ELSEVIER

Journal of Alloys and Compounds 224 (1995) 212–216

Journal of ALLOYS AND COMPOUNDS

# Structural phase transition of GaTe at high pressure

U. Schwarz [a], K. Syassen [a], R. Kniep [b]

[a] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

[b] *Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, Anorganische Chemie II, Hochschulstrasse 10, D-64289 Darmstadt, Germany*

Received 15 December 1994; in final form 18 January 1995

## Abstract

We have investigated structural stability and electronic properties of the layered semiconductor GaTe under hydrostatic pressure by X-ray powder diffraction and optical reflectivity measurements in a diamond anvil cell. The monoclinic low-pressure modification undergoes a first-order phase transition at 10(1) GPa into a high-pressure polymorph of the NaCl type structure. Thermal annealing at 475 K and 12 GPa for 12 h turned out to be essential for obtaining well-crystallized samples of the high-pressure phase. The reconstructive structural change is accompanied by a semiconductor-to-metal transition. The cubic modification is metastable with decreasing pressures down to 3 GPa and transforms to an amorphous phase at lower pressures.

*Keywords:* Structural phase transitions; High pressures; Gallium–gallium bonds; Metastable phase

## 1. Introduction

The monoclinic low-pressure modification [1,2] of GaTe is a semiconductor with a band gap of 1.65 eV [3] at ambient conditions. The layered crystal structure is isotypic to SiAs [4] and GeAs [5]. A schematic view of the crystal structure of GaTe (SG no. 12, non-conventional monoclinic setting: unique axis *c*, cell choice 2, B2/m) is shown in Fig. 1. The layers consist of condensed rings with six-membered $Ga_4Te_2$ units and five-membered $Ga_3Te_2$ cycles. The Ga atoms form $Ga_2$ groups which interconnect adjacent five-membered rings and also form two opposite edges of the six-membered rings. Within the layers tellurium is surrounded by three Ga atoms, gallium is tetrahedrally coordinated by three Te atoms and one gallium atom ($d$(Ga–Ga): 2.431(2) Å and 2.437(3) Å; $d$(Ga–Te) between 2.638(2) Å and 2.686(2) Å [1]). Te–Te contacts between adjacent layers (3.913(1) Å, 4.001(1) Å, and 4.186 Å [1]) are shorter than twice the van der Waals radius of tellurium (4.42 Å [6]). Here we report the structural properties of GaTe under hydrostatic pressure up to 22 GPa. The low coordination number of Ga (CN = 4) and the fact that high pressures can induce phase transitions into modifications with increased coordination number (pressure coordination rule [7]) suggest the possibility of polymorphic phase transitions of GaTe under pressure. The homologous phase InTe and the isotypic and isoelectronic compound GeAs undergo, at ambient temperature, discontinuous structural changes at 5 GPa [8–14] and 13 GPa [15,16]

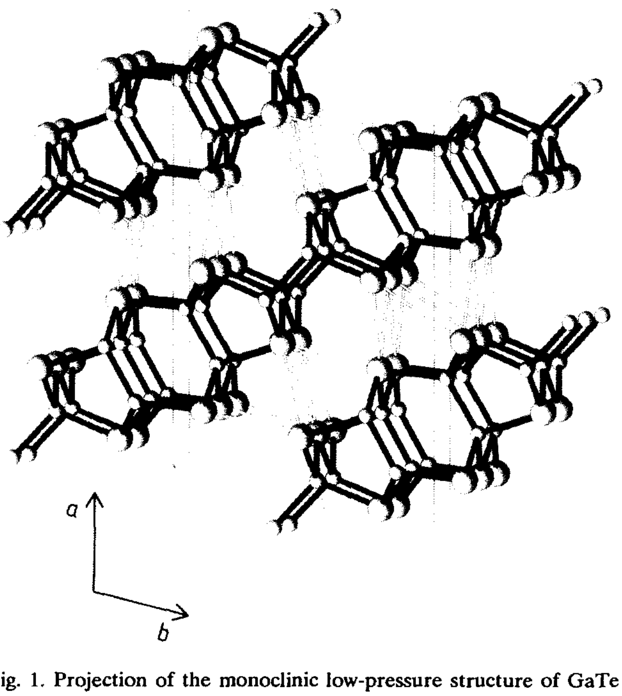

Fig. 1. Projection of the monoclinic low-pressure structure of GaTe along [001]. Ga, ○; Te, ◯; Ga–Ga bonds, dark grey; Ga–Te bonds, light grey; thin white lines indicate interlayer contacts $d$(Te–Te), which are shorter than the sum of the van der Waals radii.

