

Crystal Structure of 200 K-Superconducting Phase of Sulfur Hydride System

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ABSTRACT

Superconductivity with the critical temperature T_c above 200 K has been recently discovered by compression of H_2S (or D_2S) at pressure above 90 GPa. It was proposed that these materials decompose under pressure to elemental sulfur and hydride with higher content of hydrogen^{1,2} which is responsible for the high temperature superconductivity. Here we report the crystal structure of the superconducting compressed H_2S and D_2S by synchrotron x-ray diffraction (XRD) measurements combined with electrical resistance measurements at room and low temperatures. We found that the superconducting (SC) phase is mostly in good agreement with theoretically predicted hexagonal and body-centred cubic (bcc) structure,³ and coexists with elemental sulfur, which claims that the formation of $3H_2S \rightarrow 2H_3S + S$ is occur by the compression.³⁻⁶

Recently very high T_c of 200 K has been discovered in hydrogen sulfide. The SC was proved by the sharp drop of resistance to zero, a strong isotope effect in study of D_2S , the shift of SC transition with magnetic field and finally in the studies of magnetic susceptibility and magnetization. The structure of the SC phase was not experimentally measured but it was theoretically proposed that most likely the starting H_2S decomposes under pressure (with assistance of temperature) to pure sulfur and some sulfur hydride with higher content of hydrogen (such as SH_4 or similar to that). At the same time with a theoretical work³ appeared which considered a different starting material $(H_2S)_2H_2$ (stoichiometry H_3S) and found $R3m$ and $Im-3m$ structures under pressure above 111 GPa and 180 GPa, respectively. These structures were further carefully studied theoretically by different methods and $T_c \sim 200$ K was consistently calculated for the $Im-3m$ structure. The calculated T_c as well as its pressure dependence are close to the experimental data.^{1,2} This agreement suggests that the high T_c observed in the experiments relate to the H_3S with the $Im-3m$ structure. Later calculations supported this idea: H_2S is unstable at high pressures and decomposes to sulfur and higher hydrides, most likely to H_3S .^{5,6} The goal of the present work is to determine the structure of the superconduct-

ing hydrogen sulfide and verify, if it really corresponds to the theoretically predicted structure.

Figure 1a shows a typical x-ray diffraction image of sulfur hydride at room temperature and the integrated intensity which excludes the background. It is considered that the reflections from the sample have the anisotropy in intensity is caused by the inhomogeneous of them. The main pattern well corresponds to the theoretically predicted bcc and hexagonal phase of H_3S .³ Then the pattern can be explained by the mixture of H_3S and β -polonium (Po) structure of elemental sulfur⁷ except the peaks marked with triangle (∇), star (*) and open circle (\circ). We also carried out XRD measurements in sulfur deuteride under high pressure as shown in Fig. 1b. Structures of sulfur deuteride are the same - most of the reflections can be explained by the mixture phase of bcc and β -Po structure phases. But no peak was observed at around 13.3 degree in any sulfur deuteride which emerges in sulfur hydride (*).

We have performed that XRD and electrical resistance measurements simultaneously in sulfur deuteride at 173 GPa. Top of the fig. 1b shows the temperature dependence of the XRD patterns. The XRD patterns kept at all measured temperature region and the resistance measurement shows the drop indicates superconducting transition below 150 K (Fig. 3b). Therefore, the structure in the normal and SC states are the same - no visible structural transition at SC transition.

As shown in Fig. 1c, the obtained pattern and the calculated that which is result of Rietveld refinement using RIETAN-FP⁸ with the predicted structure in ref.³ show the good agreement as follows: $R_{\text{wp}} = 0.40\%$, $S = 1.92$ in bcc lattice and $R_{\text{wp}} = 0.41\%$, $S = 1.94$ in hexagonal lattice. It is because that both of them are of same periodicity in sulfur atoms of H_3S , which have bcc lattice. And these lattice parameters are $a_{\text{bcc}} = 3.089$ (1) Å in bcc lattice and $a_{\text{hex}} = 4.379$ (10) Å, $c_{\text{hex}} = 2.663$ (9) Å in hexagonal lattice. That of β -Po sulfur are $a = 3.696$ (1) Å, $c = 2.708$ (1) Å. In sulfur deuterides at 173 GPa at room temperature, lattice parameters are $a_{\text{bcc}} = 3.0468$ (2) Å, $a = 3.351$ (3) Å and $c = 2.659$ (3) Å with $R_{\text{wp}} = 0.28\%$, $S = 0.55$.

