bacterium, which correlates with recent 16S ribosomal RNA analysis (16). The diols also reveal a new molecular marker for assessing phylogenetic and biogeochemical relationships of prokaryotes.

REFERENCES AND NOTES

- H. Goldfine, in Current Topics in Membranes and Transport, S. Razin and S. Rottom, Eds. (Academic Press, New York, 1982), vol. 17, pp. 1-43.
 T. A. Langworthy, *ibid.*, pp. 45-77.
 , in The Bacteria, C. R. Woese and R. S. Wolfe, Eds. (Academic Press, New York, 1985), vol.
- 8, pp. 459-497. O. Kandler, Ed., Archaebacteria (Springer, New York. 1082).
- T. J. Jackson, R. F. Ramaley, W. G. Meinschein, 5.
- Int J. Syst. Bacteriol. 23, 28 (1973).
 G. J. Merkel, D. R. Durham, J. J. Perry, Can. J. Microbiol. 26, 556 (1980).

- 7. E. G. Bligh and W. J. Dyer, Can. J. Biochem. 37, 911
- G. D. B. L. (1959).
 T. A. Langworthy, *Methods Enzymol.* 88, 396 (1982).
 _____, G. Holzer, J. G. Zeikus, T. G. Tornabene, *Syst. Appl. Microbiol.* 4, 1 (1983).
 V. R. Wheatley and A. T. James, *Biochem. J.* 65, 36

- (1957).
 II. T. A. Langworthy, W. R. Mayberry, P. F. Smith, Biochim. Biophys. Acta 431, 550 (1976).
 I2. O. Wieland, in Methods of Enzymatic Analysis, H. U. Bergmeyer, Ed. (Academic Press, New York, 1965),
- pp. 211–214. T. A. Langworthy, Biochim. Biophys. Acta 487, 37 13.
- I4.
- (1977).
 P. E. Kolattukudy, in *The Biochemistry of Plants*, P. K. Stumph and E. E. Conn, Eds. (Academic Press, New York, 1980), vol. 4, pp. 571–645.
 D. H. S. Horn and F. W. Hougen, *J. Chem. Soc.*
- J. D. A. S. Arbit and T. W. Houget, J. Comm. Soc. 1953, 3533 (1953).
 J. Gibson, W. Ludwig, E. Stackebrandt, C. R. Woese, Syst. Appl. Microbiol. 6, 152 (1985).
 G. Holzer, J. Oro, T. G. Tornabene, J. Chromatogr. 20 (2017).
- 186, 795 (1979)
- 18. For example, the alkane derivative, derived from the

branched C22 diol, showed a molecular ion at a mass-to-charge ratio (m/e) = 310. The enhanced olefin peaks at m/e = 112 and 224 identified the compound as 7-methyleicosane. A 7,14-dimethylcosane could generate a similar spectrum, but the alkane from the corresponding monoalcohol showed enhanced peaks only at m/e = 112 and 210, not at m/e = 224 and 98, as would be expected. The m/e = 210 fragment confirmed also the position of the -OH groups in the diol. The observed shift of 14 amu in the spectrum of the alkane from the monoalcohol indicated that the –OH-bearing car-bon was lost from the long end of the branch. Thus, is-methyl-1.2-eicosanediol was the structure of the original diol.

Supported in part by a Senior U.S. Scientist prize from the Alexander von Humboldt Stiftung to T.A.L. and American Chemical Society grant PRF-13239 to G.H. We thank V. Menath and T. Wilharm for assistance and K. O. Stetter for advice and use of facilities during portions of this work.

18 July 1985; accepted 1 November 1985

Crystal Structures at Megabar Pressures Determined by Use of the Cornell Synchrotron Source

YOGESH K. VOHRA, KEITH E. BRISTER, SAMUEL T. WEIR, STEVEN J. DUCLOS, ARTHUR L. RUOFF

X-ray diffraction studies have been carried out on alkali halide samples 10 micrometers in diameter (volume 10^{-9} cubic centimeter) subjected to megabar pressures in the diamond anvil cell. Energy-dispersive techniques and a synchrotron source were used. These measurements can be used to detect crystallographic phase transitions. Cesium iodide was subjected to pressures of 95 gigapascals (fractional volume of 46 percent) and rubidium iodide to pressures of 89 gigapascals (fractional volume of 39 percent). Cesium iodide showed a transformation from the cubic B2 phase (cesium chloride structure) to a tetragonal phase and then to an orthorhombic phase, which was stable to 95 gigapascals. Rubidium iodide showed only a transition from the low-pressure cubic B1 phase (sodium chloride structure) to the B2 phase, which was stable up to 89 gigapascals.