0925-8388/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
*SSDI* 0925-8388(95)01559-0

respectively, into high-pressure modifications of the NaCl type. The structural phase transformations of InTe and GeAs are associated with semiconductor-to-metal transitions [8–12,15,16]. For decreasing pressures the structural phase transitions of GeAs and InTe do not reverse at room temperature [8–12,15,16].

The structural investigations of GaTe under pressure were carried out by powder X-ray diffraction at room temperature. Monoclinic GaTe is found to undergo a phase transition at 10 GPa to a high-pressure polymorph with NaCl-type structure. Optical reflectivity measurements were performed to characterize electronic changes associated with the structural phase transition.

## 2. Experimental

Monoclinic GaTe was prepared by heating mixtures of the elements (molar ratio 1:1) in a silica tube. After 20 h at 1220 K the temperature was raised to 1270 K for a short time followed by cooling down to ambient temperature [17]. High pressures were generated in gasketed diamond anvil cells (DAC) and measured by the ruby luminescence method [18]. For X-ray diffraction experiments small pieces of the compound were ground thoroughly. A 4:1 mixture of methanol/ethanol was used as pressure-transmitting medium for those experiments performed at room temperature and paraffin for those performed at elevated temperatures. X-ray powder investigations were carried out on a two-circle diffractometer with transmission geometry and Zr-filtered Mo K$\alpha$ radiation. Intensities were collected using a position sensitive detector with an active range of 12°.

Optical reflectivity measurements were performed in the photon energy range from 0.5 eV to 4.0 eV using a microoptical setup with various combinations of light sources, gratings, and detectors. A freshly cleaved chip of about 50 $\mu$m thickness was mounted in the DAC such that the sample was in direct optical contact with one of the diamond windows. The reflectivity was measured for this diamond-sample interface using a focal spot about 30 $\mu$m in diameter. In the optical experiments pressure conditions were quasi-hydrostatic due to the use of CsCl as a pressure-transmitting medium.

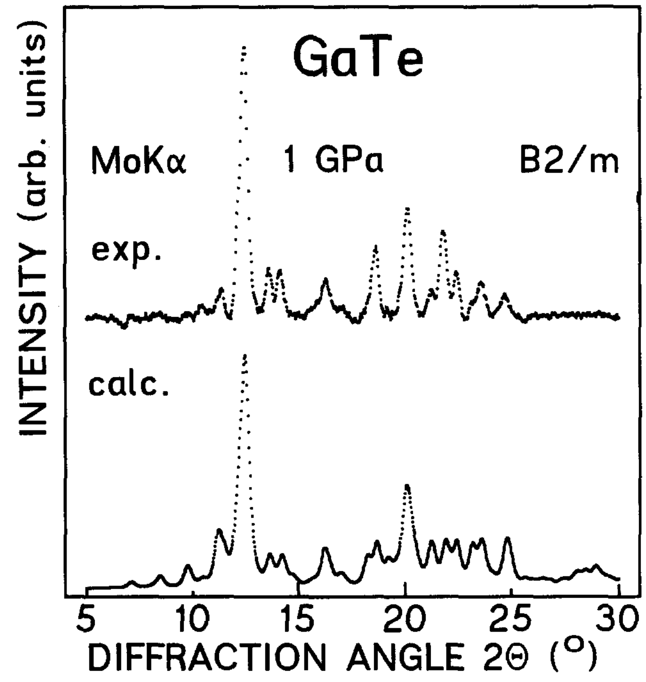

Fig. 2. Experimental and calculated diffraction diagrams of the monoclinic GaTe modification at 1 GPa.

