Doklady Physical Chemistry, Vol. 396, Part 1, 2004, pp. 111–114. Translated from Doklady Akademii Nauk, Vol. 396, No. 3, 2004, pp. 358–361.
Original Russian Text Copyright © 2004 by Boldyreva, Ivashevskaya, Sowa, Ahsbahs, Weber.

PHYSICAL CHEMISTRY

Effect of High Pressure on Crystalline Glycine: A New High-Pressure Polymorph

E. V. Boldyreva[1, 2], S. N. Ivashevskaya[1], H. Sowa[3], H. Ahsbahs[3], and H.-P. Weber[4, 5]

Presented by Academician V.V. Boldyrev January 28, 2004

Received February 11, 2004

Study of the effect of pressure on organic molecular crystals is of considerable interest for predicting the response of drugs, materials, and devices based on molecular crystals to high pressures and to other mechanical actions, as well as for upgrading theoretical models used for predicting crystal structures and molecular conformations as a function of conditions. Information obtained for crystals of small organic molecules can be used for studying biological macromolecules, in particular, for predicting the secondary structure of polypeptide chains [1].

Prominent among organic molecular crystals are crystals of amino acids. They can serve as biomimetics, as well as medicines and materials for molecular electronics. Studies of the effect of pressure on amino acids are also of importance for geo- and cosmochemistry [2]. The search for new high-pressure polymorphs is believed to be one of the most central problems; however, reliable data on pressure-induced polymorphous transformations in amino acid crystals have not hitherto been reported. The conclusion based on Raman spectra that pressure induces polymorphous transformations in L-asparagine [3] and alanine [4] was not supported by later diffraction studies of these structures (J.A. Beukes and S. Parsons, private communications). The existence of a high-pressure phase was suggested for glycine [Dawson, A., Parsons, S., Allan, D., Loveday, J., and Guthrie, M., http://www.isis.rl.ac.uk/BCA2001/Abstract%20files/bca1…]; however, neither the data supporting this suggestion nor the data describing the crystal structure of such a phase are currently available. α-Glycine was not found to undergo pressure-induced phase transitions, at least up to pressures of about 4 GPa (X-ray diffraction) [5] or 23 GPa (Raman spectroscopy) [6]. The X-ray diffraction study of α-glycine containing an impurity of γ-glycine at pressures up to 4 GPa [5] showed that, at a pressure of about 3.5 GPa, all reflections of the γ phase abruptly disappeared and no new lines were observed. It was suggested that the γ phase thereby undergoes a phase transition at this pressure and the lines of a new phase are masked by the lines of the α modification [5]. To verify this assumption, we prepared a pure phase of γ-glycine by the ad hoc procedure in [7]. This sample was studied by X-ray diffraction at hydrostatic pressures of up to 8 GPa.

The high-pressure experiments were carried out in situ in diamond anvil cells of the Merrill–Bassett type [8]. A methanol–ethanol mixture was used as the pressure-transmitting medium; this mixture was specially dried in order to rule out the possible influence of water traces on the polymorphous transformations of glycine. The X-ray powder diffraction experiment was carried out with synchrotron radiation ($\lambda = 0.7195$ Å) at the European Synchrotron Radiation Facility, Grenoble. X-ray diffraction patterns were recorded with an MAR345 image plate detector. Primary diffraction data were processed and integrated using the Fit2D software [Hammersley, A., v. V11.012, hammersley@esrf.fr]. Diffraction spectra were indexed with the TREOR program [10]. The subtraction of the background and structure solution and refinement by the Rietveld technique were performed with the MRIA program package [11]. The PowderCell program package [Kraus, W. and Nolze, G., PowderCell for Windows, v. 2.3, http://www.bam.de/a_v/v_1/powder/e_cell.html] was used for graphic representation and crystal-chemical analysis.

