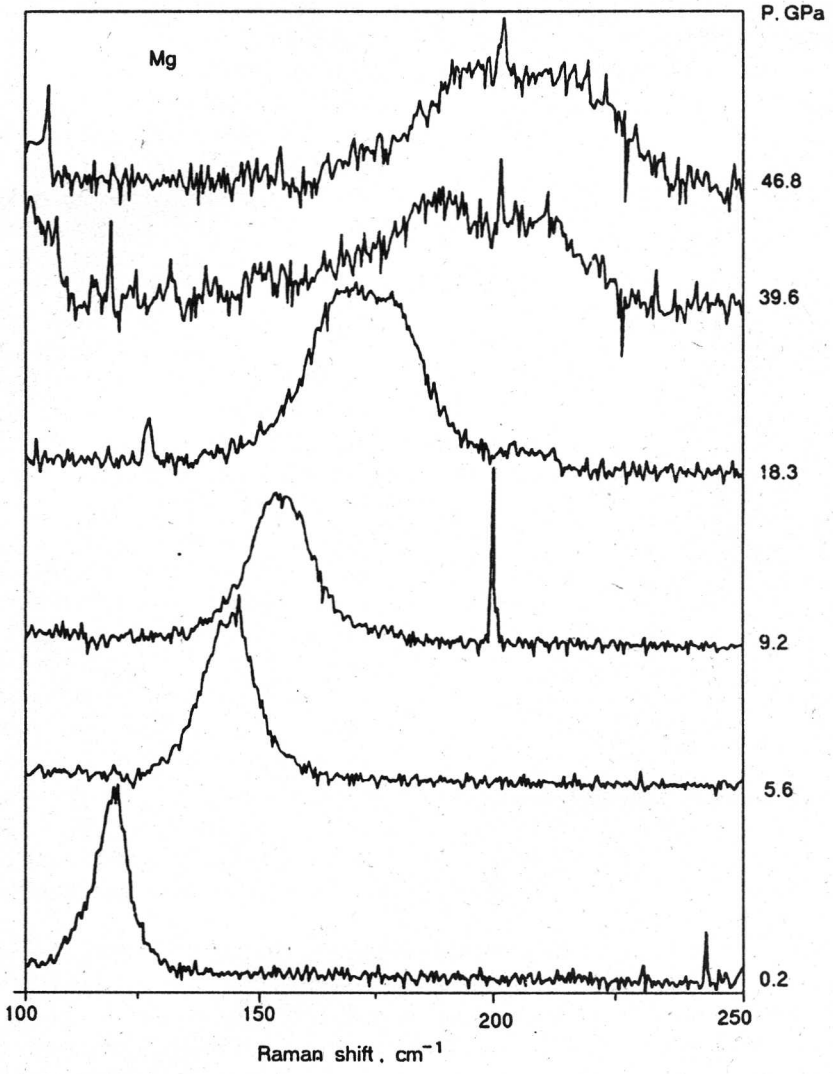

Fig. 4. Raman spectra of Mg at various pressures

expected [13], instead of the zone center LO mode, which is associated with the transition from β-tin to ph in Si and Ge.

Theoretical results for the LO mode of Si in the β-tin phase, obtained with the *ab initio* pseudopotential method [8,14], agree within 10–20% with the present experimental results. For β-Sn agreement within 3 cm^{-1} has been obtained by Christensen [15] using the LMTO-method.

In the hcp strusture (2 atoms per primitive unit cell) the doubly degenerate TO mode (Γ_6^-) is Raman active. In the case of Zn this mode shows a positive frequency shift in the investigated pressure range (see Fig. 3). A similar pressure response is observed also for the TO mode in Mg. However, this band drastically broadens with increasing pressure, and in the higher pressure range splitting of the band is observed (Fig. 4). At 50 GPa the separation of the 2 components has increased to 20 cm^{-1}. Possible reasons may be lifting of the degeneracy due to pressure inhomogeneities or slight structural modifications or loss of translational symmetry which removes the restriction to $\vec{k} = 0$. These results indicate that in hcp metals a positive pressure shift of the TO mode frequency is the "normal" behaviour. However, in the case of Gd the TO mode shifts to lower frequencies with increasing pressure (Fig. 5). Gd transforms from hcp to Sm-type at 1.5–10 GPa [16]. Both structures differ in the stacking sequence of the hexagonal layer (hcp: ABAB..., Sm-type: ABABCBCACA...), and to obtain Sm-type from hcp it is necessary to shift some of the hexagonal layers into the corresponding *A*, *B* or *C* positions. Since the TO phonon corresponds to displacements of the two hcp sublattices against each other in the basal plane, softening of this mode is associated with the phase transition.