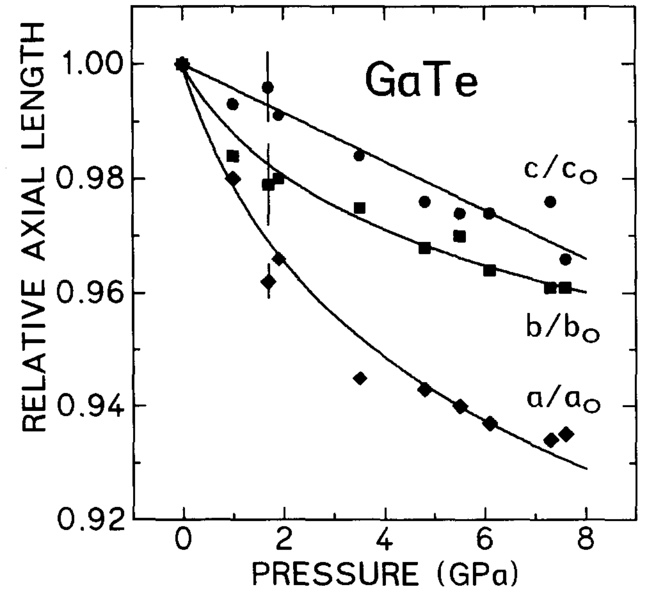

Fig. 3. Relative axial lengths for the monoclinic GaTe modification at pressures up to 7.8 GPa. Typical error bars are shown for the data at 1.7 GPa.

## 3. Results and discussion

Fig. 2 shows the X-ray powder pattern of GaTe at 1 GPa. The diagram calculated with the positional parameters of the crystal structure at ambient pressure is in good overall agreement, which indicates that at low pressures no major changes of positional parameters take place. Experimental diffraction patterns show the monoclinic modification of GaTe to be stable up to pressures of about 10 GPa. Lattice parameters and volumes of the low-pressure modification were obtained by least-squares fits using the $d$-values of reflections in the range 4.1 Å$>d>$1.5 Å. At pressures between 8 GPa and 10 GPa proper indexing was not possible due to broadening and overlap of reflections. The monoclinic angle $\gamma$ decreases linearly by 1.2° within the investigated pressure range. Fig. 3 shows the relative axial lengths for pressures up to 7.8 GPa. The change in lattice parameters is small and almost linear with pressure for the *c*-axis while it is larger and clearly nonlinear for the *a*- and *b*-axes. The pronounced anisotropy reflects the structural properties of monoclinic GaTe: compressible interlayer contacts between ${}^2_\infty(\mathrm{Te}_{3/3}\mathrm{Ga{-}GaTe}_{3/3})$ sheets are oriented along [120] whereas in the [001] direction the covalent intralayer bonds are predominant.

Near 10 GPa ($T = 300$ K) GaTe undergoes a first-order phase transition to the NaCl-type structure (SG no. 225, Fm$\bar{3}$m). Fig. 4 shows diffraction diagrams of the high-pressure modification. The diagram taken at 12 GPa exhibits broad reflections, which we attribute to a high degree of disorder. Thermal annealing in the DAC at 11 GPa and 470 K for 12 h induced a significant improvement of the diffraction pattern. Most notably, the reflections (111) and (200) become well resolved, and the intensity of the weak (311) reflection is enhanced so that it becomes clearly visible. Gaining reliable intensities of reflections with odd indices is of particular importance as these reflections indicate the ordered arrangement of Ga and Te. After applying a background correction a full-profile Rietveld refinement was carried out. The final results are $R_\mathrm{I} = 0.072$, $R_\mathrm{PR} = 0.176$, $B(\mathrm{Ga}) = 1.6(2)$ Å$^2$, and $B(\mathrm{Te}) = 1.4(2)$ Å$^2$. Here, $R_\mathrm{I}$ and $R_\mathrm{PR}$ are the residuals for refinements using integrated intensities and full profile data respectively, and $B$ is the atomic displacement factor. Although the $R$ values for our measurement in the diamond anvil cell are not as low as for free-standing samples, the quality of the refinement is sufficient to prove the rock salt structure with an ordered arrangement of Ga and Te to be reliable.

