

TABLE I. Properties of plutonium metal (1945 values, approximate).

Phase	Temperature range of stability	Crystal structure	Density g/cc at 25°C	Linear expansion coefficient (average), per °C	Electrical resistivity, microhm-cm	Temperature coefficient of resistivity
$\alpha$	below 117°C	Orthorhombic, like uranium (doubtful)	19.8	$55 \times 10^{-6}$	150 (25°)	$-29.7 \times 10^{-4}$
$\beta$	117 to 200°C	Unknown (complex)	17.8	$35 \times 10^{-6}$	110 (200°)	ca 0
$\gamma$	200 to 300°C	Unknown (complex)	...	$36 \times 10^{-6}$	110 (300°)	ca 0
$\delta$	300 to 475°C	Face-centered-cubic	16.0	$-21 \times 10^{-6}$	102 (400°)	$+ 1.5 \times 10^{-4}$
$\epsilon$	475 to 637°C	Body-centered-cubic	16.4	$4 \times 10^{-6}$	120 (500°)	ca 0
liquid	above 637 $\pm$ 5°C	...	...	...	...	...

The properties are astounding. Plutonium is unique among the elements in that there exist at least five solid allotropic modifications at atmospheric pressure. There is a 23 percent difference in atomic volume between the  $\alpha$  and  $\delta$  phases. The electrical resistivity of all phases is high—that of the  $\alpha$  phase exceeding all other “metallic” elements at room temperature. The temperature coefficient of resistance of  $\alpha$  is negative and the thermal expansivity extremely high. The *negative* expansion coefficient of the  $\delta$  phase, which is face-centered-cubic in structure, is without parallel among the elements.

Some further details are given in another paper.<sup>1</sup> These data were obtained, under the general supervision of the writer, by members of Eric R. Jette's group in the Chemistry-Metallurgy division of the Los Alamos Laboratory, operated by the University of California for the U. S. War Department. The properties quoted are preliminary values obtained under the extreme pressure of wartime conditions, and it is hoped that more recent and reliable data can soon be released.

<sup>1</sup> C. S. Smith, paper to appear in *Metal Progress*, May, 1954. For British work on the same subject, see *Nature* 173, 534 (1954).

### Superconducting Alloys

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THE superconducting elements occur in groups throughout the periodic system. One of the early attempts to prepare a superconducting compound of nonsuperconducting elements was by de Haas,<sup>1</sup> who tried to combine two normal elements on either side of a group into a superconducting phase, and he thus discovered Au<sub>2</sub>Bi. Later on, however, it became evident that the superconductivity in Au<sub>2</sub>Bi had nothing to do with averaging over a superconducting group of elements in the periodic system. Au<sub>2</sub>Bi crystallizes in a rather special crystal structure, in which no unalloyed elements can be found.

Only very recently it became apparent that such a possibility of averaging over the periodic system exists. Let us consider the following section of the periodic system:

V	VI	VII	VIII		
Nb	Mo	Tc	Ru	Rh	Pd
Ta	W	Re	Os	Ir	Pt
b.c.c.		h.c.p.		f.c.c.	

Superconducting elements are printed in boldface type.

Mo and W are at the right-hand fringe of the body-centered cubic superconductors and are not superconducting any more by themselves. On the other side of the hexagonal close-packed group of superconductors are the face-centered cubic noble metals, which again are no longer superconducting. Raub<sup>2</sup> investigated the alloys between Mo on the one side, and the noble metals on the other side. As he found intermediate phases with Rh, Ir, and Pt which are hexagonal close-packed, it becomes immediately obvious that from a crystallographic viewpoint at least we have here an

averaging over the periodic system and in particular over the superconducting hexagonal elements of the seventh and eighth columns. It suggests immediately that Mo alloys with Rh and Ir should become superconducting, an expectation which we have verified. Ru, according to Raub,<sup>2</sup> dissolves up to 35 atomic percent Mo, which is reasonable considering the tendency towards a hexagonal phase in this region. Mo-Ru alloys should therefore show superconducting properties similar to those of technetium, whose superconductivity was recently reported by Daunt and Cobble.<sup>3</sup> We have now found that the superconducting transition point of a 50-50 Mo-Ru alloy is at 10.6°K, which is 0.4° below Daunt's value for Tc. Most of this quantitative agreement is probably accidental. The superconducting transition of pure Ru is near 0.46°K.