The XRD patterns obtained on decreasing process from 150 GPa to 92 GPa in sulfur hydride are shown in Fig. 2a. No structural change was observed in main peaks. The intensity of the reflections come from β -Po structural elemental sulfur decline with decreasing pressure, and then disappear at 103 GPa. Meanwhile, a peak around 12.2 degree (\circ) which perhaps is incommensurate phase IV of elemental sulfur enhanced. The undefined peak (\bullet) around 9.5 degree disappear at 111 GPa. It is considered that other peaks around 10.5 degree (∇) and 13.3 degree (*) are from possible minor phase because these peaks shifted with the main peaks by pressure. The XRD patterns of sulfur deuteride obtained on increase and decrease from 173 GPa to 190 GPa then 180

GPa are shown in Fig. 2b. The pattern doesn't change by pressure except the shift of peak positions with pressure changes.

Pressure dependence of the atomic volume, V_{atm} , of sulfur hydride and sulfur deuteride calculated with predicted³ bcc-structures are shown in Fig. 2c. The compression curve (solid line) was fit using three experimental points, 150 GPa (sulfur hydride), 173 GPa and 190 GPa (sulfur deuteride). The other points obtained by pressure-decreasing run may show it incompressible. The solid line is drawn by the first-order Birch equation of state⁹ with the bulk modulus $B_0 = 486$ (35) GPa, and its pressure derivative $B_0' = 4$ (fixed). The value of experimentally observed V_{atm} is slightly big and the compressibility shows good agreements with the theoretically predicted one.³

Pressure dependence of the normalized atomic volume V/V_0 of β -Po structural elemental sulfur is shown in Fig. 2d. Closed circles indicate the experimental results of Luo, which are fit by the first-order Birch EOS (solid line).⁷ The deviation of the present work from the result of Luo can be considered that the lattice is expanded due to hydrogenation of β -Po sulfur which is generated from the dissociation of H_2S . As shown in broken line, the calculated result of pressure dependence of V/V_0 in $SH_{1/27}$ which has β -Po structure is able to explain the experimental result.

The temperature dependencies of the electrical resistance of sulfur hydride and deuteride measured simultaneously with XRD patterns (Fig. 1a and 1b) are shown in Fig. 3a and 3b. The summary of the values of T_c in present and previous works are plotted in Fig. 3c. The present data agree with the previous data² above 133 GPa. T_c suddenly decreased from 123 GPa and settled down. It seems that a phase transition from high- T_c phase to low- T_c occurs. In fact, the resistance at room temperature also increases suddenly at the pressure (Fig. 3a), but no evidence of this structural phase transition is detected in XRD measurements.

As Drozdov and Fujihisa have reported in ref.,^{2,10} molecular hydrogen (H_2) was not observed in the sample chamber by both Raman scattering and XRD measurements. The crystal structures of main phase of sulfur hydride and sulfur deuteride have the bcc-lattice ordering of sulfur atom. Thus, it is conceivable that H_2S/D_2S molecular are decomposed into H_3S/D_3S molecular which has bcc structure and elemental sulfur by compression as predicted by theoretical work. We claim that the bcc structural H_3S/D_3S corresponds to high- T_c phase over 200 K. Note however that the dissociated H_2S/D_2S may supply a slight amount of hydrogen atom to sulfur, and the bcc-structural H_3S/D_3S lose the hydrogen atoms like atomic vacancy. Taking into account the present theoretical work, it is expected that the chemical reaction occurs as follows: $3H_2S \rightarrow 2H_{3-\delta}S + SH_{2\delta}$, ($2\delta \sim 1/27$). The investigation of the undefined minor phases is now going on.