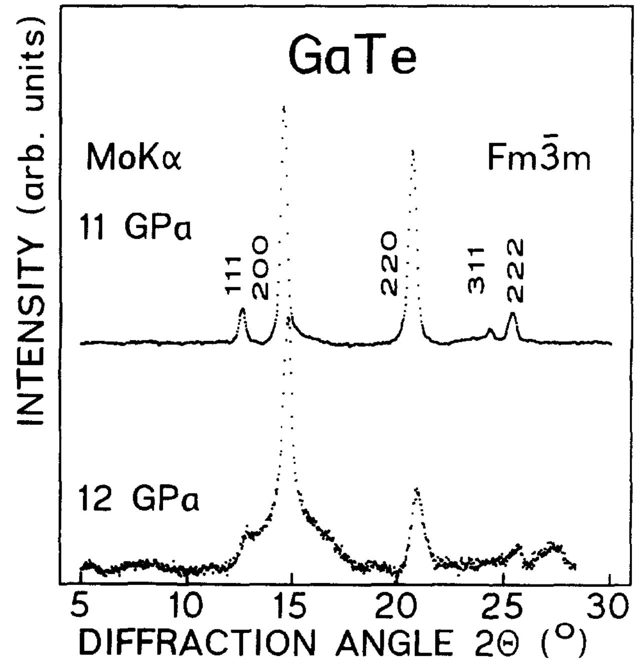

Fig. 4. Diffraction diagrams of the cubic high-pressure polymorph of GaTe after passing the phase transition at 300 K (bottom) and after thermal annealing for 20 h at 470 K (top).

In the direction of decreasing pressure the high-pressure modification is observed down to at least 3.2 GPa. After releasing pressure completely the diffraction diagram shows no sharp Bragg reflections, indicating that the translational symmetry is lost. Thus, the reverse phase transition in GaTe is not observed at room temperature, and the recovered material is amorphous.

Fig. 5 shows the pressure–volume relation for GaTe. The reconstructive phase transition results in a discontinuous volume change of 15%. Experimental volumes were fitted by a Murnaghan-type relation [19]:

$$V(P) = V_0\left(1 + \frac{B_0'}{B_0}P\right)^{-1/B_0'} \qquad (1)$$

where $V_0$, $B_0$ and $B_0'$ are volume, bulk modulus and pressure derivative of the bulk modulus respectively at zero pressure. The values of $B_0 = 30(2)$ GPa and $B_0' = 6$ of the GaTe low-pressure modification are close to the results for isotypic GeAs ($B_0 = 35.5(15)$ GPa, $B_0' = 6.5(6)$ [16]). The relatively large compressibility of the low-pressure polymorph is a consequence of the compressible contacts between the sheets of the layered crystal structure. The bulk modulus of the cubic high-pressure modification is a factor of 2 larger compared with that of the low-pressure phase. For the cubic polymorph we obtain $V_0 = 195(1)$ Å$^3$, $B_0 = 60(4)$ and $B_0' = 4.2(6)$. The extrapolated zero pressure volume of the high-pressure modification corresponds to a lattice constant of 5.80(1) Å for a hypothetical polymorph with rock salt structure at ambient conditions. Thus, the distance $d(\mathrm{Ga{-}Te})$ for octahedrally coordinated Ga atoms in

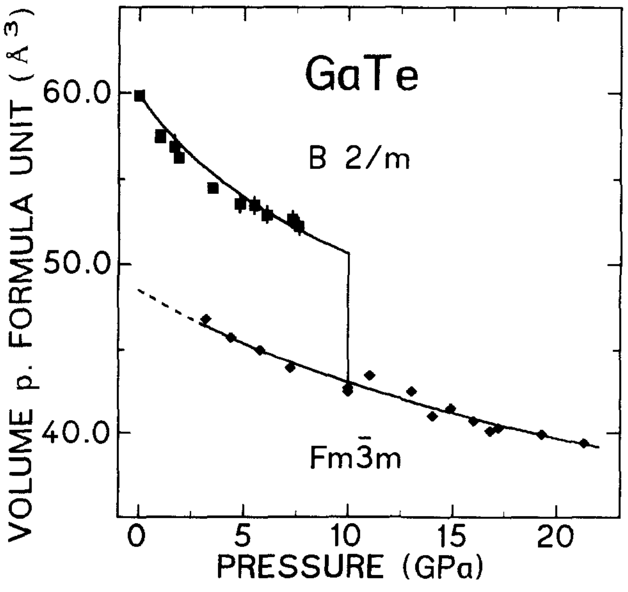

Fig. 5. Pressure–volume relation of GaTe. Solid curves represent results of least squares fits of Murnaghan-type relations; see Eq. (1).

the cubic modification is 2.900(5) Å. The distances $d$(Ga–Te) between 2.638(2) Å and 2.686(2) Å for the stable low-pressure modification are significantly smaller. The phenomenon that a phase transition with discontinuous volume reduction and increase of CN goes along with an increase in bond length is well known as the pressure-distance paradox [7].