The use of a pure sample allowed us, for the first time, to reliably detect a pressure-induced phase transition resulting in the formation of a new polymorph and to solve and refine its structure. The initial γ modification and the new high-pressure phase coexisted in a wide range of pressures. The first indications of a new

---

[1] *Molecular Design and Environmentally Safe Technologies Research and Education Center, Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*

[2] *Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences, ul. Kutateladze 18, Novosibirsk, 630128 Russia*

[3] *Philipps-Universität, Hans-Meerwein Str., Marburg/Lahn, 35032 Germany*

[4] *Swiss–Norwegian Beamlines at ESRF, PO Box 220, F-38043 Grenoble Cedex, France*

[5] *Institut de Cristallographie, Universite de Lausanne, CH-1015 Lausanne, Switzerland*

0012-5016/04/0005-0111 © 2004 MAIK “Nauka/Interperiodica”

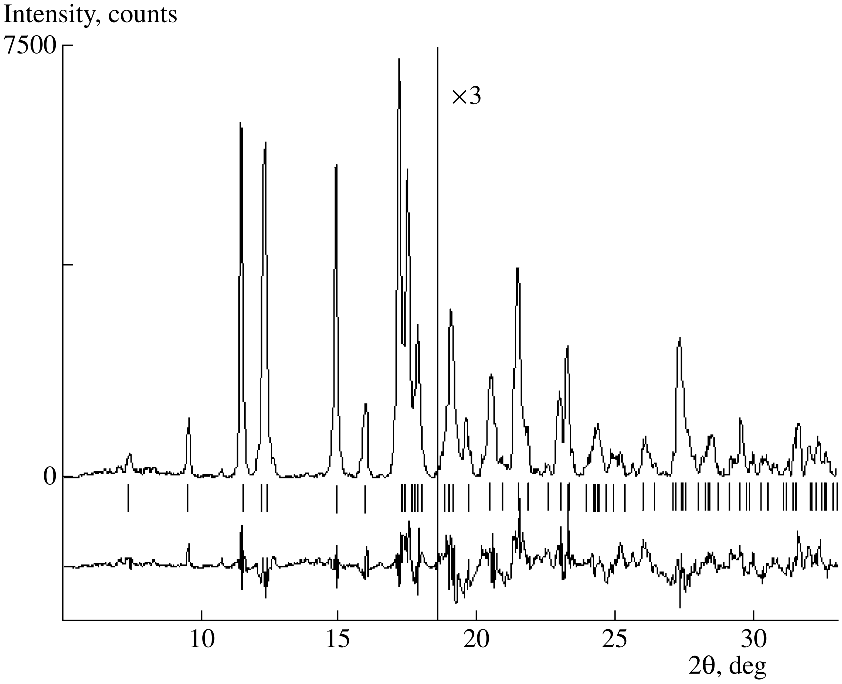

Fig. 1. Rietveld refinement profile for the glycine high-pressure phase at 7.85 GPa obtained from synchrotron radiation ($\lambda = 0.7195$ Å) diffraction data: (top) the experimental pattern minus the background and (bottom) the difference curve (observed minus calculated). Tick marks correspond to the calculated positions of reflections. For clearness, the diffraction pattern intensities are increased threefold beginning with $2\theta = 18°$.

phase were shown by the X-ray diffraction patterns at a pressure of 2.74 GPa, the initial low-pressure phase remaining the major one. The high-pressure phase dominated at pressures of 4.17–7.85 GPa. Traces of the low-pressure polymorph persisted even at 7.85 GPa, the highest pressure achieved in our experiments.

The structure of the high-pressure phase was solved in space group *Pn* ($Rp = 0.18$, $Rb = 0.18$, $Rw = 0.17$) with the use of the grid search technique [12]. Hydrogen atoms were placed in their calculated positions and were refined with a fixed $U_{\rm iso}$ parameter (0.05 Å^2) by the Rietveld method, imposing constraints on bond lengths and bond angles. Figure 1 shows the result of the refinement of the structure by the Rietveld method; the unit cell parameters, coordinates of symmetry-unrelated atoms, and atomic displacement parameters in the high-pressure phase at 7.85 GPa are summarized in the table. The packing of glycine zwitterions in the high-pressure phase appeared to be in many respects similar to the arrangement of the same zwitterions in the α ($P2_1/n$) and β ($P2_1$) glycine polymorphs [13] rather than in the initial γ phase ($P3_1$). In the γ phase, zwitterions are linked by hydrogen bonds to form a three-dimensional network based on helical chains, whereas, in the high-pressure phase, these chains are rearranged in layers. Figure 2 shows (a) the structure of a separate molecular layer in the high-pressure phase, (b) stacking of two layers, and (c) packing of the resulting double layers in the direction normal to the layers. The structure of the individual layers in the high-pressure polymorph is similar to that in the known α and β modifications, but the packing of the layers is essentially different: the layers are combined in pairs as in α-glycine, but they are related by a glide reflection plane rather than by inversion. The pressure-induced polymorphous transformation in γ-glycine can be compared with a change in the secondary structure of a polypeptide, when a helix is transformed into a sheet.

