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Pressure-induced phase transitions in L-alanine and DL-alanine, revisited

Nikolay Tumanov,^a Elena Boldyreva,^b Alexander Kurnosov,^{a,c} Raul Quesada Cabrera,^{d,e} ^a*Novosibirsk State University*. ^b*Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk*. ^c*Bayerisches Geoinstitut, University of Bayreuth (Germany)*. ^d*Swiss-Norwegian Beamline ESRF, Grenoble (France)*. ^e*University College London, Christopher-Ingold Laboratories (United Kingdom)*. E-mail: n.tumanov@gmail.com

The effect of pressure on L-alanine and DL-alanine has been studied by X-ray powder diffraction, single-crystal X-ray diffraction, Raman spectroscopy and optical microscopy. No previously reported structural phase transitions in L-alanine and DL-alanine have been observed up to 12.3 and 8.3 GPa, respectively. In both compounds at about 1.5–2 GPa (close to the pressure of the previously reported phase transition in L-alanine into a tetragonal phase, 2.3 GPa [1], [2]), the cell parameters *a* and *b* become accidentally equal to each other, but without a change in the space group symmetry. Neither could be a polymorphic transformation in L-alanine from tetragonal into a monoclinic phase at about 9 GPa confirmed, the changes in the cell parameters till the highest measured pressures being continuous and the cell metrics remaining orthorhombic. Our Raman experiments confirmed the effects described previously for the spectra of L-alanine [1] and DL-alanine [3], but we have shown that the spectral changes are continuous and are not related to structural phase transitions. During a slow decompression of L-alanine single crystal (in a methanol-ethanol 4:1 mixture as a pressure-transmitting liquid) from about 6 GPa, new phases crystallized in the diamond anvil cell in the pressure range between 0.8–4.7 GPa, which recrystallized into L-alanine below 0.8 GPa. These previously unknown phases were characterized by powder X-ray diffraction and Raman spectroscopy and seem to be a solvate of L-alanine.

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Phase Changes of H₂ and He Hydrates under High pressure and Low Temperature

Hisako Hirai,^a Akiko Umeda,^a Kousuke Shimizu,^a Taku Fujii,^a Shin-ichi Machida,^a Ayako Shinozaki,^a Taro Kawamura,^b

Yoshitaka Yamamoto,^b Takehiko Yagi,^c ^a*Geodynamics Research Center, Ehime University, Matsuyama*. ^b*National Inst. Advanced Industrial Science and Technology, Tsukuba*. ^c*Institute for Solid State Physics, Tokyo University, Kashiwa, Chiba (Japan)*. E-mail: hirai@sci.ehime-u.ac.jp

Three phases of hydrogen hydrate have been known so far. One is a clathrate hydrate, sII [1], and others are filled ice II structure and filled ice Ic structure [2]. The ratio of water to hydrogen molecules for these phases are 1:3, 1:6, 1:1, respectively. sII hydrogen hydrate is expected to be a hydrogen storage material, because it can contain relatively high hydrogen and its synthetic condition is mild comparable to industrial production. At room temperature, above about 1 GPa filled ice II and above 3 GPa filled ice Ic are formed. The latter one survives at least up to 90 GPa [3]. However, phase relations among them under high pressure and low temperature region have not yet been clarified. In this study, high pressure and low temperature experiments were performed by using diamond anvil cells and a helium-refrigeration cryostat in a region of 0.2 to 4.5 GPa and 130 to 300 K. X-ray diffractometry revealed a series of phase change from sII to filled ice Ic via filled ice II. For example, at 220K, sII transformed to filled ice II at approximately 0.6 GPa and further transformed to filled ice Ic structure at about 2.0 GPa. The present results experimentally confirmed the previous prediction.

Helium hydrate is known to form filled ice II structure [4], but the synthetic conditions reported have been limited. Similar experiments were carried in a region of 0.2 to 5.0 GPa and 200 to 300 K. The results showed that the filled ice II structure did not transform to filled ice Ic structure, but decomposed into helium and ice VI or VIII.

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Study of the behavior of alkali sulfides under pressure

David Santamaría-Pérez,^a Angel Vegas,^b Claus Muehle,^c Martin Jansen,^c ^a*Department of Physical Chemistry I, University Complutense, Madrid (Spain)*. ^b*Instituto de Química Física "Rocasolano", CSIC, Madrid (Spain)*. ^c*Max-Planck Institute for Solid State Research, Stuttgart (Germany)*. E-mail: dsantamaria@quim.ucm.es

Pressure-induced phase transitions in antiferrotype M₂S sulfides (M = Li, Na and K) into anticotunnite-type structures have recently been reported and, some of them, further transform into Ni₂In-type structures [1–3]. This high-pressure phase-transition path involves the increase of the cation coordination number from 8 in the antiferrotype structure, through 9 in anticotunnite to 11 in Ni₂In-type structure.

Theoretical *ab initio* total-energy calculations have allowed to completely characterize the high-pressure phases observed experimentally in Li₂S, Na₂S and K₂S and to predict the most likely phases that are expected to be stable below 100 GPa for all alkali metal sulfides [4].

In the present work we have studied the behavior of both, Rb₂S and Cs₂S at high-pressure and room temperature using angle-dispersive X-ray powder diffraction in a diamond anvil cell (DAC). Our measurements have allowed us to identify the existing phase transitions and confirm the previously proposed antiferrotype → anticotunnite → Ni₂In-type sequence of stable structures for M₂S sulfides with increasing pressure [5]. Strong luminescence is observed in Rb₂S above 2.6 GPa (band maximum at 703 nm) when the transition to the Ni₂In-type phase starts