-RAY DIFFRACTION STUDIES ON MAterials subjected to high pressures provide direct information about pressure-induced crystallographic phase transitions and allow measurement of pressure-volume relations (equation of state). Diamond-window, high-pressure cells have been used for x-ray diffraction studies on a variety of materials because diamonds are transparent to x-rays above 10 keV. X-ray diffraction studies in the megabar pressure range have been carried out with conventional x-ray sources (1, 2). In these studies, film techniques were used to record diffraction patterns; x-ray collimators of 50 to 150 µm are typically used, and the data collection time is 100 to 400 hours for each pressure.

Ultrahigh pressures have been generated in the diamond anvil cell, and recently static

pressures of 2.8 Mbar have been measured (3, 4) on stainless steel and ruby crystal composites. Large pressure gradients are present across the sample region between the two single-crystal diamonds, and in some situations (3, 4) gradients of 3 GPa/µm have been measured. These pressure gradients limit the maximum pressures attainable in the diamond anvil cells and also affect the quality of the x-ray diffraction data obtained. They also give rise to diffraction line-broadening in x-ray experiments, and the effect is pronounced in compressible materials. Pressure gradients can be reduced and the state of stress can be made relatively hydrostatic if a soft pressure-transmitting medium such as a rare gas solid is used. However, using such a medium somewhat reduces the maximum attainable pressures. It is important to develop experimental techniques that can be used to measure physical properties on small areas (10 µm diameter or 75 μ m²) so that the state of stress is homogeneous in the sample region.

The energy-dispersive diffraction technique coupled with a high-brilliance synchrotron source can be used to perform very rapid diffraction studies of samples in the diamond anvil cell (5). The Cornell High Energy Synchrotron Source (CHESS) is particularly suitable for this type of work because at normal operating conditions (beam energy 5 GeV; beam current 30 mA) it is an intense x-ray source in the spectral region from 10 to 50 keV (6). We have modified the experimental technique of Baublitz et al. (7) and have used an energydispersive technique at CHESS. The essential improvement is in the collimator system, where a stainless steel tube with a lead pinhole is located close to the table of the diamond (about 15 mm from the sample) and is adjusted with motor-driven motion in the two directions perpendicular to the beam. The pinhole is driven by a computer with a video display of the collimator position and can be moved with a precision of 0.2 µm. The adjustment and alignment procedures allow rapid optimization of the sample signal. Using this system, we have been able to record diffraction patterns with a pinhole 10 µm in diameter (sample volume less than 10^{-9} cubic centimeter). This volume is 0.05 to 0.1 of that used in earlier x-ray experiments. With the new collimator system, it is also possible to measure the pressure gradients across the diamond anvil face by x-ray techniques.

The alkali halides have been the subject of extensive study under high pressure because of the possibility of observing transitions from insulator to metal in some of these compounds with the present megabar capability of the diamond anvil cell. Cesium iodide (CsI) and rubidium iodide (RbI), which have band gaps of 6.4 and 6.1 eV, respectively, at ambient pressure, are highly

Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853.

compressible and are considered prime candidates for such changes. The interest in the high-pressure studies on CsI is further motivated by the fact that this compound undergoes phase transitions to noncubic crystal structures (8-12). It is now known that CsI, CsBr (13, 14), and CsCl (15) undergo a cubic-to-tetragonal phase transition under high pressures without significant change in volume (16). At the phase transition, the basis of Cs^+ at (0, 0, 0) and I^- at (1/2, 1/2, 1/2)1/2) remain unchanged; the Bravais lattice, however, changes from cubic to tetragonal. For CsI, this phase transition occurs at ~ 38 GPa. Asaumi (11) also noted the broadening of the (101) diffraction peak of the tetragonal phase in CsI, which he attributed to the formation of the orthorhombic phase at 56 GPa. Since he observed the apparent splitting of only one peak, evidence in support of the occurrence of the orthorhombic phase remained inconclusive. It is also of interest to know whether the tetragonal phase occurs in rubidium halides under high pressures or whether this phenomenon is restricted to cesium salts.

Samples of these alkali halides (25 or 50 μ m in diameter) were placed in the sample holes of the stainless steel gasket, which were made by microdrilling techniques. The diamond flats were 200 or 300 μ m in diameter. Platinum powder was mixed with the samples to provide an internal pressure marker via the isothermal equation of state



Fig. 1. The splitting of the CsI (110) diffraction peak in the tetragonal phase at 42.4 GPa and in the orthorhombic phase at 73.1 GPa. The relative intensities of the diffraction peaks in the orthorhombic phase are affected by the texture effects discussed in the text. The data were taken with a 10-µm pinhole. The upper curve is the fit of two Gaussian distributions to the data; the lower curve, of three Gaussian distributions.



