2955 Dundas Rd
Richmond 34, Va.
August 22

Hi Tracy,

Just in case you haven't already seen the enclosed article, I'm sending it to you. According to Mr Stambler, the boys at UCLA don't think much of your tetrahedral anvil. I'm curious to know what you think about their opinions and what your appraisal of their apparatus and efforts.is.

Sincerely,

Delbert

Space/Aeronautics

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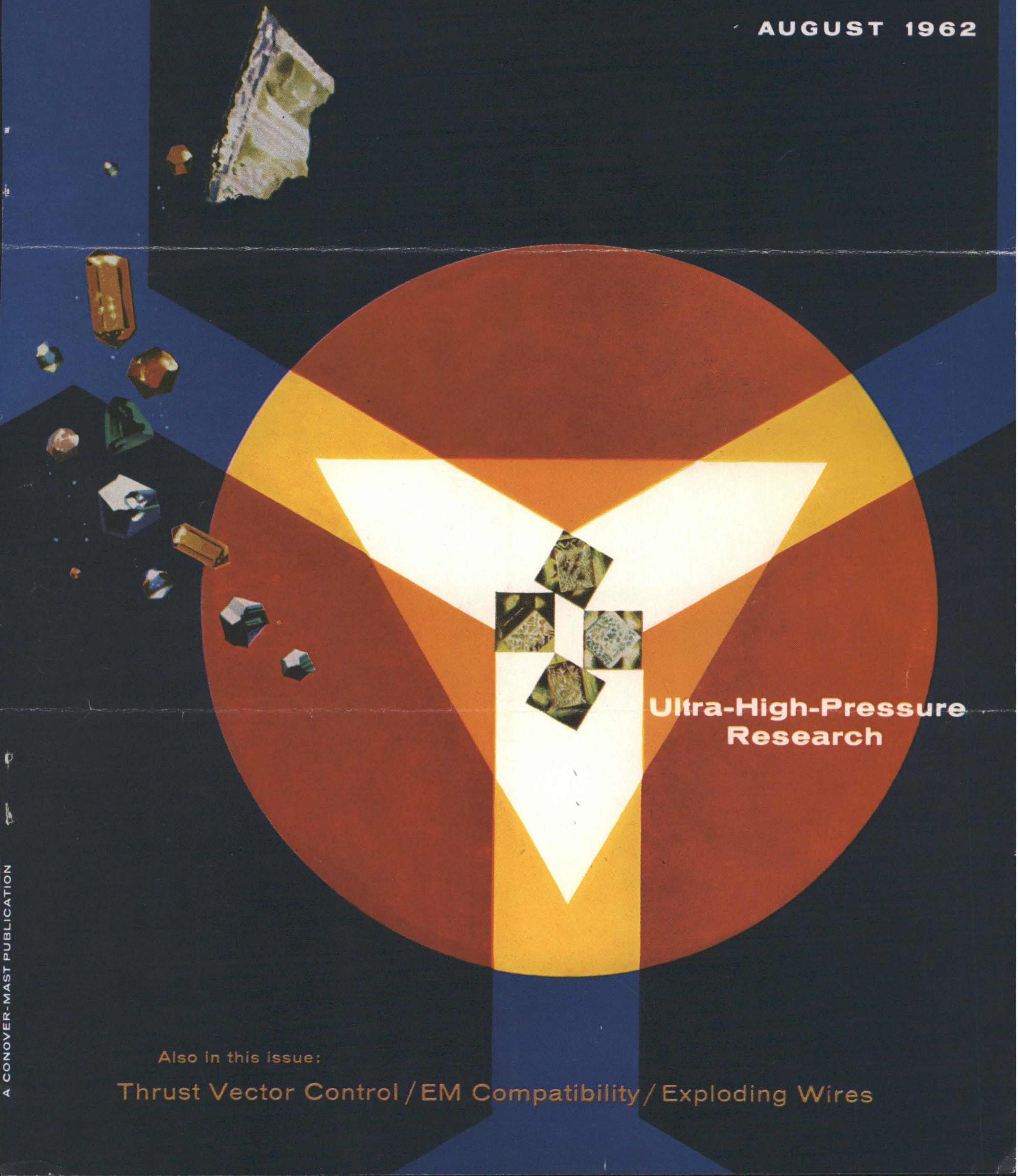
AUGUST 1962



Ultra-High-Pressure Research

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PROGRESS REPORT

Ultra-high-pressure research

by Irwin Stambler, Associate Editor

IT IS ALREADY clear that observation under ultra-high pressure has added a new dimension to the study of the physical and chemical behavior of materials. Just how much this new research technique will help us in improving existing materials and in developing entirely new ones probably no one has fully realized yet—the possibilities are too great to have been fully explored in the relatively short period since we first learned how to apply ultra-high pressure.