In an earlier paper the importance of the average valence electron per atom ratio for the magnitude of the superconducting transition temperature was pointed out.<sup>4</sup> A 50-50 Ru-Mo alloy (if it existed, though the limit according to Raub is 35 atomic percent) should thus have a ratio similar to that of pure Tc, as well as the same crystal structure. This argument is now reflected in the closely corresponding transition temperatures. In a 50-50 Mo-Rh alloy, the valence electron/atom ratio will differ much more from that of Tc, and in this alloy we therefore found a transition temperature of 1.75°K.

In the iridium case we are more fortunate. Raub finds here an additional cubic phase, having the fixed composition Mo<sub>3</sub>Ir. This composition will shift the ratio again closer to the favorable value of Tc, and we did find in fact the transition temperature for Mo<sub>3</sub>Ir at 8.8°K.

The optimum value for the valence electron/atom ratio had been found to be slightly below 5.<sup>4</sup> It is, however, difficult to evaluate this factor for the transition elements with more than 6 valence electrons. Experiments show that it seems to be symmetric with respect to the middle of a long period of the periodic system, Nb and Tc having similar ratios.

We would like to thank Mrs. A. Feri for a valuable discussion.

<sup>1</sup> de Haas, van Aubel, and Voegel, *Leiden Comm. No. 197a,c* (1929).

<sup>2</sup> E. Raub, *Z. Metallkunde*, **45**, 23 (1954).

<sup>3</sup> J. G. Daunt and J. W. Cobble, *Phys. Rev.* **92**, 507 (1953).

<sup>4</sup> B. T. Matthias, *Phys. Rev.* **92**, 874 (1953).

### Compression to 10,000 Atmos of Solid Hydrogen and Deuterium at 4.2°K\*

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WE have completed measurements on the hydrostatic compression of solid hydrogen and deuterium at liquid helium temperatures, and present here a brief discussion of the results. The gases were condensed into a  $\frac{1}{4}$ -in. diameter piston and cylinder combination at low temperatures, and were solidified by im-

TABLE I. The relative volume change and compressibility of solid H<sub>2</sub> and D<sub>2</sub> at 4.2°K.

Pressure (atmos)	Hydrogen		Deuterium	
	$\frac{\Delta V}{V_0}$	$-\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T \times 10^5$ (atmos <sup>-1</sup> )	$\frac{\Delta V}{V_0}$	$-\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T \times 10^5$ (atmos <sup>-1</sup> )
0	0	50	0	31
200	0.076	29	0.056	21
400	0.123	20	0.093	16
600	0.159	15.8	0.121	13.4
1000	0.209	10.7	0.165	10.0
1500	0.252	7.8	0.205	7.4
2000	0.292	5.8	0.242	5.5
3000	0.341	4.0	0.288	4.0
4000	0.374	3.0	0.323	3.0
6000	0.423	2.0	0.373	2.0
8000	0.457	1.5	0.406	1.5
10 000	0.481	1.2	0.430	1.2

mersing the apparatus in liquid helium. A compressive force was applied to the sample holder piston by means of stainless steel compression and tension members which were connected to a low-friction hydraulic press at room temperature. Measurements of the relative motion of the press piston in its cylinder, when compared with a blank run, gave both the length of the sample and its change of volume with pressure. Data were taken for each run with increasing and decreasing pressure to provide a correction for the not inconsiderable friction encountered.

Preliminary extrusion experiments had shown that solid hydrogen is highly plastic at 4.2°K, so our one-sided compression is effectively translated into a purely hydrostatic pressure. The plasticity was so great that, until a seal of the Bridgman type (using metallic potassium as the gasket material) was placed on the piston, an unstable extrusion, which usually resulted in complete loss of the sample, was observed at about 2000 atmospheres for both hydrogen and deuterium. The clearance between piston and cylinder when this occurred was less than 5 microns.

Most of the work on these substances has been done at pressures up to 4000 atmos at Harvard. Single runs were made on each substance with a similar but larger setup at M.I.T. which confirmed the other results and extended them to 10 000-atmos pressure.