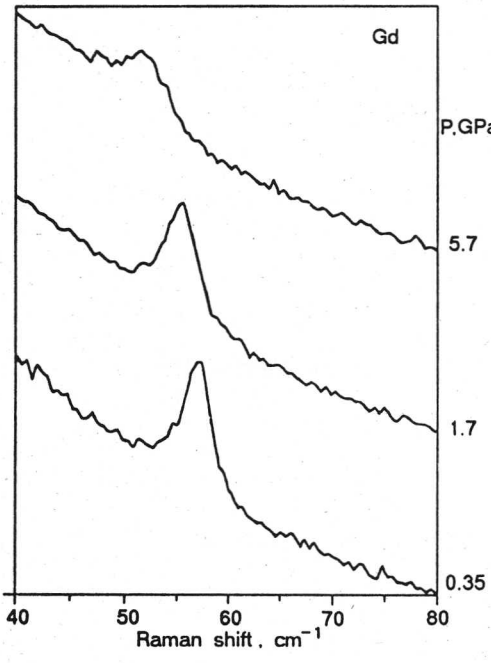

Fig. 5. Raman spectra of Gd in the hcp phase at various pressures

For the hcp metals theoretical investigation are available for Mg [17]. The generalized pseudopotential theory (GPT) was used to predict the pressure shift of the TO mode. Agreement with 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 values of the 2 components.

Conclusion. In summary, the present results show that Raman spectroscopy is a powerful tool for the investigation of phonons in metals up to very high pressures, especially with respect to phase transitions and soft modes involved in them, including systems which metallize only at higher pressures. In addition, such data provide a stringent test on various theoretical methods in their ability to predict dynamical properties.

1. *D. W. Feldman, J. H. Parker, Jr., and M. Ashkin*, Phys. Rev. Lett. **21**, 607 (1968).
2. *J. E. Pemberton, R. L. Sobocinski, M. A. Bryant, and D. A. Carter*, Spectrosc. Int. **2**, 26 (1990).
3. *G. Huber, K. Syassen, and W. B. Holzapfel*, Phys. Rev. **B15**, 5123 (1977).
4. *G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman*, J. Appl. Phys. **46**, 2274 (1975).
5. *S. H. Chen*, Phys. Rev. **163**, 532 (1967).
6. *J. M. Rowe*, Phys. Rev. **163**, 547 (1967).
7. *H. Olijnyk*, Phys. Rev. Lett. **68**, 2232 (1992).
8. *K. J. Chang and M. L. Cohen*, Phys. Rev. **B31**, 7819 (1985).
9. *H .Olijnyk, S. K. Sikka, and W. B. Holzapfel*, Phys. Lett. **103 A**, 137, (1984).
10. *J. Z. Hu and I. L. Spain*, Sol. State Comm. **51**, 263 (1984).
11. *Y. K. Vohra, K. E. Brister, S. Desgreniers, A. L. Ruoff, K. J. Chang, and M. L. Cohen*, Phys. Rev. Lett. **56**, 1944 (1986).
12. *H. Olijnyk*, Phys. Rev. **B46**, 6589 (1992).
13. *M. J. P. Musgrave*, J. Phys. Chem. Solids **24**, 557 (1963).
14. *R. J. Needs and R. M. Martin*, Phys. Rev. **B30**, 5390 (1984).
15. *N. E. Christensen*, preprint (1992).
16. *T. Krüger, B. Merkau, W. A. Grosshans, and W. B. Holzapfel*, High Press Res. **2**, 193 (1990), and references therein.
17. *J. D. Althoff, P. B. Allen, R. M. Wentzcovitch, and J. A. Moriarty*, preprint (1992).
18. *H. Olijnyk and W. B. Holzapfel*, J. Phys. (Paris) Colloqu. **45**, Suppl. 11, C8–153 (1984).