It is interesting to compare the high-pressure structural properties of GaTe with those of the homologous compound InTe. InTe crystallizes at ambient conditions in the TlSe-type structure [13,20] and should be formulated as In(I)[In(III)$Te_2^-$]. Although the crystal structures of GaTe and InTe are different at ambient pressure they form isotypic high-pressure modifications. The energetic differences of oxidation states at normal pressure, which lead to a mixed valent In(I)/In(III) compound in the case of InTe and to a pure Ga(II) phase with covalent Ga–Ga bonds in the case of GaTe, are not relevant for the high-pressure modifications. At high pressure, non-directional interactions dominate the structural properties and lead to homodesmic high-pressure crystal structures with octahedral coordination for all atoms.

On the other hand, a difference in behaviour is observed for GaTe and InTe when releasing the pressure. The structural phase transformation of InTe is not reversed, and, in contrast to GaTe, the high-pressure polymorph can be retained at normal pressure [8]. The lattice constant of NaCl type InTe ($a$ = 6.177 Å) results in a distance $d$(Te–Te) of 4.368 Å. This is almost equal to the distance $d$(Te–Te) of 4.42 Å for close-packed $Te^{2-}$ anions as estimated from the ionic radius of the $Te^{2-}$ anion [6]. In the case of GaTe the distance $d$(Te–Te) corresponding to the extrapolated zero pressure volume is significantly smaller (4.10 Å). Thus, for GaTe it is energetically less favorable to form a metastable NaCl-type phase at ambient conditions. This qualitative argument explains why a metastable cubic phase of GaTe is not observed at ambient conditions.

The fact that an amorphous phase of GaTe at ambient conditions was obtained may indicate that the back transformation to the ambient pressure monoclinic modification is kinetically hindered [21]. The thermal activation at room temperature may just not be sufficient to overcome the energy barrier associated with the reconstructive structural change [22]. Empirically, the formation of disordered phases is favored in situations where tetrahedrally coordinated cations exist in different modifications, e.g. $SiO_2$ [23–27]. For GaTe this appears to be the case because a metastable hexagonal modification has been reported at ambient pressure [2].

Structural phase transformations of InTe and GeAs to the NaCl-type structure are accompanied by semiconductor-to-metal transitions [8–12,15,16]. We have investigated the optical reflectivity of both the low- and high-pressure modification of GaTe in order to gain some insight concerning electronic structure changes at the phase transition. Optical reflectivity spectra of GaTe at different pressures are shown in Fig. 6(a). We need to emphasize here that the reflectivity is measured at the interface between diamond window and sample. Owing to the large refractive index of diamond the absolute reflectivity values are different from those corresponding to a standard reflectivity measurement at a sample–vacuum interface.