Fig. 2. Energy-dispersive x-ray diffraction pattern from CsI at a pressure of 81 GPa taken with a 25- μ m pinhole. Seven diffraction peaks from the orthorhombic phase of CsI and three peaks from the platinum marker are indexed. The unlabeled peak at 21 keV is an escape peak from the intrinsic germanium detector.

of platinum (17). Both CsI and RbI are good scatterers of x-rays because of the large number of electrons, and both give good diffraction patterns. The typical data collection time at each pressure was 30 minutes for the cubic phase and 1 hour or more for noncubic structures. We used large diffraction angles $(2\theta = 21^\circ)$ in these experiments in order to observe more diffraction peaks.

For CsI, (110), (200), (211), (220), and (310) diffraction peaks were observed in the cubic B2 phase at low pressures. At pressures of 20 GPa and above, the (200) peak becomes weak (18) and is known to disappear under hydrostatic conditions if argon (19) or xenon (20) is used as a pressure medium. At \sim 38 GPa, the (110) and (211) peaks of the cubic phase first broadened and then split into two peaks. The splitting of the (110) peak into (101) and (110) peaks of the tetragonal phase is shown in the upper curve of Fig. 1. The relative intensity ratio of the (101) and (110) peaks at this pressure is approximately 2:1, as it should be on the basis of the multiplicity of the diffraction planes.

At higher pressure (~50 GPa), the (110) peak increased in intensity. From this we infer the development of texture, with the c axis of the tetragonal phase tending to orient in the plane of the diamond anvil. The peculiar nature of the texture in the CsI sample can be qualitatively understood as follows. After the tetragonal phase transition, the c axis increases with increasing pressure and therefore tends to align normal

to the maximum compressive stress direction. At ~56 GPa, the (101) and (121) peaks of the tetragonal phase first broadened and then split into two peaks. The lower curve in Fig. 1 shows the details of the (110)-related peaks in the orthorhombic phase. Figure 2 shows the full diffraction pattern at 81 GPa; the seven diffraction peaks from CsI and the three peaks from the platinum marker are well resolved. The CsI peak labeled (202) appears after the orthorhombic transition, an indication that the (022) peak of the tetragonal phase also splits at the orthorhombic phase transition.



Fig. 3. Interplanar spacings for various diffraction peaks as a function of pressure for CsI.

REPORTS 1137



1.0

Fig. 5. The measured equation of state for RbI to 89 GPa. The data shown are for the B2 phase, and the curve is the fit of the Birch first-order equation to the data with parameters listed in the text.



Figure 3 shows the interplanar spacings d(shift of diffraction peaks) as a function of pressure. The occurrence of the orthorhombic phase is indicated by the splitting of the (211)-related peaks (~60 GPa). Only at higher pressure (70 GPa and above) does the splitting of (110)-related peaks become clear.

Figure 4 shows the equation of state of CsI to 95 GPa (fractional volume of 46 percent), based on a series of experiments. The compression curve of CsI is insensitive to the phase transitions at 38 and 56 GPa as the transitions appear to be isovoluminal; however, small volume changes of less than 0.5 percent may occur. The curve in Fig. 4 is the fit of Keane's equation to the combined data with $B_0 = 11.89$ GPa, $B'_0 = 5.93$, and $B_0'' = -0.86 \pm 0.01 \text{ GPa}^{-1}$. B_0 and B_0' were constrained to ultrasonic values (21). B_0 is the isothermal bulk modulus; B'_0 and B''_0 are its first-order and second-order partial derivatives with respect to pressure, respectively. The fitted value of $B_0'' = -0.86 \text{ GPa}^{-1}$ is

from ultrasonic data (21). The Birch firstorder equation, when fitted to our data to 95 GPa with fixed $B_0 = 11.89$ GPa, gives $B'_0 = 6.27 \pm 0.1$; the earlier data (11) to 65 GPa gave $B_0 = 11.1 \pm 0.8$ GPa and $B'_0 = 6.9 \pm 0.4.$ Rubidium iodide, which crystallizes in the

slightly lower than the value (-0.73 GPa^{-1})