Crystallographic coordinates (rel. units) and atomic displacement parameters (Å^2) of symmetry-unrelated atoms in the high-pressure glycine at 7.85 GPa (space group *Pn*, $a = 5.379(1)$ Å, $b = 5.557(1)$ Å, $c = 4.780(1)$ Å, $\beta = 118.25(1)°$, $V = 125.86(1)$ Å^3, $Z = 2$)

Atom	*x*	*y*	*z*	$U_{\rm iso}$
O(1)	0.9533	0.806(2)	0.2824	0.018(1)
O(2)	0.308(2)	0.6525(14)	0.767(2)	0.018(1)
N(1)	0.780(3)	0.724(2)	0.734(2)	0.018(1)
C(1)	0.224(3)	0.763(3)	0.519(2)	0.018(1)
C(2)	0.484(3)	0.853(2)	0.496(3)	0.018(1)
H(1)	0.516	0.022	0.549	0.051
H(2)	0.433	0.825	0.294	0.051
H(3)	0.753	0.560	0.690	0.051
H(4)	0.945	0.782	0.708	0.051
H(5)	0.850	0.756	0.943	0.051

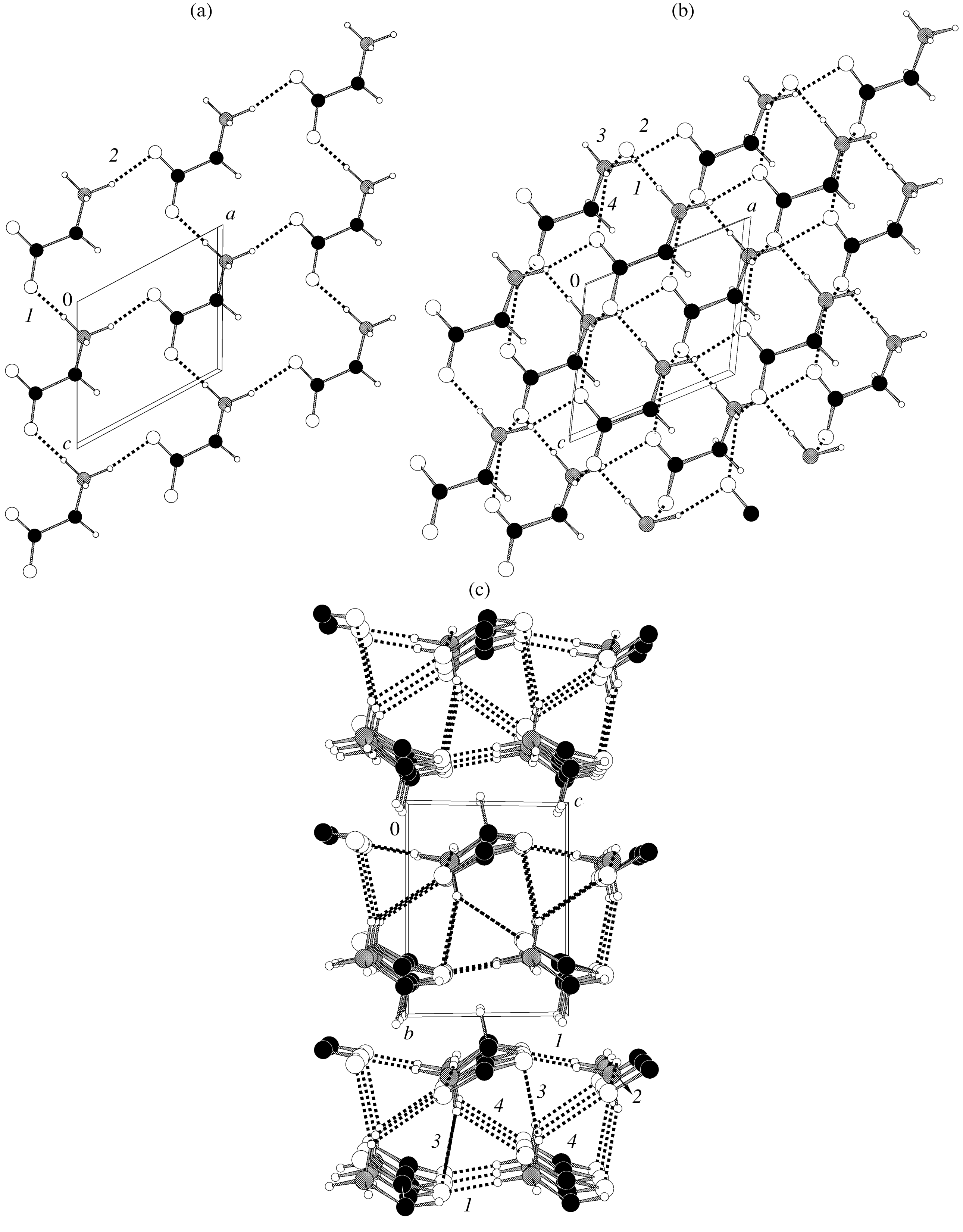

Fig. 2. Fragments of the crystal structure of the glycine high-pressure phase: (a) an individual layer formed by zwitterions, (b) stacking of two layers ($a \times c$ projection), and (c) packing of double layers ($a \times b$ projection). NH···O hydrogen bonds are shown by dashed lines (numbered in order of increasing length).

Thus, our findings allow us to draw the following conclusions:

(1) γ-Glycine undergoes a first-order phase transition accompanied by an abrupt change in the unit cell volume; the phase transition commences at a hydrostatic pressure of 2.74 GPa and is not completed even at 7.85 GPa.

(2) The structure of the high-pressure phase is described in space group *Pn*. The glycine zwitterions in the structure are linked by hydrogen bonds to form layers, which are combined in pairs.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 02–03–33358), the CRDF (award no. NO–008–X1), the Ministry of Education of the Russian Federation (grant no. Ch0069 of the program "Integration," grant no. 1–67–01, and grant no. ur.05.01.021 of the program "Universities of Russia"), and the Foundation for Support of Russian Science. Diffraction experiments were supported through grants from the Swiss–Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble (experiment nos. 01–02–656 and 01–02–671).