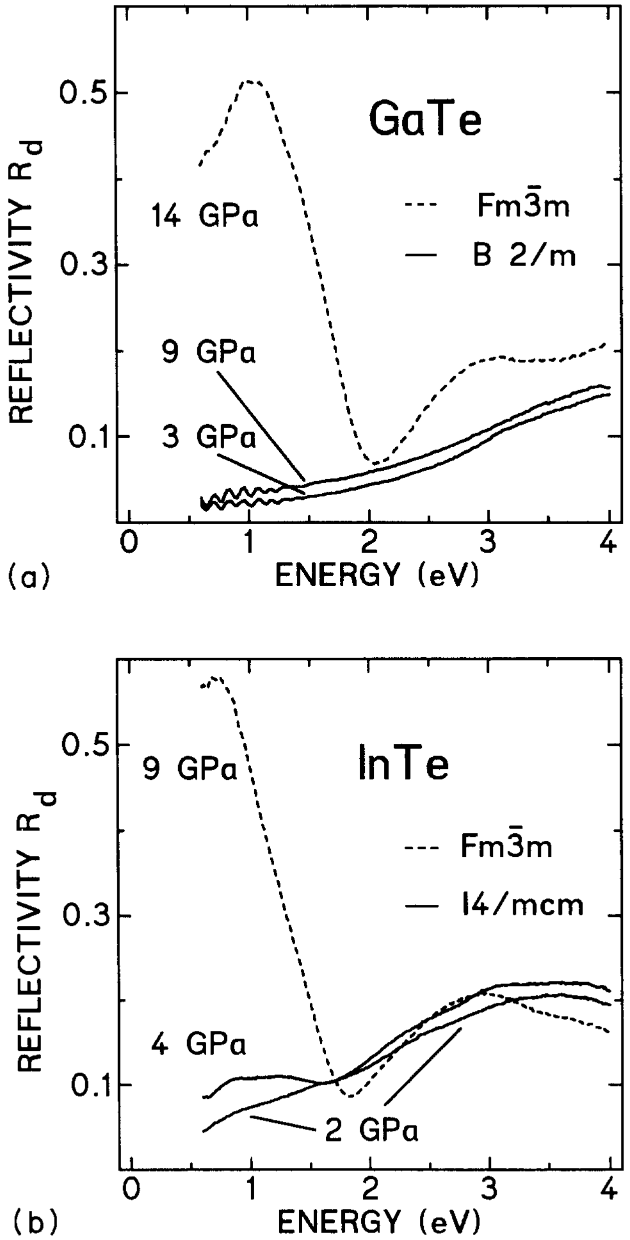

Fig. 6. (a) Optical reflectivity spectra of GaTe at different pressures. 3 GPa and 9 GPa: semiconducting low-pressure phase; 14 GPa: the enhanced reflectivity in the near IR region indicates the metallic character of the high-pressure polymorph with NaCl-type structure. (b) Optical reflectivity spectra of InTe at different pressures. 2 GPa and 4 GPa: semiconducting low-pressure modification; 9 GPa: metallic high-pressure modification.

At pressures up to 9 GPa the overall reflectivity is low, which indicates semiconducting behavior throughout the stability range of the low-pressure phase. The oscillations below 1.5 eV are caused by interferences because the sample is transparent for light with energies below the lowest optical gap. For pressures above the structural phase transition the reflectivity in the low energy region is significantly larger. A reflectivity edge similar to a Drude-like edge appears in the near-infrared spectral range. The corresponding screened plasma frequency is close to 2 eV.

For comparison, we have also performed optical reflectivity measurements of InTe which are shown in Fig. 6(b). The behaviour is quite similar to that of GaTe. The spectra measured up to 4 GPa are consistent with a semiconducting character of the low-pressure phase. Spectra measured at pressures above the structural phase transition at 5 GPa [13] show a Drude-like reflectivity edge, which is consistent with a metallic character of the high-pressure polymorph. Thus, the results of our optical reflectivity measurements on InTe are in agreement with earlier conductivity experiments [9,10].

In terms of independent-electron band structure theory, metallic properties are expected for III–VI compounds with NaCl-type structure. At least one energy band originating from hybridized sp states of the trivalent cation can only be partly filled. Most likely, however, several bands cross the Fermi energy [28], giving rise to electron as well as hole pockets. In such a situation the optical response is a complicated superposition of intra- and interband transitions. The intraband part is primarily responsible for a high reflectivity in the infrared spectral range, while the onset energy for strong direct interband transitions determines the energetic position of the reflectivity edge and the corresponding screened plasma frequency, which is close to 2 eV in GaTe and InTe. The fact that the reflectivity of GaTe decreases slightly near the low-energy limit of the present experiment is possibly a consequence of disorder, since the reflectivity data have been measured with samples that were not thermally annealed.

In conclusion, we observe for monoclinic GaTe a phase transformation from a heterodesmic layered low-pressure modification into a homodesmic high-pressure rock salt structure at 10(1) GPa (increasing pressure). The structural phase transformation is associated with a semiconductor-to-metal transition. For decreasing pressures the high-pressure polymorph is metastable down to 3.2 GPa. At ambient temperature, the discontinuous structural change is not reversed in the direction of decreasing pressures, and a phase without translational symmetry is formed at zero pressure.