B1 phase at ambient conditions, transforms to the B2 phase at a pressure of 0.4 GPa. The B2 phase of RbI was stable up to the highest pressure (89 GPa), and no phase transition to the tetragonal phase was observed. Thus the tetragonal and orthorhombic phase transitions at high pressures may be characteristic of cesium halides only. However, other alkali halides and ionic solids must be studied to ultrahigh pressures before any definite conclusions can be drawn. Figure 5 shows the equation of state of RbI to 89 GPa (fractional volume compression to 39 percent). The fractional volume at 89 GPa is 45 percent if only the B2 phase is considered. The curve in Fig. 5 shows the fit of the Birch first-order equation to the data with $B_0 = 15.7 \pm 2.0$ GPa and $B'_0 = 4.8 \pm 0.1$, and the density of the B2 phase is higher by 13 percent than that of the B1 phase at ambient pressure. These data are in reasonable agreement with earlier measurements on RbI up to 67 GPa (22), which gave $B_0 = 16.0 \pm 0.6$ GPa and $B'_0 = 4.6 \pm 0.1.$

Our results demonstrate that it is possible to carry out x-ray diffraction measurements on alkali halide samples 75 μ m² in area in the diamond anvil cell by using the energydispersive technique with a high-brilliance synchrotron source. This technique has also been used to study other materials such as barium chalcogenides (23), semiconductor compounds from groups III and V of the periodic table (24), and germanium, the group IV semiconductor (25), to ultrahigh pressures.

REFERENCES AND NOTES

- H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Stienberg, *J. Appl. Phys.* 49, 3276 (1978).
 J. A. Xu, H. K. Mao, P. M. Bell, paper presented at the 10th International Association for the Advancement of High Pressure Science and Technology International High Pressure Conference, Amster-
- dam, 8-11 July 1985. P. M. Bell et al., Science 226, 542 (1984). K. A. Goettel, H. K. Mao, P. M. Bell, Rev. Sci. Instrum. 56, 1420 (1985)
- E. F. Skelton, *Phys. Today* **37** (No. 9), 44 (1984). B. W. Batterman and N. W. Ashcroft, *Science* **206**, 6.
- M. Baublitz, Jr., V. Arnold, A. L. Ruoff, Rev. Sci. 7. Instrum. 52, 1616 (1981). T. L. Huang and A. L. Ruoff, in High Pressure in
- 8 Science and Technology, Proceedings of the Ninth AIR-APT International High Pressure Conference, Materials Research Society Symposia Proceedings vol. 22, part 3, C. Homan, R. K. MacCrone, E. Whalley,
- Eds. (North Holland, New York, 1983), p. 11. T. L. Huang and A. L. Ruoff, *Phys. Rev. B* 29, 1112 9. (1984)
- E. Knittle and R. Jeanloz, Science 223, 53 (1984). **I**O.
- K. Asaumi, *Phys. Rev. B* **29**, 1118 (1984). Y. K. Vohra, S. T. Weir, K. E. Brister, A. L. Ruoff, п. 12
- Phys. Rev. Lett. 55, 977 (1985). E. Knittle et al., Phys. Rev. B 31, 588 (1985)
- T. L. Huang, K. E. Brister, A. L. Ruoff, ibid. 30, 2968 (1984)
- K. E. Brister, Y. K. Vohra, A. L. Ruoff, ibid. 31, 15. 4657 (1985). Y. K. Vohra, S. J. Duclos, A. L. Ruoff, *Phys. Rev.*
- 16.
- Lett. 54, 570 (1984).
 J. C. Jamicson, J. Fritz, M. H. Manghnani, Adv. Earth Planet. Sci. 12, 27 (1980).
 D. E. Hammond, thesis, University of Rochester 17.
- T. L. Huang, thesis, Cornell University (1984). A. N. Zisman, I. V. Aleksandrov, S. M. Stishov. TQ.
- 20. Phys. Rev. B 32, 484 (1985). G. R. Barsch and Z. P. Chang, Natl. Bur. Stand. 21.
- (U.S.) Spec. Publ. 326 (1971), p. 173. K. Asaumi, Y. Kondo, T. Mori, T. Suzuki, in Solid 22
- State Physics under High Pressure, S. Minomura, Ed. (KTK Scientific Publications, Tokyo, 1985), p. 63. S. T. Weir, Y. K. Vohra, A. L. Ruoff, Phys. Rev. B, 23.
- in press Y. K. Vohra, S. T. Weir, A. L. Ruoff, ibid. 31, 7344 24.
- (1985). Y. K. Vohra, S. Desgreniers, A. L. Ruoff, in 25.
- preparation. preparation. Supported under NSF grant DMR-8305798. One of us (K.E.B.) thanks the NSF for support through the Cornell Materials Science Center. S.T.W. thanks the Eastman Kodak Company for support. We thank the entire CHESS staff for their help. 26.

2 August 1985; accepted 7 January 1986

SCIENCE, VOL. 231