Methods

The sample preparations in DACs are almost same setup with those of ref.² with diamond mount with wider diffraction angle. Angle-dispersive powder x-ray diffraction measurements were carried out in beamline BL10XU of the SPring-8. The sample in the DACs was irradiated using synchrotron radiation beams monochromatized to energy of 30.0 keV ($\lambda \sim 0.412 - 0.414 \text{ \AA}$). Simultaneous measurements of XRD and electrical resistance were carried out in D₂S at 173 GPa under low temperature region, 13 - 300 K. DAC set in a cryostat. Each diffraction pattern was recorded using an imaging plate with an exposure time between 120 and 300 seconds. The electrical resistance was measured by a commercial AC-resistance bridge (Linear Research Inc., LR-700) with four probe method.

We determined the amount of hydrogen impurity in β -Po sulfur by comparing pressure-volume curve between experiments and first-principles calculations. The Quantum ESPRESSO code¹¹ was utilized for the calculations based on the density functional theory, in which the Perdew-Burke-Ernzerhof generalized gradient approximation¹² was used for the exchange-correlation functional and the Vanderbilt ultrasoft pseudopotential¹³ was employed. We calculated the pressure-volume curve of β -Po sulfur with hydrogen impurity by setting a hydrogen atom in the supercell of sulfur and performing the structural optimization. The position of the hydrogen atom, the size of the supercell, and the number of k-points are as follows: (i) $(1/4, 1/4, 1/4)$, $2 \times 2 \times 2$ primitive cells, and $12 \times 12 \times 12$, and (ii) $(1/6, 1/6, 1/6)$, $3 \times 3 \times 3$ primitive cells, and $8 \times 8 \times 8$. The energy cut-off of the plane wave basis was set at 80 Ry.

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Author contributions

M.E. performed the whole XRD measurement and the data interpretation and writing the manuscript. M.S. performed the cryogenic operations and XRD data collections. K.S. performed the in situ electrical resistance measurements in XRD measurements and writing the manuscript. T.I. performed the support calculations for the data interpretation. M.I.E. designed the study and participated in XRD experiments. A.P.D. and I.A.T. prepared the sample in DAC for whole experiments. N.H. and Y.O. performed the optimization of synchrotron XRD and cryogenic operations. M.E., K.S. and M.I.E. contributed equally to this paper.

Competing financial interests

The authors declare that they have no competing financial interests.

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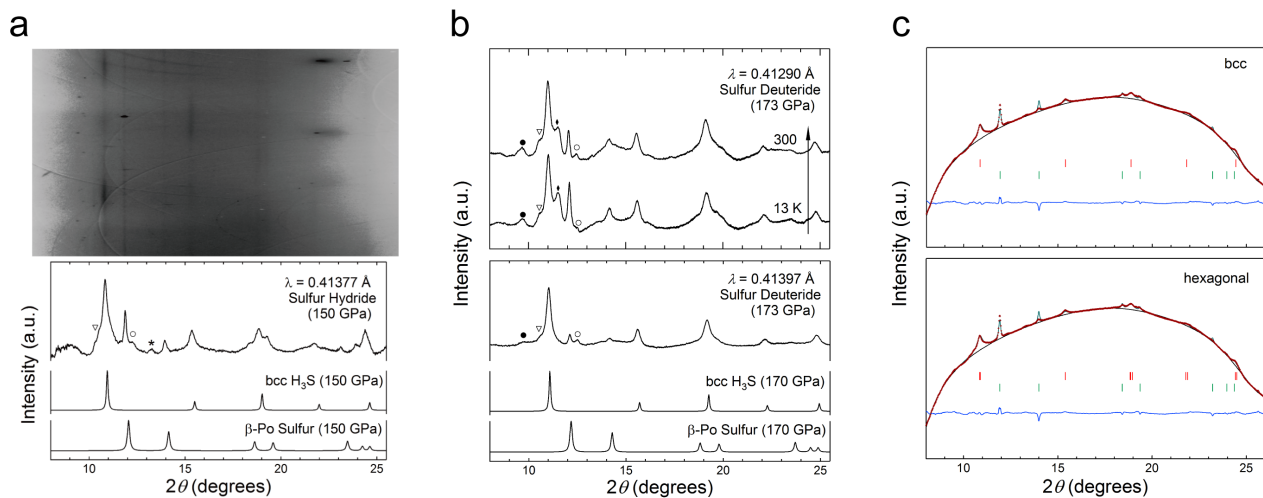