## References

[1] M. Julien-Pouzol, S. Jaulmes, M. Guittard and F. Alapini, *Acta Crystallogr. B, 35* (1979) 2848.

[2] The hexagonal polymorph is a metastable phase; see S.A. Semiletov and V.A. Vlasov, *Sov. Phys. Crystallogr., 8* (1964) 704.

[3] J.L. Brebner, G. Fischer and E. Mooser, *J. Phys. Chem. Solids, 23* (1962) 1417.

[4] T. Wadsten, *Acta Chem. Scand., 19* (1965) 1232.

[5] T. Wadsten, *Acta Chem. Scand., 21* (1967) 593.

[6] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr. B, 25* (1969) 925.

[7] A. Neuhaus, *Chimia, 18* (1964) 93.

[8] A.J. Darnell, A.J. Yencha and W.F. Libby, *Science, 141* (1963) 713.

[9] M.D. Banus, R.E. Hanneman, M. Strongin and K. Gooen, *Science, 142* (1963) 662.

[10] A.J. Darnell and W.F. Libby, *Phys. Rev., 135* (1964) A1453.

[11] S. Geller, A. Jayaraman and G.W. Hull, *Appl. Phys. Lett., 4* (1964) 35.

[12] S. Geller, A. Jayaraman and G.W. Hull, *J. Phys. Chem. Solids, 26* (1965) 353.

[13] T. Chattopadhyay, R.P. Santandrea and H.G. v. Schnering, *J. Phys. Chem. Solids, 46* (1985) 351.

[14] G.B. Demishev, S.S. Kabalkina and T.N. Kolobyanina, *Sov. Phys. Solid State, 29* (1987) 1985.

[15] P.C. Donohue and H.S. Young, *J. Solid State Chem., 1* (1970) 143.

[16] U. Schwarz and K. Syassen, *High Pressure Res., 9* (1992) 148.

[17] S. Paashaus and R. Kniep, *Z. Naturforsch., 45b* (1990) 667.

[18] G.J. Piermarini, S. Block, J.D. Barnett and R.A. Forman, *J. Appl. Phys., 46* (1975) 2774.

[19] F.D. Murnaghan, *Proc. Nat. Acad. Sci. USA, 50* (1944) 697.

[20] J.H.C. Hogg and H.H. Sutherland, *Acta Crystallogr. B, 32* (1976) 2689.

[21] R. Zuber and K.G. Weil, *Ber. Bunsenges. Phys. Chem., 93* (1989) 162.

[22] U. Pittermann, S. Ripper and K.G. Weil, *Z. Metallkd., 79* (1988) 561.

[23] N. Binggeli, N. Troullier, J.L. Martins and J.R. Chelikowky, *Phys. Rev. B, 44* (1991) 4771.

[24] J.R. Chelikowky, N. Troullier, J.L. Martins and H.E. King, *Phys. Rev. B, 44* (1991) 489.

[25] N. Binggeli and J.R. Chelikowky, *Phys. Rev. Lett., 69* (1992) 2220.

[26] R.W. Winters, A. Garg and W.S. Hammack, *Phys. Rev. Lett., 69* (1992) 3751.

[27] K.J. Kingma, C. Meade, R.J. Hemley, H.K. Mao and D.R. Veblen, *Science, 259* (1993) 666.

[28] A rough idea of the overall features of the band structure of cubic GaTe may be obtained by interpolating between band structures calculated for II–VI and IV–VI compounds with NaCl-type structure. See: S. Ves, U. Schwarz, N.E. Christensen, K. Syassen and M. Cardona, *Phys. Rev. B, 42* (1990) 9113; J.S. Melvin and D.C. Henry, *J. Phys. C: Solid State Phys., 12* (1979) 3003; G. Martinez, M. Schlüter and M.L. Cohen, *Phys. Rev. B, 11* (1975) 651; G. Martinez, M. Schlüter and M.L. Cohen, *Phys. Rev. B, 11* (1975) 660; Y.W. Tung and M.L. Cohen, *Phys. Rev., 180* (1969) 823; F. Herman, R.L. Kortum, I.B. Ortenburger and J.P. van Dyke, *J. Phys. Coll., C4* (1968) 62; M.L. Cohen, Y. Tung and B. Allen, *J. Phys. Coll., C4* (1968) 163.