Of course, high pressure alone isn't enough. In most cases, high temperature is needed, too. As C. M. Schwartz and W. B. Wilson, of Battelle, explain, pressure normally affects not only the equilibrium conditions of a material but also the reaction rate. "However, in the case of solids with ionic or covalent bonding . . . there are no molecules as such to be aligned by pressure; instead, the effect is to increase bond strengths and thus to lower the reactivity. . . . Raising the temperature has the opposite effect on bond strength, owing to the increased thermal vibrations and separations of the atoms or ions. This increases the chemical reactivity and thus counteracts the effect of pressure. In fact, most [of the] reactions [that] form materials . . . would be much too sluggish at room temperature to be of economic value, and thus the use of heat simultaneously with pressure appears mandatory."

The need to combine high pressures and temperatures severely restricts the designer of ultra-high pressure apparatus. This was shown already by the work that led up to the first major breakthrough in high-pressure technology, the synthesis of diamonds. Dr. Percy Bridgman, generally considered the father of ultra-high-pressure technology, in the forties achieved pressures of 3,000,000 PSI and more. Nevertheless he was unable to make diamonds from graphite. It was not until 1955, when F. P. Bundy, H. T. Hall, and others at GE added high temperatures to speed up the reaction rate, that the production of synthetic diamonds became reality. By now it is a commercial process—rows of machines at firms like de Beers and GE have been turning out over

IN BRIEF

The trend in materials research for some time has pointed to more intensive study of the fundamental properties of matter. The goal of this work is the creation of materials tailored to perform specific functions, many of them of critical importance for aerospace development. Ultra-high pressures, which we have only recently begun to achieve, are proving invaluable in this effort.

This survey reports on the methods developed so far for producing very high pressures and discusses the problem of combining these pressures with high temperatures. It also gives details on, and assesses the significance of, the most important results of ultra-high-pressure to date, reviews current basic and applied research at ultra-high pressures, and outlines the possibilities for more ambitious projects in the future.