The  $\Delta V/V_0$  data for both hydrogen and deuterium are given as a function of pressure in Table I. These results can be conveniently represented within the estimated experimental accuracy (better than 5 percent in  $\Delta V/V_0$ ) in terms of equations developed by Birch<sup>1</sup> from Murnaghan's theory of finite strain. The general expression is of the form

$$P = \frac{3}{2}K_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left[ 1 - \xi \left\{ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right\} \right], \quad (1)$$

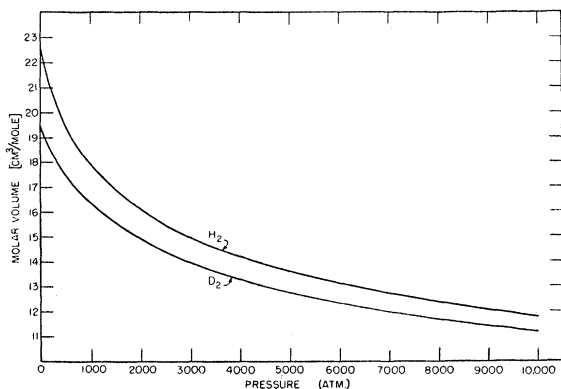


FIG. 1. The molar volumes of solid hydrogen and deuterium as a function of pressure at 4.2°K.

where  $K_0$  is the reciprocal of the initial compressibility and  $\xi$  is a constant which is adjusted for best fit to the experimental data. We find for hydrogen  $K_0=1990$  atmos and  $\xi=-1.9$ , and for deuterium,  $K_0=3180$  atmos and  $\xi=-1.6$ .

The compressibilities,  $-(1/V_0)(\partial V/\partial P)_T$ , for hydrogen and deuterium were obtained by differentiation of Eq. (1). The agreement at low pressures with the work of Megaw<sup>2</sup> is satisfactory. It is interesting to note that the volume of hydrogen is reduced by roughly 50 percent in the first 10 000 atmos, but that an extrapolation of Eq. (1) beyond the experimental range indicates that 180 000 atmos would be required to obtain reduction by another factor of two.

The equality of the compressibilities of hydrogen and deuterium at the higher pressures is fortuitous, since one should actually compare values of  $(\partial V/\partial P)_T$  for the same molar volumes of the two, and not  $(1/V_0)(\partial V/\partial P)_T$ . Such a comparison can be made from Fig. 1 where the molar volumes of solid hydrogen and deuterium are plotted as a function of pressure. We have used Megaw's<sup>2</sup> values at zero pressure, namely 22.65 cc/mole for hydrogen and 19.56 cc/mole for deuterium. Classically these two curves should be the same, but the quantum-mechanical zero-point energy produces a repulsive energy which is larger for hydrogen than for the heavier isotope deuterium under comparable conditions. Since the two curves approach each other as the pressure increases, the relative importance of the zero-point energy must decrease with increasing pressure. However, an extrapolation of Eq. (1) indicates that the two molar volumes never actually become equal, so that the effect of the zero-point energy does not disappear completely.

A more complete account of these experiments and results will be published later. We are indebted to Professor Bridgman for suggesting this work initially, and to both him and Professor H. Brooks for many helpful discussions.

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<sup>1</sup> F. Birch, *J. Geophys. Research* **56**, 227 (1952).

<sup>2</sup> H. D. Megaw, *Phil. Mag.* **28**, 129 (1939).

## Molecular Field Treatment of Magnetic Ordering Transitions

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IN a recent paper, Smart<sup>1</sup> has given an interesting treatment of magnetic ordering transitions on the basis of an assumed temperature dependence of the parameters specifying the interactions. The expression for the free energy, upon which his considerations are based, is, however, in error. A less arbitrary evaluation of the free energy (by methods similar to those used by the author<sup>2</sup> in a collective electron treatment of antiferromagnetism) leads to a substantially different and much simpler condition for the occurrence of a transition.

For simplicity and definiteness the case of a body-centered lattice containing  $8N$  atoms having spin  $S_0 = \frac{1}{2}$  will be considered. In the usual way, the lattice is subdivided into four sublattices  $A_1, A_2, B_1, B_2$ , such that a given atom has neither nearest or next-nearest neighbors on its own sublattice and only one kind of neighbors on any other sublattice. The nearest-neighbor interaction will be taken as ferromagnetic and the next-nearest-neighbor interaction as antiferromagnetic (Smart,<sup>1</sup> mode IV). The zero-order interaction energy ( $J$ ), apart from terms independent of the ordering which will have no effect on the results to be obtained, may be written as

$$J = N \{ k \varphi' [\zeta_{A_1} \cdot \zeta_{A_2} + \zeta_{B_1} \cdot \zeta_{B_2}] - \frac{k \theta'}{2} [\zeta_{A_1} + \zeta_{A_2}] \cdot [\zeta_{B_1} + \zeta_{B_2}] \}, \quad (1)$$

where the  $\zeta$ 's are the relative magnetizations of the various sublattices and  $\theta'$  and  $\varphi'$  are (positive) parameters specifying the