

Lawrence Berkeley National Laboratory

Recent Work

Title

HIGH PRESSURE INVESTIGATION OP SULFUR

Permalink

<https://escholarship.org/uc/item/3r8636xc>

Authors

Harris, Robert E.
Jura, George.

Publication Date

1965-04-01

University of California
Ernest O. Lawrence
Radiation Laboratory

HIGH PRESSURE INVESTIGATIONS OF SULFUR

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted as a Chapter in the
Proceedings of 1964 Sulfur
Conference

UCRL-16075

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

HIGH PRESSURE INVESTIGATIONS OF SULFUR

Robert E. Harris and George Jura

April, 1965

High Pressure Investigations of Sulfur

Robert E. Harris and George Jura

Department of Chemistry, and Inorganic Materials Research Division,
Lawrence Radiation Laboratory, University of California
Berkeley, California

Abstract

The high pressure investigations on sulfur are reviewed. The only unusual property exhibited by sulfur under pressure is the transformation to the rubbery form when the crystals are subjected to shear under pressure, presumably at pressures as low as 10 kbars. The electrical properties show that the energy gap in sulfur decreases with pressure, but that the element has not been found to become metallic even at pressures as high as 400 kbars.

A number of measurements have been made on sulfur to high pressures and somewhat elevated temperatures. Both static and dynamic methods of generating the pressure have been used. The present paper is a review of the available data and the presentation of the measurements of the electrical resistance made by the present authors. Insofar as high pressure measurements have been made, sulfur has shown no properties or behavior that make the investigation of this element particularly interesting. It does not exhibit an abnormally high compressibility such as those of the alkali metals, nor as low as the incompressible metals such as beryllium or uranium. No one has found any polymorphic modification with a variation in pressure. In short, with one exception, to be discussed later, sulfur shows a continuous variation with pressure of all of its properties, and the variation is neither sufficiently great nor small to distinguish it from the great bulk of elements or compounds.

Volume measurements: Rather extensive pressure-volume measurements were made by Bridgman. At room temperature, the highest pressure at which determinations were made was 98 kbars.¹ Measurements were made at 125° C up to pressures of 49 kbars.² He also investigated the directional effect of the rhombic structure to pressures of 11.8 kbars.³ None of these measurements showed any indication of any change in the crystal structure of sulfur. At room temperature, there was a 27.4% decrease in volume at 98 kbars. This volume decrement is only slightly larger than that observed for the alkaline earth metals. Bridgman also observed that the compressibility in the plane of the rhombic faces to be larger than in the direction normal to this plane. He has made many other volume measurements on

sulfur, but the results of the other determinations are in accord with the three references cited. The pressure-volume determinations to 98 kbars are given in Table I.

Table I.

Volume of Sulfur as a Function of Pressure at Room Temperature

$P(\text{Kg cm}^{-2})^*$	$\Delta V/V_0$
0	0.000
10,000	0.083
20,000	0.131
30,000	0.163
40,000	0.188
50,000	0.208
60,000	0.225
70,000	0.240
80,000	0.253
90,000	0.264
100,000	0.274

Shear strength: In addition to the compressibility, Bridgman also investigated the shear strength of elemental sulfur as a function of pressure. In these experiments the material under study was placed between movable and fixed discs, and the force required to rotate a disc with respect to a fixed disc was measured. The minimum force required to rotate the disc was then related to the shear strength of the material.

* $(\text{Kg cm}^{-2}) = .9806 \text{ kbar}$

These experiments were carried out to pressures of 49 kbars.⁴ The results are reproduced in Table II.

Table II.

Shear Strength of Sulfur as a Function of Pressure

Pressure (Kg cm ⁻²)	Shear Stress (Kg cm ⁻²)
10,000	1,840
20,000	3,300
30,000	4,700
40,000	6,000
50,000	7,100

Apart from an expected increase in shear strength, there is no indication of any phase transition in sulfur. The apparatus was loaded with crystalline sulfur. The material that was recovered was "sticky, like amorphous sulfur". Bridgman noted that since the same curves for shear were obtained at increasing and decreasing pressure, the transformation to the amorphous form must have occurred at a low pressure. This transformation to the amorphous form is certainly worthy of comment. It is also unique in that such a transformation is not noted for any other material that has been investigated. At the present time, there is no reasonable explanation for this transformation. Bridgman made several other investigations of the shear properties of sulfur, and the results are in agreement with those which have been quoted. The technique used to measure the shear may have some interesting applications which have not as yet been reasonably explored.

Bridgman observed that when sulfur and copper were mixed in the apparatus that a detonation ensued at 20 kbars. The product that was recovered was black indicating the formation of copper sulfide. The transition to the amorphous form of sulfur and the reaction of sulfur with copper when the apparatus is at ambient temperature almost certainly indicates that the local temperature in the system under shear must be considerably above that of the surrounding air. Since the charge is small compared to the apparatus for making the determinations, it is possible to develop a high temperature in the sample for a short period of time without appreciably changing the temperature of the container. If such a temperature increase occurs when the sulfur is sheared under pressure, it becomes possible to understand these two observations.