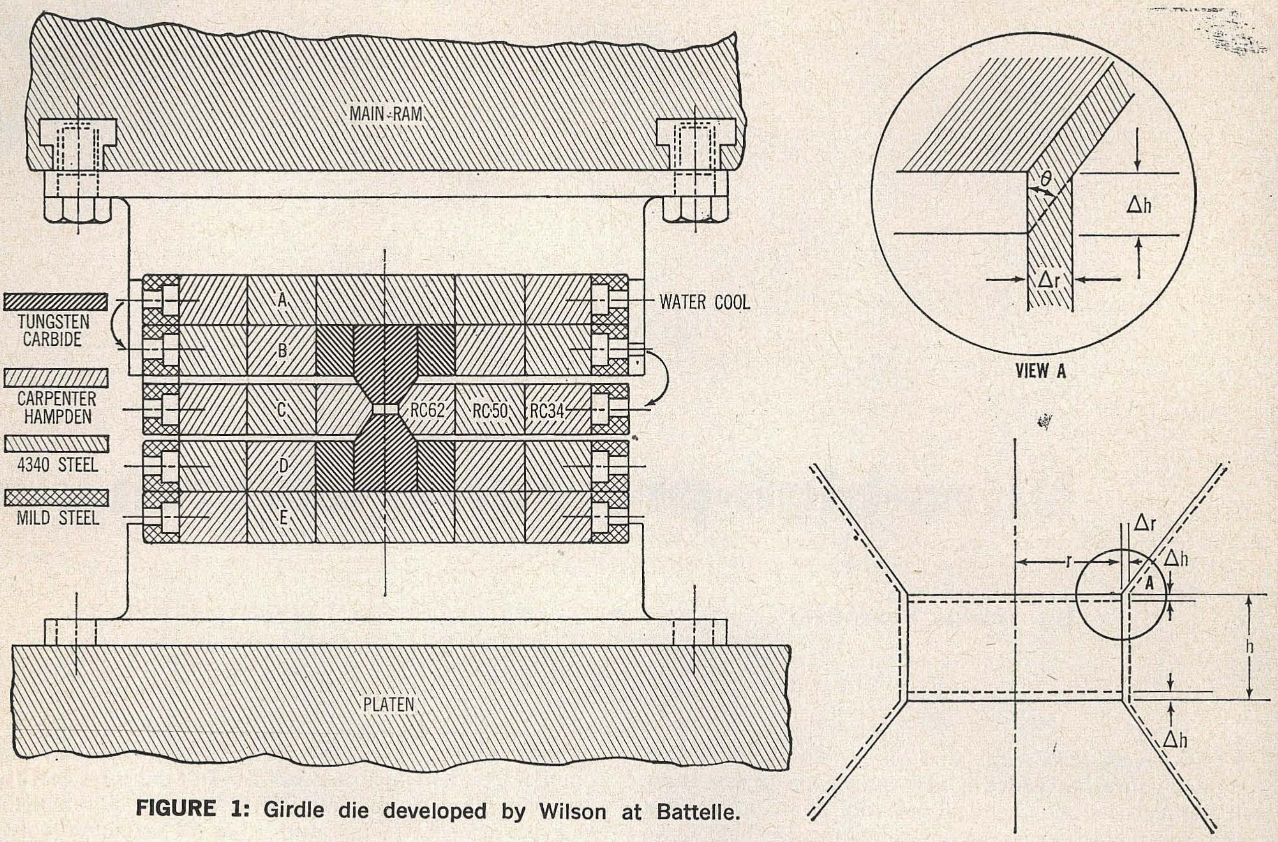


FIGURE 1: Girdle die developed by Wilson at Battelle.

3,000,000 carats a year at pressures of 1,500,000 PSI.

Bridgman's pioneering work was done with a simple, right circular cylinder vessel and piston. The cylinder had outer binding rings forced onto a cemented tungsten carbide insert, which thus was placed under compression. Bridgman achieved pressures on the order of 100,000 atm, or about 1,500,000 PSI, at room temperature by surrounding the piston and cylinder with a liquid under hydrostatic pressure. A recent improvement on Bridgman's design that provides high temperatures, too, is the "girdle" invented at Battelle (*Fig. 1*).

First design used steel parts

For GE's work on diamond synthesis, the Bridgman apparatus was found to be inadequate (*Fig. 2*). A series of modifications eventually led to Hall's successful belt apparatus (*Fig. 3*). Hall's first design used steel belt parts and achieved 60,000 atm; later he used Carboloy anvils and cylinders and got pressures originally put at about 100,000 atm but now revised to about 75,000 atm on the basis of new data compiled by George Kennedy and others at UCLA. The temperatures provided by Hall's final apparatus are more than 4000 deg C for short periods and about 2000 deg C for long ones (over one hour). The pressure and temperatures of diamond synthesis have been postulated as 55,000-130,000 atm and 1400-2350 deg C.

In many studies, the tetrahedral anvil die is used, which consists of four pistons with triangular faces that nest together. The pistons are hydraulically actuated to close on the sample, which is in a heater tube supported in a pyrophyllite tetrahedron. In most, if not all, cases the anvil material is cemented carbide.

In this early stage of work with ultra-high pressures, it's all-important that we improve our understanding of the basic principles that determine how pressures affect materials. This in turn means that we must have precise and reliable measurements, Kennedy told SPACE/AERONAUTICS. To the researcher, he said, the mere production of high pressure is meaningless—he must know exactly how much pressure is produced and exactly how much of it is actually applied to the sample.

Much of the data based on work with the tetrahedral anvil, for example, now has become suspect, Kennedy points out. If the sample is compressible, the anvils of this die bear on each other, and in the test results the anvil-to-anvil pressure may be added to the pressure on the sample. In some cases, pressure data for tetrahedral

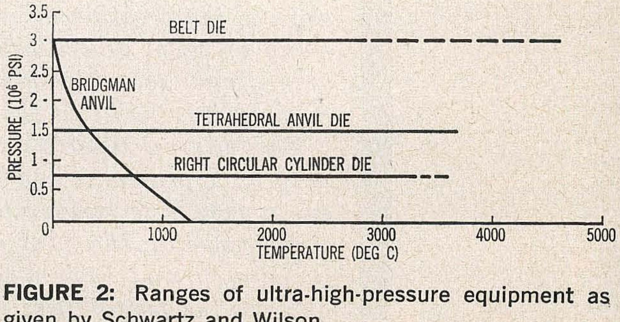


FIGURE 2: Ranges of ultra-high-pressure equipment as given by Schwartz and Wilson.

