Structural Studies on Novel Materials Synthesized at High Pressures

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Introduction

Recent improvements in synchrotron-based powder diffractometry on samples in diamond anvil cells [1] and parallel progress in laser heating techniques [2] have opened avenues to synthesize entirely new classes of compounds at elevated pressures and to examine their structure by means of a combination of optical spectroscopy and Rietveld refinement of model structures.

The microdiffraction beamline station 16-ID-B at the APS is among the most advanced facilities for examining powder diffraction of micrometer-sized samples confined in diamond anvil cells. Our recent work at this beamline focuses on three topics: (1) synthesis of new quasi-organic polymers at high pressures, (2) pressure-induced modifications of materials, and (3) examination of pressure-induced changes in bonding character.

Two examples of studies belonging to the second and third kind are synthesis of a pressure-induced phase transition in MgB_2 and preliminary results on pressure effects on bonding character in sulphur.

Methods and Materials

All studies were performed on samples loaded in diamond anvil cells with wide-angle openings, optimized for powder diffraction studies. The pressurized samples were heated with the YLF-laser heating setup at APS sector 16 (MgB_2) and with the CO_2-laser heating system at UNLV (sulphur). In case of sulphur, the temperature range between 300 and 500K had been explored by external heating of the diamond anvil cell.

X-ray diffraction patterns were collected at APS beamline station 16-ID-B by using MAR image plate- and charge-coupled device (CCD) detectors. The x-ray beam was focussed onto the detector.

Results and Discussion

Phase Transition in MgB_2 at Elevated Pressure and Temperature

(O. Tschauner, D. Errandonea, G.C. Serghiou)

The recently reported superconductivity in MgB_2 has been described by the Bardeen Cooper-Schrieffer (BCS) mechanism in a system with two almost independent bands of pair-forming electrons. Calculations indicate that the size of the larger of the two superconducting gaps depends pronouncedly on direction [3]. The E_{2g} phonon regarded to be involved in the Fröhlich interaction with the two-dimensionally confined boron σ-electron bands has been found to be extremely anharmonic, and the coupling itself has been found to be nonlinear [4]. This coupling induces the larger of the two superconducting gaps and is responsible for the transition around 40K. Hence, static lattice distortion in the boron layer is expected to strongly affect superconductivity in MgB_2. Structural modifications of the MgB_2 basic structure can then open synthesis paths for new related superconductors with high T_c.

We recently observed and characterized a phase transition in MgB_2 at pressures above 9 GPa induced by short-term heating to 1500K by using x-ray diffraction at beamline station 16-ID-B, and Raman spectroscopy [5]. The observed changes in optical spectra and diffraction are interpreted as a group-subgroup transition resulting in a doubling of the cell along c and partial reduction of the boron site symmetry.

Pressure-induced Changes in Bonding Character in Sulphur

(O. Tschauner, Z. Trautt, G. May, M. Nicol)

At ambient pressure, sulphur assumes several crystalline structures, all based on ring-shaped molecules or, at high temperature, chains. Around 100 GPa, sulphur is a structurally simple metallic solid [6]. This metallic phase is anticipated by a semimetallic crystalline phase at slightly lower pressure [7]; however, the range of pressure between ~ 25 and 80 GPa did not yield any indication of a crystalline structure upon compression and decompression at 300K. This has been interpreted by a pressure-induced amorphization [7, 8], which convolutes the detailed mechanisms and intermediate states of the fundamental change in bonding character from molecular to normal metallic. By application of CO_2-laser and external

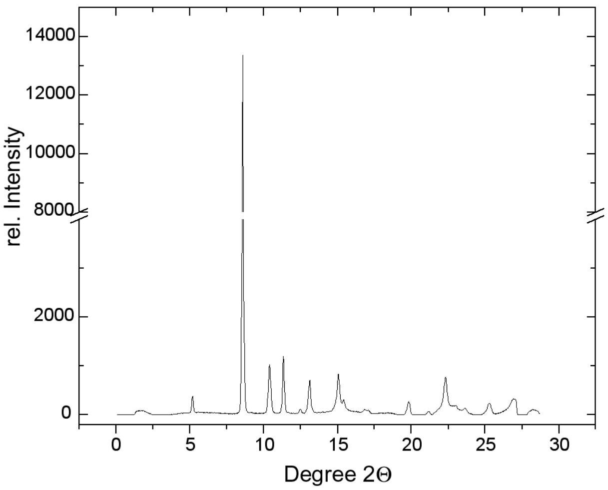

FIG. 1. Diffraction pattern of sulphur, heated to between 500 and 1200K at 28 GPa. The data were collected at APS beamline station 16-ID-B.

heating on γ-S_8, the stable phase of sulphur at ambient conditions, we show that sulphur recovers a crystalline structure between 25 and 30 GPa after heating to temperatures between 500 and 1200K. This new phase of sulphur is characterized by more than 20 diffraction peaks occurring in the angular range of 5° to 27° 2Θ, which can be indexed by large, low symmetric unit cells. The Raman spectra of this phase are characterized by a strong first-order Raman shift at 800 cm^{-1}, markedly higher than any first-order Raman shift in the lower-pressure phases of sulphur. The details of this complex structure could not yet be resolved, but the findings indicate that sulphur still remains a molecular solid under these conditions, while the size and configuration of the molecular unit are different from those of S_8. The amorphous state occurring upon compression at 300K then reflects the kinetic barriers of the transition from the low-pressure S_8 molecules to a molecule with a different number of atoms at high pressure. We will examine further changes in the atomic arrangement of sulphur at higher pressures and temperatures in order to map out the transition from molecular to a simple metallic state through various intermediate states.

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