Miller, Kleinman, and Savage.[3]) Also, it should be noticed that for ZnS which occurs with zinc blende as well as hexagonal structure, the largest of the nonlinear coefficients, i.e., d_{14} for zinc blende ZnS and d_{33} for hexagonal ZnS, are nearly equal.

Trigonal-crystal selenium (space group $P3_{1,2}21$) is somewhat more interesting as compared with the crystals discussed above because phase matching is possible. (Thus Se is the second such nonlinear crystal at 10.6 μ, the first being Te.[1]) No reliable dispersion curves or birefringence data exist for single-crystal selenium other than data of Caldwell and Fan.[7] Phase matching was achieved at $\theta_m \approx 10°$ with the fundamental E vector polarized in the yz plane at θ_m from the y axis. Then the second harmonic is polarized along the x axis. [See Eq. (1) of Ref. 1 for an explanation.] Because of the large birefringence ($n^o = 2.78 \pm 0.02$, $n^e = 2.58 \pm 0.02$),[7] phase-matched SHG and other parametric experiments can be carried out up to wavelengths as short as 8000 Å. The accuracy of the nonlinear coefficient measurement for selenium is poor (possible error ~50%) because large single-crystal samples of Se are difficult to obtain.

The author thanks A. Ashkin, G. D. Boyd, and R. C. Miller for critical comments on the manuscript, R. J. Kerl for skilled technical assistance, and A. Albert and V. C. Wade for polishing the crystals.

---

[1] C. K. N. Patel, Phys. Rev. Letters, 15, 1027 (1965).

[2] J. Ducuing and N. Bloembergen, Phys. Rev. Letters 10, 474 (1963); R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Letters 15, 415 (1965); see also N. Bloembergen, Nonlinear Optics (W. A. Benjamin, Inc., New York, 1965), p. 135.

[3] R. C. Miller, D. A. Kleinman, and A. Savage, Phys. Rev. Letters 11, 146 (1963); see also R. Soref and W. P. Moos, J. Appl. Phys. 35, 2152 (1964).

[4] C. K. N. Patel, P. K. Tien, and J. H. McFee, Appl. Phys. Letters 7, 290 (1965); D. Moeller and J. D. Rigden, Appl. Phys. Letters 7, 276 (1965); and references cited therein.

[5] M. A. Kovacs, G. W. Flynn, C. K. Rhodes, and A. Javan, Bull. Am. Phys. Soc. 11, 128 (1966).

[6] J. T. Yardley and C. B. Moore, Appl. Phys. Letters 7, 311 (1965).

[7] R. S. Caldwell and H. Y. Fan, Phys. Rev. 114, 664 (1959); see also J. S. Blakemore, D. Long, K. C. Namura, and A. Nussbaum, in Progress in Semiconductors, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1962), Vol. VI, pp. 37-84.

[8] P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Letters 8, 21 (1962).

[9] G. D. Boyd and C. K. N. Patel, to be published.

[10] O. G. Lorimor and W. G. Spitzer, J. Appl. Phys. 36, 1841 (1965).

[11] R. C. Miller, Appl. Phys. Letters 5, 17 (1965).

[12] D. A. Kleinman, Phys. Rev. 126, 1977 (1962).

CRYSTAL STRUCTURE OF DEUTERIUM AT LOW TEMPERATURES*

A. F. Schuch and R. L. Mills
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

(Received 2 March 1966)

Previous structure determinations of normal deuterium are in apparent conflict. Kogan and co-workers[1] analyzed their earliest x-ray and neutron diffraction measurements at helium temperatures in terms of a body-centered tetragonal (bct) structure. Their latest x-ray studies,[2] however, suggest a structure which is hexagonal closest packed (hcp). Curzon and Pawlowicz[3] obtained electron diffraction patterns at about 7°K which they indexed on the basis of a face-centered cubic (fcc) lattice. Mucker and collaborators[4] at Ohio State recently reported neutron diffraction studies of deuterium at 13°K which clearly show the hcp structure.

The disagreements may have arisen because some of the studies[2,4] were made on bulk solid condensed in a cell and others[1,3] were made on thin layers of deuterium condensed on cold substrates. These substrates apparently cause crystallites to form with preferred orientations such that the intensities of the diffraction lines are altered. Recently it was discovered[5,6] that the structure of hydrogen near 1.3°K can be either fcc or hcp, depending upon the ortho-para ratio. The question of whether deuterium has a similar phase change prompted the present study by x-ray diffraction of solid deuterium.