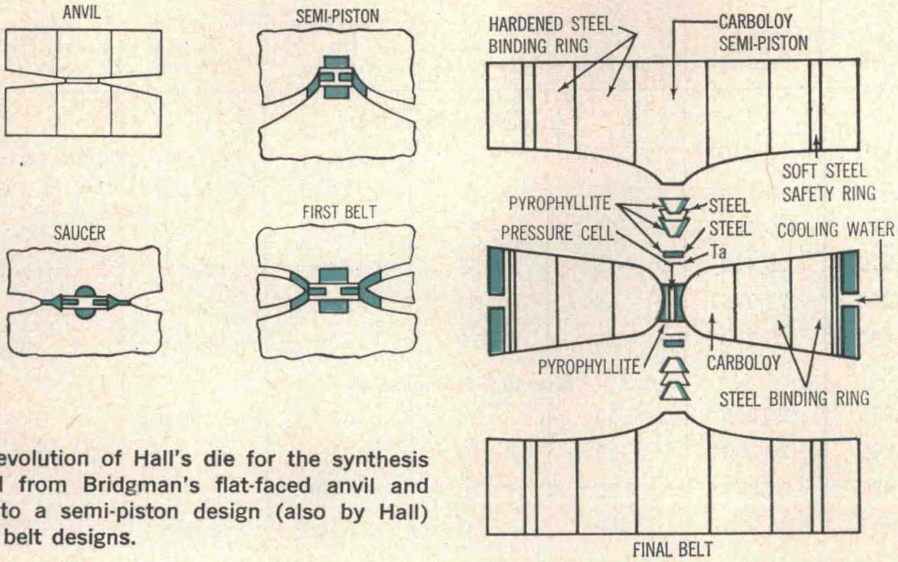


FIGURE 3: The evolution of Hall's die for the synthesis of diamonds led from Bridgman's flat-faced anvil and Bundy's saucer to a semi-piston design (also by Hall) and then to two belt designs.

anvils appear to be twice what they should be (though in other cases they seem to be just right).

Kennedy thinks that the highest verified pressures produced so far are about 84,000 atm for the upper bismuth transition and perhaps 135,000 atm in certain other experiments. He and his colleagues have designed several machines that they believe give accurate pressure data (*Fig. 4*).

The physical properties of a solid depend strongly on its phases. Under ultra-high pressure, many new phases can be produced in a number of materials. Very often, however, these phases are reversible—they disappear as pressure is removed, and the original phase reappears. The researchers, of course, want to reduce the pressure once a new phase is created, since they need something like room temperature to analyze the results they have gotten.

Reversibility is sometimes slow

Reversibility varies widely—it occurs at about room temperature with metals, at about 1500 deg C with diamonds. In some cases it takes place slowly, so that the high-pressure phase can be retained at study temperatures if the sample is cooled quickly enough.

Schwartz and Wilson point out that the temperature stability of many elements and compounds existing in two or more crystalline forms increases as their structure becomes more nearly symmetrical and their atoms therefore are packed together more closely. From this they deduce that, "in a few instances, it is possible by chemical additions to stabilize a high-temperature form so that it is retained at lower temperature. Thus, addi-