Electronic Structure: Two techniques have been used to seek any possible electronic change in solid sulfur, electrical resistance and optical measurements. The electrical resistance measurements show that there is no detectable change by this measurement. The optical measurements again indicate that there is only a change in the magnitude of the gap between the valence and conduction bands.

Haman^{5,6} has investigated the electrical resistance of sulfur using shock waves. He observed that at about 230,000 atm. the resistance of the sample became less than 0.03 ohm cm, the limit of the sensitivity of his equipment. Although his sensitivity was not sufficiently good to measure a resistance which could be uniquely identified with the metallic state, Haman suggested that the sulfur might have reached the metallic state. His reasoning was based on the fact that phosphorous became metallic at a pressure somewhat over 100 kbars, and that iodine certainly

approached this state.⁷ It was this statement which instigated our investigation of the resistivity of sulfur.

The techniques that were used in this investigation are fully described in Ref. 7. The specific resistance of sulfur is very high, and ordinary resistance measurements are not applicable for a determination of the resistance of sulfur. The instrumentation necessary to determine high resistances such as that of sulfur has not been developed where it can be used in high pressure determinations. Consequently, the actual resistance measurements have little or no significance. However, if there had been a change to the metallic state, or to a semiconductor with a low gap energy, it would have been simple to determine the pressure at which such a change occurred. Thus, even though the individual resistance measurements are incorrect, if a change had occurred to where the resistance measurements were significant, it could be unequivocally stated that a phase change had occurred. The sulfur used in the experiments was supposedly 99.999% pure. The sulfur was used as received, and also it was heated to form the rubbery sulfur.

Since phosphorous,⁷ selenium,⁸ and tellurium⁹ become metallic under pressures that are accessible, it is not unreasonable to make similar measurements to determine whether the metallic transition is also accessible for sulfur. Our measurements on ordinary and μ sulfur were negative even though the pressures studied extended to 400 kbars. The only statement we can make as a result of our work is that at all pressures, for both forms of sulfur, the specific resistance is over 10^7 ohm cm.

These results are not necessarily in contradiction to the low figure quoted by Haman at 230,000 atm. It must be remembered that the shock measurements are made under adiabatic conditions and that the temperature is increased. Since the resistance of a semiconductor decreases exponentially with an increase in temperature, the two sets of data can be in complete accord. Thus electrical conductivity indicates that there are no major electronic changes in sulfur.

Slykhouse and Drickamer¹⁰ have determined the change in the gap energy of sulfur as a function of pressure by spectroscopic methods. Their measurements extend to about 160 kbars. At this pressure, the instrumentation became too insensitive for the determination of the band edge. They found that the gap decreased linearly with pressure to about 100 kbars. They found the decrease in the gap to be 7.2×10^{-6} ev atm⁻¹ in this pressure region. Above this pressure, the gap begins to decrease more slowly with pressure. At the maximum pressure at which they made the measurements, the gap has been reduced to 60% of its value at one atmosphere.

When these authors plotted the change in gap as a function of volume instead of pressure, they found a very strong volume dependence. By extrapolating their gap measurements, and using Bridgman's volume data to 100 kbars, they estimated that sulfur would become a metal at a pressure of 400-500 kbars at room temperature.

The three different determinations which are related to the electronic structure of rhombic sulfur are not in contradiction. The only conclusion that can certainly be reached from the present data is that there is no electronic change in sulfur in the pressure-temperature region so far investigated.

Acknowledgment

This work was performed under the auspices of the United States Atomic Energy Commission.

References

1. Bridgman, P. W., Proc. Amer. Acad. Arts and Sci., 76, 1 (1945).
2. Bridgman, P. W., Proc. Amer. Acad. Arts and Sci., 72, 207 (1938).
3. Bridgman, P. W., Proc. Amer. Acad. Arts and Sci., 62, 207 (1927).
4. Bridgman, P. W., Proc. Amer. Acad. Arts and Sci., 71, 387 (1937).
5. Haman, S. D., Australian Journal of Chemistry, 11, 391 (1958).
6. David, H. G., and Haman, S. D., J. Chem. Phys., 28, 1006 (1958).
7. Harris, R. E., Valsnys, R. J., Stromberg, H., and Jura, G.,
"Resistance and Thermal Gap Measurements to 400,000 atmospheres"
in Progress in Very High Pressure Research, Bundy, F. P.,
Hibbard, W. R., Jr., and Strong, H. M., eds. John Wiley and Sons,
New York, 1961.
8. Riggleman, B. M., and Drickamer, H. G., J. Chem. Phys. 37, 446 (1962).
9. Bridgman, P. W., Proc. Amer. Acad. Arts and Sci., 81, 165 (1952).
10. Slykhouse, T. E., and Drickamer, H. G., J. Phys. and Chem. of Solids,
7, 275 (1958).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

