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in a state very close to the native one.

Blood samples from seven patients who had received doses varying from 2 to 6 mc of I^{131} for hyperthyroidism were collected 24 and 48 hours after the dose and allowed to clot. The serum removed after centrifugation was treated with an anionic exchange resin (Amberlite IRA-400 in its chloride phase) to remove the inorganic I^{131} and was then brought to a density of 1.063 g/ml with dry sodium bromide (*7*). All densities were measured at 25°C with a 1-ml pycnometer. Enough serum was used to fill a 13.5-ml Lusteroid centrifuge tube. The tube was centrifuged for 18 hours at 105,000*g*. At the end of this period a density gradient was found; the minimum density (at the top) was 1.050 g/ml, and the maximum density (at the bottom) was 1.076 g/ml. The tube was cut into 10 equal portions. The volume of each portion was measured, and its activity was determined with a well-type scintillation counter.

The beta lipoproteins (low-density lipoproteins), with density varying from .980 to 1.040 g/ml, appeared at the top as a very yellow layer, while all other serum proteins sedimented toward the bottom of the tube. Only the first fraction contained beta lipoproteins (*8*). The layer next to the first contained negligible radioactivity. The contents of the remaining nine portions were pooled, the volume was brought to 13 ml with saline solution and the density was brought to 1.216 with dry sodium bromide.

This solution was centrifuged for 36 hours and then cut into ten approximately equal portions. A density gradient was found, with a minimum density at the top (1.190 g/ml) and a maximum at the bottom (1.248 g/ml). The high-density lipoproteins appeared at the top of this layer as a very yellow band (*9*). Once again, the layer next to the first contained negligible radioactivity. The high-density proteins (1.220 g/ml or higher) sedimented toward the bottom.

Our results in eight experiments (*10*) showed that under the above-mentioned experimental conditions the low-density lipoproteins (or slow-moving lipoproteins in electrophoresis at *p*H 8.6) bind very little of the circulating thyroid hormone. The range varied from 0.5 to 2.0 percent of the total radioactivity. The binding of thyroid hormones by the high-density lipoproteins (or fast-moving lipoproteins in electrophoresis at *p*H 8.6) was appreciably higher, being from 8 to 12 percent of the total radioactivity. The bulk of the radioactivity was bound to proteins of density higher than 1.23 g/ml; these proteins obviously are not lipoproteins. The possibility exists that the binding of thyroid hormones by proteins may be affected by high concentrations of salt. If this were so, it could explain the difference between our results and those of Clausen and Munkner (*5*). Although experiments performed in our laboratory show that high salt concentrations do not diminish the capacity of serum to bind thyroid hormones, alterations in the binding by lipoproteins caused by high concentrations of salt, if any, are not known. This may merit further study (*11*).

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7. The thyroxine nature of the iodinated compounds found in the circulation of patients receiving therapeutic doses of radioiodine for the treatment of hyperthyroidism has been established by Robbins *et al.* [*J. Biol. Chem.* 212, 403, (1955)]. As a check, we also performed descending paper chromatographic analyses of the butanol-extractable portion of sera obtained from two of the patients with butanol, acetic acid, and water (4:1:5) as solvent in Whatman No. 1 paper. The activity appeared to be located in one spot corresponding to that of commercial radioiodinated thyroxine in control runs. The latter commercial preparations were supplied by Abbott Laboratories, Chicago, Ill. The fact that we were dealing with thyroid-binding proteins was verified in each experiment by continuous flow electrophoresis in barbital buffer at *p*H 8.6, ionic strength 0.02, followed by paper electrophoresis (barbital buffer, *p*H 8.6; ionic strength 0.05) of each of the fractions so obtained. The bulk of the radioactivity was found in the fractions containing alpha-2 and alpha-1 proteins.
8. We verified that no other protein was present in this fraction. This was determined by paper electrophoresis in barbital buffer at *p*H 8.6, the strips being stained both for protein with bromphenol blue and for lipid with oil red O.
9. The presence of only lipoproteins in this fraction was also determined by electrophoresis in barbital buffer at *p*H 8.6 and staining of the paper strips both for protein and lipids.
10. The eighth was an additional experiment performed in which serum from a normal patient was tagged in vitro with commercial radioactive thyroxine. The results did not differ from those obtained in the other seven.
11. Support by the National Institutes of Health (research grant A-4251) is acknowledged.