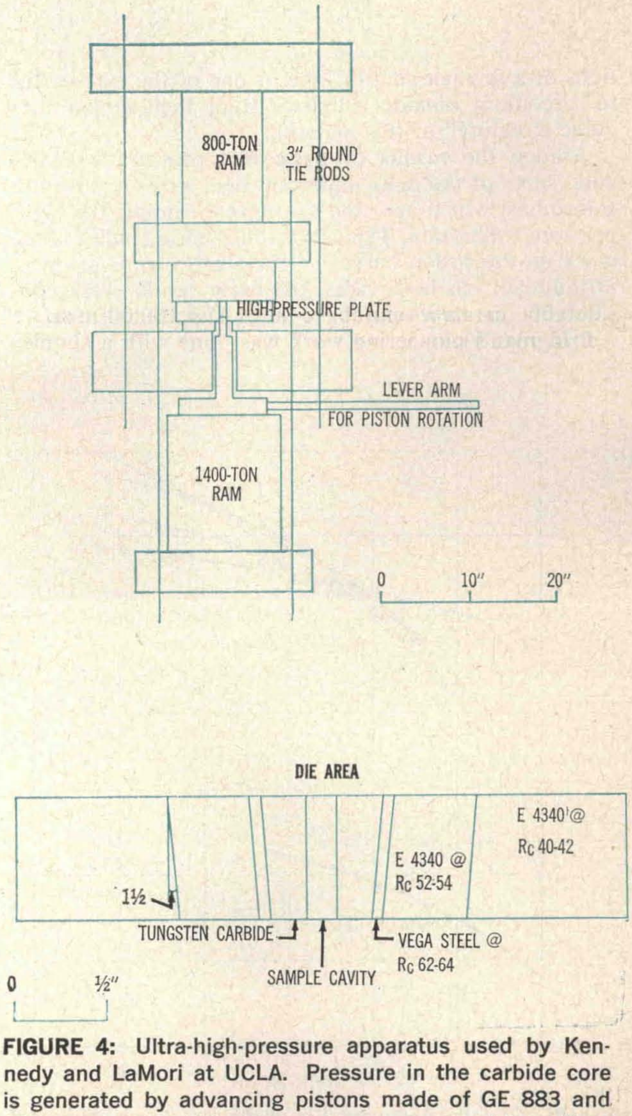


FIGURE 4: Ultra-high-pressure apparatus used by Kennedy and LaMori at UCLA. Pressure in the carbide core is generated by advancing pistons made of GE 883 and 999 tungsten carbide. The pistons are ground to a fit of better than 0.0003 in. to lapped bores in the core.

Table I: Bismuth Transition Pressures (bars)*

Temp. (deg C)	Up-Pressure	Down-Pressure	Ram Correction	Temp. Correction	Corrected Up-Pressure	Corrected Down-Pressure	Mean Pressure at 25° C	Uncertainty
				Bismuth I to Bismuth II				
23.4	25,800	25,370	−55	−70	25,615	25,245	25,430	±185
23.6	25,645	25,425	−55	−70	25,520	25,300	25,410	±110
23.8	25,590	25,480	−55	−55	25,480	25,370	25,425	±55
23.8	25,590	25,410	−55	−55	25,480	25,300	25,390	±90
24.5	25,620	25,385	−55	−30	25,535	25,380	25,460	±80
24.5	25,450	25,370	−55	−30	25,375	25,285	25,330	±45
				Bismuth II to Bismuth III				
24.6	27,235	26,865	−55	−10	27,170	26,800	26,985	±190
24.6	27,225	26,850	−55	−10	27,160	26,785	26,975	±190
24.6	27,250	26,835	−55	−10	27,185	26,770	26,975	±190
24.6	27,250	26,820	−55	−10	27,185	26,755	26,970	±190

*From Kennedy for a piston diameter of 0.4963+0.0001 in.

tions of a few per cent of lime or one of the rare earths to zirconium dioxide stabilizes [the] high-temperature cubic structure" of this material.

Among the results of basic high-pressure work to date, some of the most important deal with the bismuth transitions, which are used as reference points for high-pressure calibration. Typical of other basic studies is the work on the fusion curves of the alkali metals at up to 50 kilobars. In both cases, the early results were considerably in error and have been superseded (*Tables I & II, Fig. 5*).

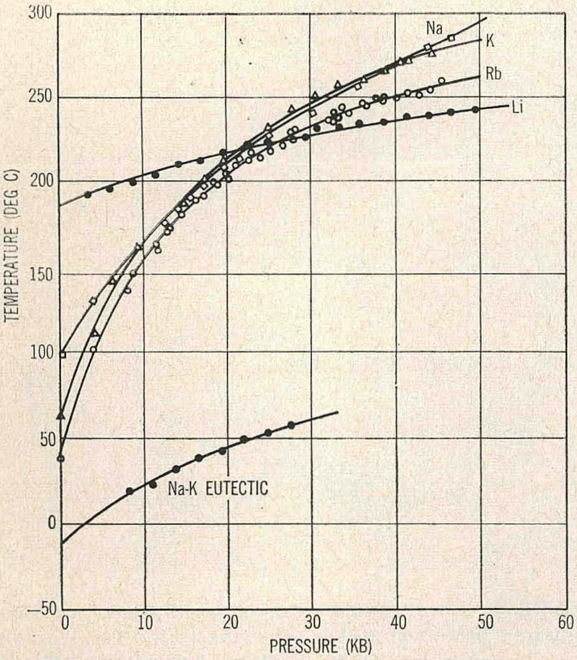


FIGURE 5: Fusion curves for alkali metals as given by Newton, Jayamaran, and Kennedy.

