RAMAN SPECTRA OF METASTABLE Ge

Helmut Olijnyk

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 101252, W-8580 Bayreuth, FRG

Raman spectra of Ge, *pressurized into the β-tin phase, were measured during unloading between 8.8 and 0.4 GPa, using red light excitation. The spectral features are different from those reported ealier for metastable* Ge *phases. The large number of observed bands (at least 13) may suggest an assignment to the tetragonal ST12-structure, for which 21 Raman active modes are predicted. There is evidence that this phase is not stable under green light irradiation.*

Introduction. Metastable phases of Ge can be prepared by depressurizing Ge from its metallic high pressure phase. The crystal structures of these phases, determined at ambient pressure, are the tetragonal ST12–($Z = 12$) [1,2] and the cubic BC8-structure ($Z = 8$) [3]. Another allotropic modification, allo-Ge (orthorhombic, $Z = 128$), has been prepared by chemical processes [4]. Phase transitions from this phase into hexagonal 4H-Ge and then into the cubic diamond structure were observed at 420 K and 770 K, respectively [4].

Raman spectra at ambient pressure for ST12-Ge were reported by Kobliska et al. [5] and for allo-Ge and 4H-Ge by Lopez-Cruz and Cardona [6]. Raman spectra during pressure release from the metallic phase were studied by Hanfland [7] and Hanfland and Syassen [8], who observed two phases with different spectral features. They found that the spectra of the first phase are strikingly similar to that of Ge in the BC8-strusture in stead of to the ST12-structure, which should be stable in this pressure range [9]. Below about 5 GPa a phase transition into the hexagonal diamond structure was observed. Mernagh and Liu [10] observed one strong band, and Asaumi and Minomura [16] observed two bands in Ge samples recovered from the metallic phase. The frequencies of observed Raman bands as well as available pressure coefficients from these studies are summarized in the upper part of Table.

For ST12-Ge with 12 atoms per primitive unit cell a large number of Raman bands (21) should be observed [5]. However, only two peaks have been identified [5], and puzzling enough, the frequency values agree with frequencies reported by Hanfland [7] and Hanfland and Syassen [8] for the "BC8"-phase. Therefore, the Raman spectroscopic characterization of ST12-Ge is still an open question.

Experimental. In the present study Ge powder was pressurized into the metallic phase using a gasketed diamond anvil cell of the Syassen-Holzapfel type [11] and 4:1 methanol:ethanol as pressure transmitting medium. Raman spectra were recorded during unloading and reloading. The spectra were excited by the 647 nm line of a Kr^+ laser. Backscattered light was analyzed using a triple spectograph (Spex, model 1877) equipped with a liquid nitrogen cooled CCD multichannel detector (Photometrics Ltd.). Pressure was determined by the ruby fluorescence method [12].

Rezults and discussion. Raman spectra, which were recorded between 8.8 and 0.4 GPa, are shown in Figure. They are very different from those reported earlier. At least 13 bands can be clearly distinguished. At ambient pressure some frequencies agree with frequencies given by Kobliska et al. [5] and Hanfland [7] and Hanfland and Syassen [8], however the pressure coefficients deviate considerably (see Table).

The large number of observed Raman bands suggests an assignment to the ST12-structure, for which 21 modes should be Raman active. This assignment is given further support by a comparison with theoretical predictions for ST12-Ge by