17 December 1962

FEBRUARY 1963 JAMI-JC 63-0309

Crystal Structures at High Pressures of Metallic Modifications of Silicon and Germanium

Abstract. *Studies of germanium and silicon by x-ray diffraction reveal that their crystal structure changes at high pressures from the semiconducting diamond-type structure to the metallic white tin structure, in analogy to the known "gray" to "white" transition in tin itself.*

The development of a new x-ray diffraction technique (*1*) has made it possible to obtain useful information about the crystal structure of materials while they are exposed to pressures above 100 kilobars. I have obtained results with silicon, germanium, indium antimonide, indium arsenide, gallium antimonide, aluminum antimonide, indium phosphide, and tin (*2*). The common-structure Sn-type transitions in these elements and compounds indicates that there is a systematic variation in the pressures at which the group IV elements and certain group III–V compounds attain the metallic state. I now report work on silicon and germanium (*3*).

The x-ray diffraction cameras operate on the same physical principle as that described previously (*1*). However, to improve the quality of the picture and the precision, a camera diameter of 114.6 mm is now used in conjunction with commercial collimators (*4*). The film holder is fixed in position with respect to the sample, and diffraction lines may be obtained at 2θ values from 10° to 170°. But, since the sample is encased in "amorphous" boron, which cuts down on the diffracted line intensity, and since filtered Mo radiation is used, the high pressure patterns seldom have useful lines above 2θ equals 60°.

An annulus of "amorphous" boron

constructed with an outside diameter of 0.125 inch, an inside diameter of 0.015 inch, and a height of about 0.025 inch. A pressed pellet of the sample, diluted with the boron (to minimize absorption) and about 0.020 inch long, was loaded into the center of the annulus. The assemblage was compressed between carbide pistons to a load of 10 to 60 kb. Under these conditions the porous boron collapses and extrudes laterally so that the initial load bears primarily on the sample. However, because of the high internal friction of the boron grains and also friction at the carbide-boron interface, a state of quasi equilibrium is reached when the pistons are still about 0.010 inch apart. The pressure distribution within the annulus is exponential in form, rising to a peak at the position of the sample in the center. The pressures attained are a function of the compressibility of the mixture of sample and boron. Collimated x-rays are passed through the annulus laterally, and the resulting diffraction pattern is recorded on film. The pattern consists of diffraction lines from the sample superimposed on a background arising from incoherent scattering from the boron, broad bands resulting from the partial crystallinity of the boron, and some trace of a diffraction pattern from the carbide pistons.

The major improvement in the current technique is the use of two different piston configurations, each of which serves a different purpose. In one configuration, the load-bearing areas are 3/16 inch in diameter and flat across their faces. After the boron annulus is extruded, a hand tool is used to remove excess boron and trim the "pressure vessel" back to a diameter of 1/8 inch. These pistons have the advantage because the sample becomes a two-phase mixture when the transitions are above about 60 kb. Further increase in load is sustained mostly by the boron, and only a small amount more of the low-pressure phase transforms to the high-pressure phase. When the high-pressure structures are known, we have accurate measure of both the change in volume (ΔV) of the transition and the compression of the low-pressure phase at transition. This has the disadvantage of providing a complicated pattern to unravel when the structure of the high-pressure phase is not known. A second piston configuration has now provided single-phase patterns of high-pressure phases at least as high as 130 kb, greatly reduced exposure time, and improved picture quality. In this configuration the piston faces are again 3/16 inch in diameter. However, the pistons rise at a 5° angle from the edge to a 1/32-inch flat in the center. The mixture of boron and sample is made as usual and lightly loaded. Again the excess boron is removed after extrusion. Since the boron on the tapered edge is not as compressed as that in the sample region, an increase in load compresses the central region more and transitions are completed. The lower density boron absorbs x-radiation less, and exposure times are shorter. Both configurations have been used in the following studies. The Ge and Si used were of semiconductor grade (*5*).

Diffraction patterns of Ge diluted with boron revealed a second phase when the loads were sufficiently high. Flat pistons were used. The ratio of the volume at high pressure (V_p) to the original volume (V_o) for the diamond structure form, compared with a graphical extrapolation of Bridgman's (*6*) data for 10^6 kg/cm^2 on the compression of Ge, gave a pressure for the appearance of the new phase which was in excellent agreement with the figure of 120 kb obtained by Minomura and Drickamer (*7*). At no time was total conversion achieved, and at most seven lines of the new phase could be recognized.