In the hydrogen work, the temperature of the structure change was found to decrease with decreasing concentration of orthohydrogen (lowest rotational level $J = 1$) and to occur near the λ anomaly in specific heat.[7] An analogous specific-heat λ anomaly[8] occurs in solid deuterium when the concentration of paradeuterium (lowest rotational level $J=1$) exceeds about 60%. It seemed desirable, therefore, to investigate the structure of solid deuterium in the neighborhood of its λ anomaly.

Enriched paradeuterium was prepared in a two-stage apparatus, similar to that of Cunningham, Chapin, and Johnston,[9] by selective adsorption of n-D_2 on alumina at liquid-hydrogen temperature. Compositions in the range of 33 to 65% paradeuterium were produced. Gas samples were analyzed for para content with a Grilly-type[10] thermal conductivity bridge. The analyzer was calibrated with mixtures of n-D_2 (33.3% para), 75°K equilibrium D_2 (29.3% para), and 19.4°K equilibrium D_2 (1.8% para). Enriched samples were diluted with 19.4 or 75°K deuterium until they fell within the calibrated range. With this technique, changes of 0.5% in para concentration could be observed, but the absolute concentration was known only to about ± 2% out of 65%. Although enriched paradeuterium could be stored at room temperature for a month in copper cylinders at ~50 psi (gauge) without measurable change in composition, the para content decreased from 65 to about 61.5% when solid D_2 was held for 6 h at helium temperature in the x-ray apparatus. To establish gas purity, a mass spectrographic analysis was made which showed only 0.38% HD present in the enriched D_2.

The x-ray apparatus and cryostat were those used in the hydrogen work.[6] The deuterium specimens were solidified in a short beryllium cell of 0.8-mm bore by 0.4-mm wall. Filtered radiation from iron and copper targets was used and 44-deg oscillation photographs were taken with a cylindrical camera at exposure times of from 3 to 12 h. The previous filling technique[6] was altered to permit low-pressure D_2 to condense in the Be cell. After the sample gas was admitted to the cell at ~50 psi (gauge) and 75°K, the inlet capillary was heated electrically, whereupon liquid He was transferred into the cryostat. A subsequent drop in D_2 pressure to about zero indicated that the capillary remained unplugged while gas liquefied and solidified in the cell. The cryostat was quickly pumped down to operating temperature, usually below 1.5°K, and the solid D_2 was allowed to equilibrate for about one hour before exposure to the x-ray beam. The addition of a Roots blower to the He pumping system made it possible to attain bath temperatures as low as 0.95°K. Several experiments were carried out around 18°K with a liquid-hydrogen bath. When samples were collected for analysis of para content following an x-ray exposure, gas in the filling line was first pumped away before the solid D_2 specimen in the Be cell was vaporized and collected.

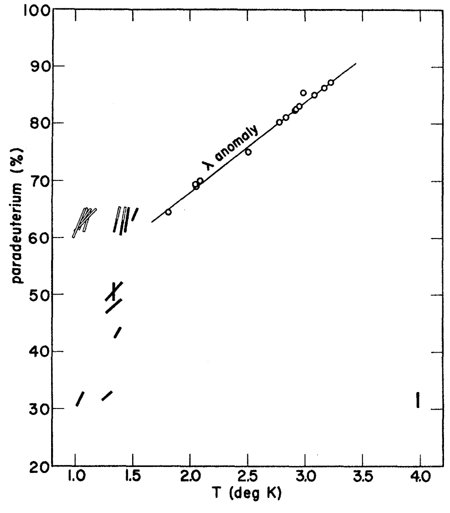

FIG. 1. Crystal structure of D_2 at zero pressure as a function of temperature and para concentration. Open bars signify fcc structure; solid bars, hcp structure; open and solid bars indicate both structures observed; open circles are data of Grenier and White (Ref. 8) showing λ anomaly in specific heat.

Altogether 23 photographs were made under various conditions of para concentration and temperature. As in the H_2 case, the diffraction photographs of D_2 showed a series of spots, not continuous lines, indicating that the solid was a conglomeration of crystallites. The deduced structures were sometimes hcp and sometimes fcc and, in several cases, diffraction patterns from both crystal forms were observed on a film. The results are plotted in Fig. 1 together with the locus of the λ anomaly in specific heat.[8] For 60-65% paradeuterium, the structure changed from hcp to fcc below about 1.4°K. At para concentrations of 52% and less the structure was hcp. Photographs of n-D_2 made at 17 and 19.4°K also gave the hcp structure.