Figure 1. XRD measurement in sulfur hydride and sulfur deuteride systems. **a**, (top) Unrolled powder diffraction image of sulfur hydride at 150 GPa at room temperature recorded on imaging plate. These arcuate lines and dots come from the Kossel line from diamond anvils. (bottom) X-ray diffraction pattern which is obtained by integration of top, which excludes background. The marks of open triangle and star indicate the undefined minor phase. Open circle indicates the reflection from other high pressure phase. Calculated patterns of bcc H_3S and β -Po elemental sulfur at 150 GPa from ref.^{4,7} lie below. **b**, (top) Temperature dependence of XRD patterns of sulfur deuteride at 173 GPa. Dot and open triangle are reflection comes from undefined minor phase. Diamond are from gasket. Open circle indicates the reflections from other high pressure phases. (bottom) X-ray diffraction pattern at room temperature and 173 GPa which excludes background. **c**, Rietveld fit of diffraction pattern of Fig. 1a with bcc/hexagonal structural H_3S and β -Po elemental sulfur at 150 GPa and room temperature. Red Dots, green and black lines represent the observed, calculated intensity and back ground, respectively. Blue line at the bottom indicates the residual error. Top and bottom ticks are peak position of the reflection from H_3S and elemental sulfur, respectively.

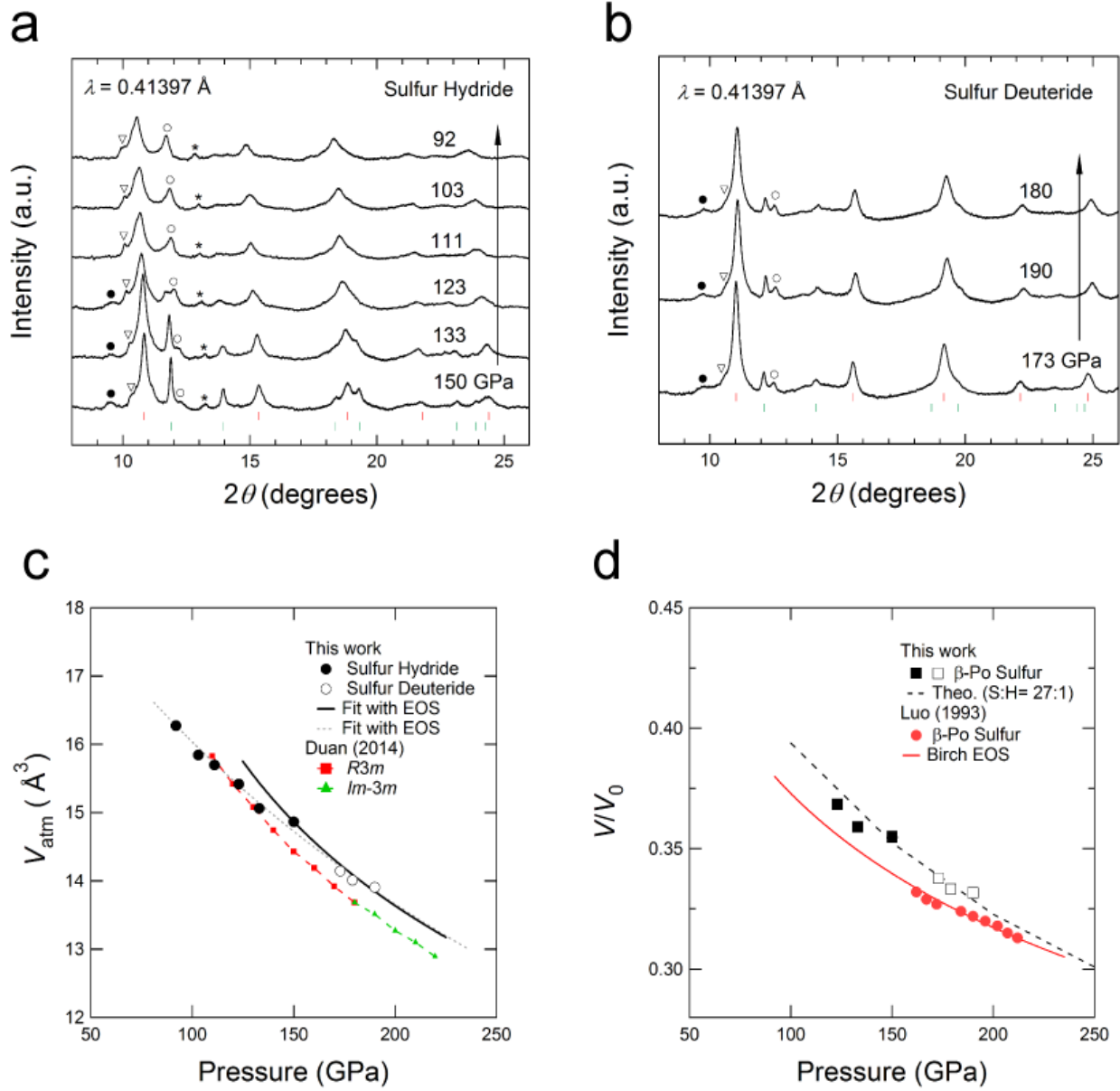