Patterns taken at high pressure with the tapered pistons gave the diffraction lines listed in Table 1. The patterns were readily indexed as tetragonal with $c/a = 0.551$. The structure is presumably the white tin structure. This structural transition (diamond type to white tin) has already been suggested for InSb under pressure by Jayaraman *et al.* (*8*) and found for that substance by Smith and Martin (*9*), Kasper (*10*), and me (*2*). The line 101 was abnormally weak and in the studies with the flat pistons only appeared at the highest load. I believe that this is either a stress orientation effect or a nucleation phenomenon such as appeared to a greater extent in Si (see below). No additional lines appeared in the patterns obtained with the tapered pistons.

Because of its low absorption of molybdenum radiation, Si required no dilution. This, together with its small compressibility (*6*), guaranteed that exceedingly high pressures would be reached with the boron annulus technique. This was found to be so, and

Table 1. Data on germanium.

hkl	Calculated (Å)	Observed (Å)
200	2.442	2.442 S+
101	2.358	2.358 W
220	1.727	1.720 S
211	1.696	
301	1.393	1.393 M
112	1.254	
400	1.221	1.218 M+
321	1.210	
420	1.092	1.089 M
411	1.085	
312	1.0149	
501	0.9182	0.9271 W
103	.8826	.8705 W (band)
332	.8750	
440	.8634	
521	.8595	
213	.8300	.8315 W-
600	.8140	
303	.7858	.7779 W (band)
512	.7803	
620	.7722	
611	.7694	

at high pressures with flat pistons four new lines appeared on the pattern at spacings of 2.337, 1.628, 1.160, and 1.038 Å. These could be indexed 200, 220, 400, and 420 of a tetragonal tin structure with appropriate density. Needless to say, there would be a large uncertainty in this identification because of the lack of all *hkl* spacings with $l \neq 0$. The use of tapered pistons resolved this difficulty. In addition, it revealed that there may be previously unsuspected complications in the study of polymorphic transitions at high pressures.

The initial patterns taken with tapered pistons were similar to (but of better quality than) those taken with flat pistons since a phase mixture of diamond structure lines together with additional lines indexing as before, ap-

Table 2. Data on silicon.

Diamond type		Observed		Sn type	
a_o (Å)	*hkl*	lines (Å)		Calc. (Å)	*hkl*
5.343	111	3.085	S+		
	X	2.613	S		X
		2.351	S	2.343	200
		2.265	M+	2.263	101
5.275	220	1.865	S		
	X	1.713	W+		X
		?		1.657	220
		?		1.628	211
5.280	311	1.592	S		
	400	1.326	M+	1.337	301
	331	1.209	M+	1.204	112
		1.159	W	1.172	400
				1.161	321
5.281	422	1.078	M+		
		1.040	W	1.048	420
				1.040	411
5.271	511	1.0145	M		
		0.9737	W-	0.9740	312
5.268	440	.9312	W		
5.282	531	.8929	W+		
5.272	620	.8335	W+		
	533				
	444				
	711				
5.286	642	.7064	W		
5.288	731	.6885	W-		

Table 3. Crystallographic parameters.

c (Å)	a (Å)	c/a	V_p/V_o	$\Delta V/V_p$ (%)	$\Delta d/d$ (%)
		Silicon			
2.585	4.686	0.554	0.918	22.7	+6.3
		Germanium			
2.692	4.884	.551	.875	20.7	+8.6
		Tin			
3.182	5.831	.546		20.9	+7.5

peared. Patterns taken over a 3-day period at constant pressure revealed a change in the added pattern until ultimately that given in Table 2 appeared. Of particular note was the appearance of $l \neq 0$ lines for a white tin tetragonal indexing such as 101, 301, 112, and 312, while diffraction peaks previously indexable as 400 and 420 shifted positions, indicating now unresolved lines with additions of 321 and 411. The line indexing 220, which had been strong, was too faint to measure in the background between 1.713 Å (labeled *X*) and 211 (tin) which blended with 311 (diamond). A glance at Table 2 reveals that two further lines appeared, at 2.613 Å and 1.713 Å. Neither of these fit a white tin structure. When the pressure was lowered, all lines indexable as white tin disappeared, while these two lines persisted, indicating that they belonged to a separate phase. The nature of this phase, as well as its relationship to the now reasonably-well proved white tin structure for Si at high pressure, is not known. Such an indexing is given in Table 2. The collected crystallographic data for Ge and Si are given in Table 3, together with those of Sn (*11*) at zero pressure for comparison (d is interatomic distance).