In addition to diamonds, a number of minerals found in the earth's crust have been synthesized under ultrahigh pressure. According to S. V. Radcliffe, of Manufacturing Labs, Cambridge, Mass., the most interesting of these materials include coesite (a dense, highly stable form of silica) cubic boron nitride, and cubic molybdenum carbide. "In all cases," he points out, "synthesis could be achieved only by chemical reaction at pressures and temperatures of at least 40-50 kilobars and 1000-1500 deg C, and not by a physical transition."

Effects on structure are promising

GE has been working on the effects of high pressure and temperature on metallic elements, binary alloys, and some vitreous ceramic materials (*Table III*). Its results show that highly significant phase changes may be achieved in alloy systems. In addition, the effects on the grain structure look very promising. In experiments

Table II: Melting Points of Alkali Metals*

Pressure (kb)	Melting Point (deg C)					
	Li	Na	K	Rb	Cs	Na-K eutectic
5	195	134	120	109	104	7
10	203	164	111	103	106	22
15	211	189	189	183	184	34
20	218	209	211	203	196	44
25	223	226	229	218	193	53
30	229	241	244	231	198	60
35	233	255	256	241	193	
40	236	268	266	249	169	
45	239	281	274	255	124	
50	242	294	281	260	97	

*From Kennedy, Jayaraman, Newton.

with tool steel at 2400 deg F, the grain size of a pressure-treated specimen remained fine (ASM 11) while that of a conventionally treated specimen coarsened to ASM 3 (*Table IV*). Obviously, finer grain sizes could lead to marked improvements in the properties of conventional alloys.

A high hope of ultra-high pressure work is very dense material structures virtually free of voids. As even the use of relatively low pressures has increased the densities of materials like aluminum oxide and beryllia enough to lead to markedly improved properties, higher pressures should have extremely rewarding results.

New elements may be created

GE is trying to find out whether ultra-high pressures can be used to transform the chromium structure from its usual body-centered cubic form to the face-centered cubic form. If this proves possible, it might solve the problem posed by the metal's brittleness—the face-centered structure would be much more ductile. Aside from theoretical studies, very little effort has been devoted to atomic compressibility, perhaps the most fascinating of the many aspects of ultra-high-pressure work. There's no doubt that the outer electrons of many of the basic solids can be forced inward if you go about it the right way. The big stumbling block is reversibility. If it is overcome, completely new elements could be the result, and we might have to draw up a new periodic table.

A more practical matter at present is that the synthesis of diamonds points the way to the development of improved cutting tools. If very fine diamonds could be bonded together, they would make better tools than tungsten carbide. The major problem is that we don't yet know how to clean the diamond surface so that it can be bonded to metal. Ultra-high-pressure studies are also underway that may lead to even better tools that can be made from diamonds and tungsten carbide. Boron, carbon, phosphorus alumina and silica are among the materials that would be used for these tools.

At the moment, states Kennedy, synthetic diamonds are not necessarily better for production applications than are natural ones, except for the dressing of tungsten carbide and a few other special cases.

A direct aerospace application of synthetic diamonds might be rocket nozzle linings—layers of diamonds bonded together theoretically could provide very good abrasion resistance at very high temperatures.

Table III:
Summary of High-Pressure Experiments with Vitreous Silica and Germania*

Pressure (atm)	Temp. (deg C)	Refractive Index	Density	Density Increase (per unit)
		Silica		
90,000	150	1.510	2.470	11.2
80,000	400	1.522	2.524	13.7
80,000	500	1.528	2.558	15.2
100,000	300			
100,000	500			
100,000	150			
100,000	300		2.550	
100,000	600		2.595	
		Germania		
100,000	250	1.694	4.16	13.3
100,000	400	1.720	4.25	15.8
100,000	RT	1.668	4.00	9.0

*From Claussen et al.