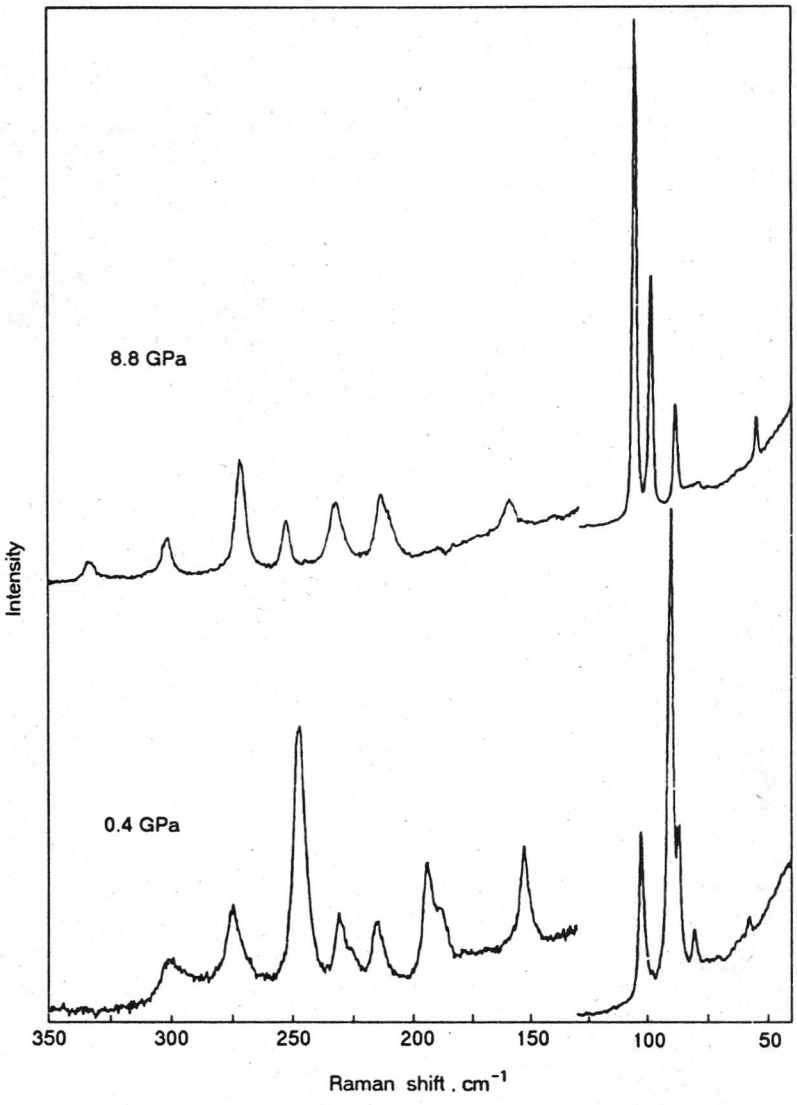

Fig. Raman spectra of metastable Ge at different pressure

Winer and Wooten [13]. Though the calculated frequencies are generally higher than the observed ones, the frequency distribution of calculated and experimental frequencies is very similar. On the other hand, theoretical investigations propose the existence of additional metastable phases for Ge [14]. For Si, which behaves very similar to Ge, two metastable phases with tetragonal symmetry different from the ST12-structure have been reported by Zhao et al. [15]. Taking into account these results the above assignment should be considered as a tentative one.

On total release of pressure these spectral features disappeared, and only a relatively broad feature around 293 cm^{-1} was observed. On reloading, the former spectrum reappeared. Irradiation with the 514 nm line of an Ar^+ laser at 6.5 GPa resulted in the formation of the cubic diamond and another not yet identified phase.

Table. Observed Raman phonons of metastable Ge phases. ν_0 are the phonon frequencies at ambient pressure and $d\nu_0/dp$ the linear pressure coefficients.

ν_0 [cm^{-1}]	$d\nu_0/dp$ [cm^{-1}/GPa]	Structural assignment	Reference
246 273	– –	ST12	Kobliska et al. [5]
110 130 160 225 265 280		allo-Ge	Lopez-Cruz & Cardona [6]
287		4H-Ge	
85 95 201 223 246 274 290	0.0 0.0 1.1 1.0 1.6 3.2 2.9	BC8 ?	Hanfland [7]
286 296	4.2 4.1	hexagonal diamond	
292		ST12	Mernagh & Liu [10]
250 298		?	Asaumi & Minomura [16]
55 78 85 88.5 100 150.5 186 192 213 228 245 274 300	-0.3 0.0 0.2 1.0 0.3 0.8 2.5 2.2 2.0 2.6 2.8 3.1 3.6	ST12 ?	[a] present study

[a] The frequencies and the pressure coefficients were obtained by linear least square filts.

This observation may explain why the spectral features, observed in the present study, have not been observed in the previous Raman studies, which all used the 514 or 488 nm line for exciting the Raman spectra.

1. *F. P. Bundy and J. S. Kasper*, Science 139, 340 (1960).
2. *J. S. Kasper and S. M. Richards*, Acta Cryst. 17, 752 (1964).
3. *C. H. Bates, F. Dachille and R. Roy*, Science 147, 860 (1965).
4. *A. Grüttner, R. Nesper and H. G. v. Schnering*, Angew. Chem. 94, 993 (1982).
5. *R. J. Kobliska, S. A. Solin, M. Selders, R. K. Chang, R. Alben, M. F. Thorpe, and D. Weaire*, Phys. Rev. Lett. 29, 725 (1972).
6. *E. Lopez-Cruz and M. Cardona*, Sol. St. Comm. 45, 787 (1983).
7. *M. Hanfland, Ph. D. Thesis*, University of Düsseldorf (1989).
8. *M. Hanfland and K. Syassen*, High Press. Res. 3, 242 (1990).
9. *C. S. Menoni, J. Z. Hu and I. L. Spain*, Phys. Rev. B34, 362 (1986).
10. *T. P. Mernagh and L. G. Liu*, J. Phys. Chem. Solids 52, 507 (1991).
11. *G. Huber, K. Syassen and W. B. Holzapfel*, Phys. Rev. B15, 5123 (1977).
12. *G. J. Piermarini, S. Block, J. D. Barnett and R. A. Forman*, J. Appl. Phys. 46, 2774 (1975).
13. *K. Winer and F. Wooten*, Phys. stat. sol. (b) 136, 519 (1986).
14. *D. J. Chadi*, Phys. Rev. B32, 6485 (1985).
15. *Y.-X. Zhao, F. Buehler*, J. S. Sites and I. L. Spain, Sol. St. Comm. 59, 679 (1986).
16. *K. Asaumi and S. Minomura*, J. Phys. Soc. Japan 45, 1061 (1978).