It now becomes possible to discuss the mode of transition of Ge and Si under the stress conditions of the x-ray experiments. It must be remembered that the samples are encased in confined boron which will apparently support quite high shearing stresses. Musgrave and Pople (*12*) have suggested that the mode of transition of a diamond structure to a white-tin structure can be a mechanical one, namely a compression along any one of the cubic axes and an expansion along the direction (110). This means that in the pressure experiments on the average, the c axis of the new phase will be normal to the piston faces, while the a axes will be parallel. Hence the diffraction pattern will consist of intensified a reflections and diminished c until recrystallization with lateral relief of the sample can occur. This makes it difficult to say precisely what the pressure of transition (in Si especially) is. If the V_p/V_o for Si from Table 3 is plotted on a graph containing Bridgman's curve for V_p/V_o vs. pressure to 10^5 kg/cm^2 (*6*), it seems to correspond to a pressure of about 160 kb or so rather than Minomura and Drickamer's figure of 195 to 200 kb (*7*). However, Minomura and Drickamer also reported that some Si samples, confined in pyrophyllite, showed exceedingly low resistivities starting as low as 135 to 150 kb, while samples confined in the low-shear-strength material AgCl consistently transformed at 195-to-200 kb. The present study is mechanically more analogous to their study of the pyrophyllite cell. Hence, on the basis of the x-ray study, it does not seem inappropriate to suggest that the Si transition is actually displaced by a nonhydrostatic stress system. Such a displacement is metastable, for with time the system relaxes by recrystallization to a more "hydrostatic" condition. This in turn suggests that in studies of polymorphic transitions at high pressures with solid pressure-transmitting media, transition pressures *lower* than those of hydrostatic equilibrium may be reported. This is contrary to what would be expected from the thermodynamics of the hydrostatic case in which a reported pressure of transition must be equal to or above the true equilibrium pressure on increasing pressure.

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2. A portion of this work was presented at the Houston meeting of the Geological Society of America, November 1962. This work has been supported by grant G19744 from the National Science Foundation and also by a grant from the Petroleum Research Fund of the American Chemical Society.
3. A report on the group III–V compounds is in press (*Science*). A report on tin is in preparation.
4. North American Philips Co. collimator for their 114.58 mm powder camera.
5. I thank Prof. N. H. Nachtrieb for the Ge, Prof. J. V. Smith for the Si.
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18 January 1963

Tremoctopus violaceus Uses Physalia Tentacles as Weapons

Abstract. *Immature octopods* (Tremoctopus violaceus) *have been found with numerous fragments of tentacles of the coelenterate* Physalia *attached to the suckers of their dorsal arms. The probable method of acquisition, the evidence of adaptation for holding the tentacles, and the possibility that the octopod uses these coelenterate tentacles as offensive and defensive weapons are discussed.*

Several workers (*1*, *2*) have reported the occurrence of portions of unidentified coelenterate tentacles on the arms of young *Tremoctopus violaceus* Delle Chiaje (Cephalopoda: Tremoctopodidae), a pelagic octopod. Naef (*2*) was unable to determine whether this association was the accidental result of an encounter with the coelenterate or an advantageous behavior pattern whereby the stinging cells could be used as weapons by the octopod. He proposed that the latter was probably the case.

This report presents some similar observations in which the coelenterate fragments are identified, and Naef's hypothesis of an advantageous behavior pattern is supported.

During cruise No. 38 of the Bureau of Commercial Fisheries' research vessel *Hugh M. Smith* in February 1957, night-light stations were conducted in the vicinity of latitude 13°S, longitude 110° to 112°W. Among the frequent visitors to the submerged light were a number of immature female octopods, *Tremoctopus violaceus*. I dip-netted one of these from the water and lifted it by hand out of the net. I experienced sudden and severe pain and involuntarily threw the octopod back into the water. To determine the mechanism responsible for this sensation 10 or 12 small (40 to 72 mm total length) octopods were captured and I purposely placed each one on the tender areas of my hands. The severe pain occurred each time, but careful observation indicated that I was not being bitten by the octopod. The pain and the resulting swelling and inflammation, which lasted several days, resembled the stings of the coelenterate *Physalia*, the Portuguese man-of-war, which was quite abundant in the area.

Subsequent examination of one of these female octopods, 72 mm long, which had been preserved, revealed