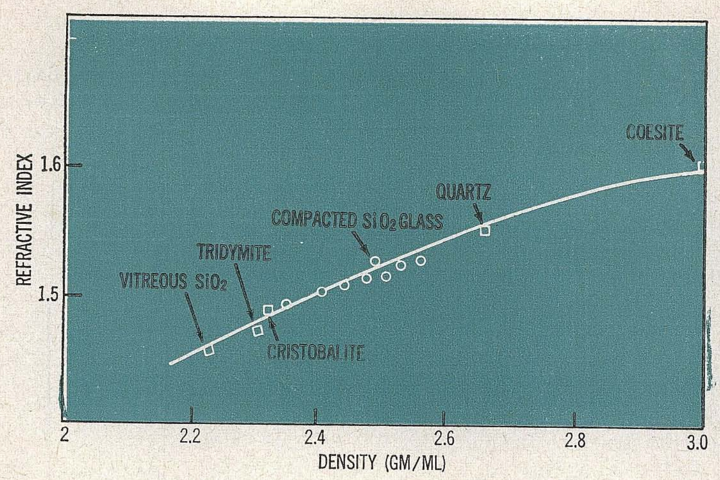
Among the problems being studied in recently started ultra-high-pressure programs are the analysis of synthetic jade, the synthesis of fluorine polymers, and the development of better explosive charges. (If you take a very dense element and lock in a still denser polymorph, an extremely powerful explosive should result.) Several groups of researchers are trying to determine the density and compression numbers needed to measure shock wave velocity.

Electronics has provided excellent opportunities for ultra-high-pressures, which are being used, for instance, in studies of the growth of silicate semiconductors and of thin-film properties as well as in attempts to find new semiconductor materials. There's also a very good chance that the upper temperature limit at which superconducting materials are still superconducting can be raised substantially by development work at high temperature and pressures.

Table IV: Results of Conventional and Pressure Treatments of Tool Steels*

Treatment	Quenched (deg F)	Hardness (R_C)	Grain Size (AMS)	Tempered (deg F)	Hardness (R_C)	Grain Size (AMS)	Double Temper (deg F)	Hardness (R_C)	Grain Size (AMS)
Pressure	2000	61.5		900	63.0		1000 + 700	62.0	
Conventional	2000	61.5		900	63.0		1000 + 700	63.0	
Pressure	2300	64.0	11	900	66	11	1000 + 700	65	12
Conventional	2300	65.5	11	900	66	12	1000 + 700	66	11
Pressure	2400	66.0	11	900	63.5	8	1000 + 700	62	5
Conventional	2400	62.0	3	900	64.0	3	1000 + 700	62	5
Pressure	2500	60.0	5						
Pressure	2600	60.0	3						

*From Goliber et al. Where only hardness values are given, the grain size was not visible.



DENSITY of crystalline and compacted materials, as given by GE.

Of course, crystals with special electronic properties, such as the garnets of lasers, can be produced only at high pressures. As ultra-high-pressure methods are improved, the development of new crystals with radically new properties becomes a distinct possibility.

What further opportunities are offered by ultra-high pressures will become clear once the restrictions are lifted under which we are laboring today. As Radcliffe notes, "a substantial effort" is in the offing that should result in two highly important developments:

- the achievement of "truly hydrostatic conditions at high pressure and temperature" (specially valuable for the study of structure-dependent properties);
- the construction of pressure chambers with large volumes (a feat that at least one firm, Engineering Supervision, of New York City, is already trying to bring off).

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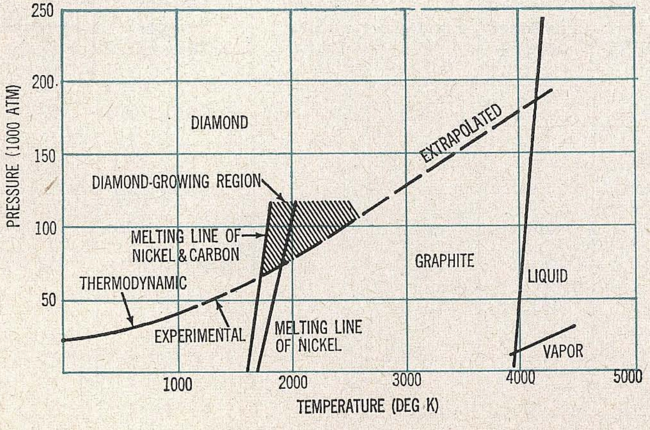

CARBON phase diagram showing theoretical and actual diamond-growing areas, as given by Bovenkerk et al.