Figure 2. Pressure dependence of XRD patterns in sulfur hydride and sulfur deuteride systems. **a**, Pressure dependence in decreasing pressure of XRD patterns in pressurized sulfur hydride at room temperature. Upper (red) and lower (green) ticks indicates the peak position of predicted bcc structure and β -Po elemental sulfur, respectively. The peaks marked with dot and open triangle, and star are undefined minor phase. Open circles indicate the reflection from other high pressure phase. **b**, Pressure dependence in decreasing pressure of XRD patterns in pressurized sulfur deuteride at room temperature. Upper (red) and lower (green) ticks indicates the peak position of predicted bcc structure and β -Po structural elemental sulfur, respectively. The peaks marked with star are undefined peak. Dot and open circle indicate the reflection from other high pressure phase. **c**, Pressure dependence of the atomic volume of sulfur hydride and deuteride which are marked with solid and open symbol, respectively. Experimentally obtained data are fit with first-order Birch EOS indicated with the black solid line (increasing process) and dotted line (all). The theoretical predicted volumes of hexagonal ($R3m$) and bcc ($Im-3m$) structures are shown in solid square (■) and triangle (▲) with broken line, respectively.³ **d**, Pressure dependence of the normalized volume V/V_0 in β -Po structural elemental sulfur (■, □). Broken line indicates the simulated V/V_0 which contains 1/27 hydrogen atoms per a sulfur atom in the present work. Close circle indicates the experimentally obtained volume and solid line is the fitting curve with first-order Birch EOS with $B_0 = 30.6 \text{ GPa}$, $B_0' = 6$, $V_0 = 25.64 \text{ \AA}^3$ in ref.⁷