Average values of the observed interplanar spacings d, the cell dimensions a and c, and the molar volume $\bar{V}$ derived therefrom are listed in Tables I and II for each structure. The cell dimensions for the hcp lattice were determined from a least-squares fit of eight

Table I. Deuterium hcp data from five photographs taken between 1.40 and 1.50°K with copper radiation.

hkl	d(obs) (Å)	d(calc) (Å)
100	3.110	3.117
002	2.938	2.929
101	2.750	2.752
102	2.142	2.135
110	masked	1.800
103	1.652	1.655
112	1.536	1.533
201	1.506	1.506
202	1.375	1.376

$a = 3.600 \pm 0.004$ Å, $c = 5.858 \pm 0.007$ Å, $c/a = 1.627$
$\bar{V} = 19.79$ cc/mole

interplanar spacings. Values of d(calc) were computed from the fitted dimensions. For hcp D_2 the 110 reflection was masked by a diffraction line from the Be cell. Similarly, the fcc 220 reflection could not be observed.

Within experimental error, the computed molar volumes for the two structures in Tables I and II are not significantly different. However, they are both almost 1.5% larger than the value 19.51 cc/mole which is interpolated from pycnometer data listed by Woolley, Scott, and Brickwedde[11] for n-D_2 at $p = 0$ and $T = 1.4$°K. Molar volumes computed from the present x-ray photographs made at 17 and 19.4°K likewise were 1.5% larger than the volumes of Woolley, Scott, and Brickwedde.[11] The neutron diffraction data[4] at 13°K also gave a molar volume that was larger than the pycnometer value,[11] but only by about 0.5%. There seemed to be no trend in the hcp molar volume with para concentration, within the rather large scatter of ±0.2 cc/mole for individual photographs.

Investigations of the crystal structure changes of hydrogen and deuterium are continuing.

Table II. Deuterium fcc data from six photographs taken between 0.95 and 1.40°K with copper radiation.

hkl	d(obs) (Å)	a (Å)
111	2.932	5.078
200	2.537	5.074
220	masked	
131	1.534	5.087
222	1.468	5.085

Average cell edge = 5.081 ± 0.006
$\bar{V} = 19.75$ cc/mole

---

*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] V. S. Kogan, B. G. Lazerov, and R. F. Bulatova, Zh. Eksperim. i Teor. Fiz. 31, 541 (1956); 37, 678 (1959) [translations: Soviet Phys.—JETP 4, 593 (1957); 10, 485 (1960)]. R. P. Ozerov, V. S. Kogan, G. S. Zhdanov, and O. H. Kuto, Kristallografiya 6, 631 (1961) [translation: Soviet Phys.—Cryst. 6, 507 (1962)]. V. S. Kogan, B. G. Lazerov, R. P. Ozerov, and G. S. Zhdanov, Zh. Eksperim. i Teor. Fiz. 40, 1022 (1961) [translation: Soviet Phys.—JETP 13, 718 (1961)]. R. P. Ozerov, V. S. Kogan, G. S. Zhdanov, and B. G. Lazerov, J. Phys. Soc. Japan 17, Suppl. B-II, 385 (1962).

[2] V. S. Kogan, A. S. Bulatov, and L. F. Yakimenko, Zh. Eksperim. i Teor. Fiz. 46, 148 (1964) [translation: Soviet Phys.—JETP 19, 107 (1964)].

[3] A. E. Curzon and A. T. Pawlowicz, Proc. Phys. Soc. (London) 83, 499, 888 (1964).

[4] K. F. Mucker, S. Talhouk, P. M. Harris, David White, and R. A. Erickson, Phys. Rev. Letters 15, 586 (1965).

[5] M. Clouter and H. P. Gush, Phys. Rev. Letters 15, 200 (1965).

[6] R. L. Mills and A. F. Schuch, Phys. Rev. Letters 15, 722 (1965).

[7] G. Ahlers and W. H. Orttung, Phys. Rev. 133, A1642 (1964).

[8] G. Grenier and David White, J. Chem. Phys. 40, 3015 (1964).

[9] C. M. Cunningham, D. S. Chapin, and H. L. Johnston, J. Am. Chem. Soc. 80, 2382 (2382 (1958).

[10] E. R. Grilly, Rev. Sci. Instr. 24, 72 (1953).

[11] H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. 41, 379 (1948).