The experimental assistance of the staff of the SNBL is gratefully acknowledged. We are grateful to V.V. Chernyshev and V.B. Zlokazov for their help in subtracting the background of integrated diffraction spectra and to T.N. Drebushchak for help in preparing illustrations.

REFERENCES

1. Boldyreva, E.V., in *High Pressure Crystallography. NATO ASI Series*, Dordrecht: Kluwer, pp. 495–512.
2. Peterson, E., Horz, F., and Chang, S., *Geochim. Cosmochim. Acta*, 1997, vol. 61, pp. 3937–3950.
3. Moreno, A.J.D., Freire, P.T.C., Melo, F.E.A., *et al.*, *Solid State Commun.*, 1997, vol. 103, pp. 655–658.
4. Teixeira, A.M.R., Freire, P.T.C., Moreno, A.J.D., *et al.*, *Solid State Commun.*, 2000, vol. 116, pp. 405–409.
5. Boldyreva, E., Ahsbahs, H., and Weber, H.-P., *Z. Kristallogr.*, 2003, vol. 218, pp. 231–236.
6. Murli, C., Sharma, S.M., Karmakar, S., and Sikka, S.K., *Physica B* (Amsterdam), 2003, vol. 339, pp. 23–30.
7. Boldyreva, E., Drebushchak, V., Drebushchak, T., *et al.*, *J. Therm. Anal. Calorim.*, 2003, vol. 73, pp. 409–428.
8. Merrill, L. and Bassett, W.A., *Rev. Sci. Instrum.*, 1974, vol. 45, pp. 290–294.
9. Piermarini, G.J., Block, S., and Barnett, J.D., *J. Appl. Phys.*, 1973, vol. 44, pp. 5377–5382.
10. Werner, P.-E., Eriksson, L., and Westdahl, M., *J. Appl. Crystallogr.,* 1985, vol. 18, pp. 367–370.
11. Zlokazov, V.B. and Chernyshev, V.V., *J. Appl. Crystallogr.*, 1992, vol. 25, pp. 447–451.
12. Chernyshev, V.V. and Schenk, H., *Z. Kristallogr.*, 1998, vol. 213, pp. 1–3.
13. Boldyreva, E., Drebushchak, T., and Shutova, E., *Z. Kristallogr.*, 2003, vol. 218, pp. 366–376.
14. Knorre, D.G. and Myzina, S.D., *Biologicheskaya khimiya* (Biological Chemistry), Moscow: Vysshaya Shkola, 2000.