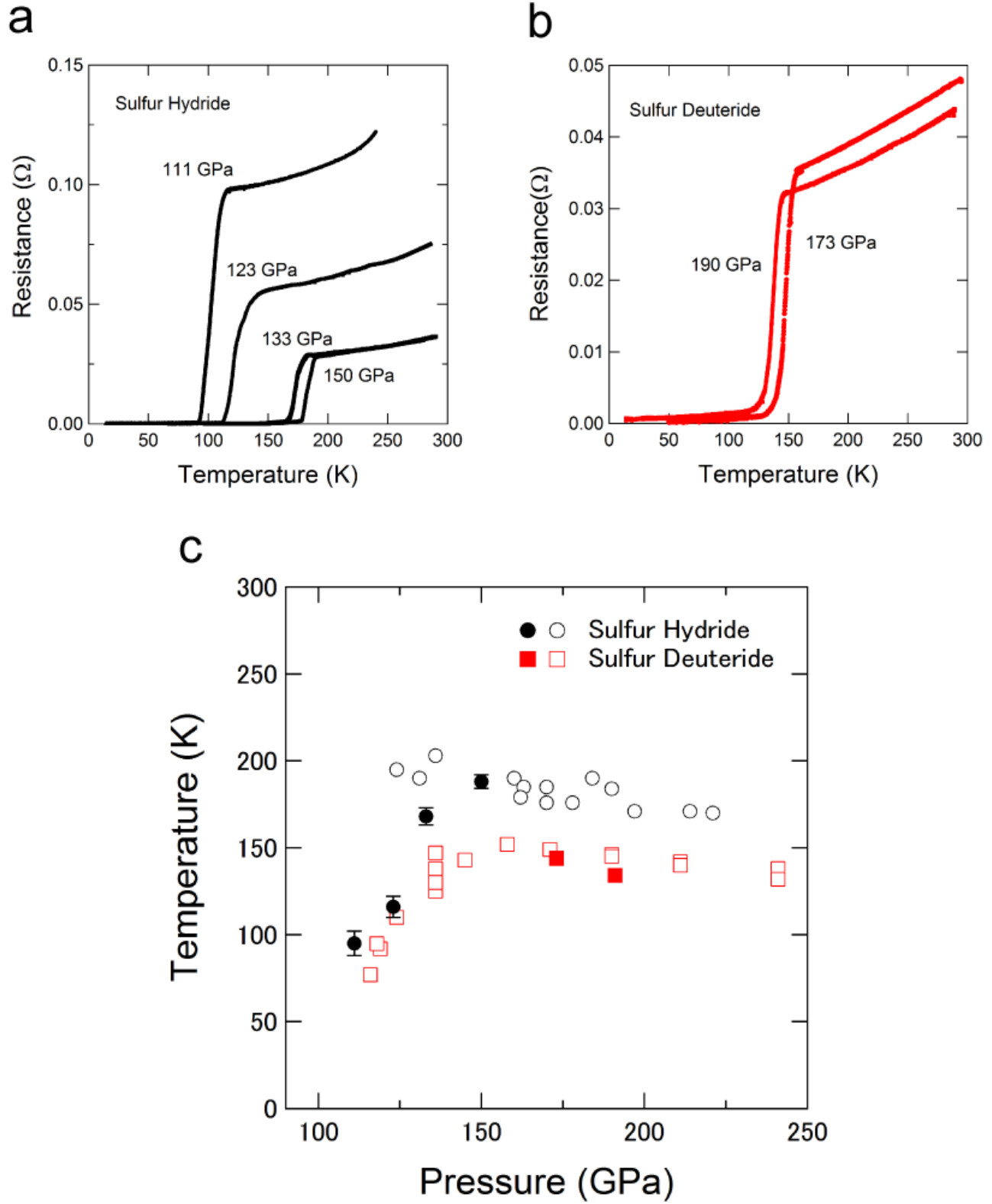


Figure 3. Pressure dependence of T_c in sulfur hydride and sulfur deuteride. **a**, Temperature dependence of resistance in sulfur hydride on heating process. **b**, and sulfur deuteride. **c**, Pressure dependence of T_c of sulfur hydride and sulfur deuteride which are marked with circle and square symbol, respectively. Open circles, square and triangles are obtained in increasing pressure process.² Closed circles and squares are the data in increasing and decreasing pressure that of this work, respectively.