

High-Field Effects in Germanium

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(Received April 1, 1954)

IN the light of some of the results obtained in a recent study of *n*-type germanium,¹ it appears necessary to re-examine the interpretation of high-field effects found at 20°K in *n*-type germanium samples.^{2,3} The effect in question, a sharp increase in current density with field at around 10 volts/cm, was interpreted as an increase in mobility due to the decreased effectiveness of impurity scattering for hot electrons. It has since been suggested that it is due instead to impact ionization of neutral donors by the hot electrons.⁴

In the experiment the high voltage was applied in pulses of 10^{-6} or 10^{-7} second duration, and the resulting current pulses were found to be flat. Thus, carrier multiplication, if this were the mechanism, would have to be substantially complete in about 10^{-8} second. A crude estimate of the time required for this process can be obtained by use of the hydrogen-like model. The cross section for ionization of hydrogen by slow electrons is of the order of the geometrical cross section. The ionization cross section for a neutral donor should be $\kappa^2 (m/m^*)^2$ times this. It has been shown that the hydrogen-like model predicts reasonably well the ionization energy and scattering of electrons by neutral donors if m/m^* is taken to be 4. This value leads to a sufficiently large ionization cross section to make it not implausible that ionization could have been complete in 10^{-8} second in the sample considered.

There is also reason to believe that a given impurity concentration is less effective in scattering at these temperatures than theoretically expected.¹ To maintain the ratio of lattice mobility to impurity mobility at the value required to explain the data as a mobility change would then require a higher value of minority impurity concentration than previously considered, and one that begins to look implausibly high.

It has been argued that the heating of the electrons required to produce substantial impact ionization would first (i.e., at lower fields) have to be manifest as a change in mobility. It is worth pointing out, however, that this change might well be small enough to be easily missed experimentally. If only lattice and impurity scattering were operative, and these in amounts such that the respective low-field mobilities were equal, theory³ predicts that in the course of a change in electron "temperature" by a factor 4 the mobility would first increase by about 20 percent, then decrease by 10 percent. It is possible that the sample in question had a low enough minority impurity concentration so that lattice and impurity scattering were balanced in this way.

The type of experiment performed by Ryder may make it possible to decide between these alternatives if data from different samples at the same temperature, or the same sample at different temperatures, are available. For the particular sample investigated it was found that at fields beyond the region of the steep increase the current density varied as \sqrt{E} . This dependence on E is characteristic of the high field variation of drift velocity under lattice scattering, and indicates that carrier concentration is constant in this range. For two different samples, 1 and 2, at the same temperature, theory³ predicts that at any E for which both are in \sqrt{E} range: $j_1/j_2 = n_1/n_2$. Thus the high-field value of the ratio n_1/n_2 can be obtained from the experimental j_1/j_2 , and compared with the low-field value, obtainable from Hall data for the individual samples. If the two samples have somewhat different impurity concentrations, say $10^{13}/\text{cm}^3$ and $10^{15}/\text{cm}^3$, this should be conclusive. Similarly, in the case where data at different temperatures are available for the same sample, and the fields used are high enough to attain the \sqrt{E} range at both temperatures, theory³ predicts $j(T_1)/j(T_2) = [\mu_{Lo}(T_1)/\mu_{Lo}(T_2)]^2 n(T_1)/n(T_2)$. The quantity μ_{Lo} is the low-field lattice mobility, and $[\mu_{Lo}(T_1)/\mu_{Lo}(T_2)]^2 \approx (T_2/T_1)^{0.8}$. Again, this enables comparison of the high-field ratio of carrier concentrations to the low-field

ratio, obtainable from the usual Hall measurements as a function of temperature. If feasible, experiments of this type in which suitable infrared radiation is used to ionize the donors would also be conclusive.

¹ P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954)

² E. J. Ryder, Phys. Rev. **90**, 766 (1953).

³ E. M. Conwell, Phys. Rev. **90**, 769 (1953).

⁴ Sclar, Burstein, and Davisson, Phys. Rev. **92**, 858 (1953).

Properties of Plutonium Metal

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(Received March 5, 1954)

SOME early information on the structure and physical properties of plutonium metal has recently been declassified by the Atomic Energy Commission. The data, as they were known to the Los Alamos metallurgists in 1945, are given in Table I. Figure 1 shows the dilatation and Fig. 2 the electrical resistivity of a slightly impure sample as a function of temperature.

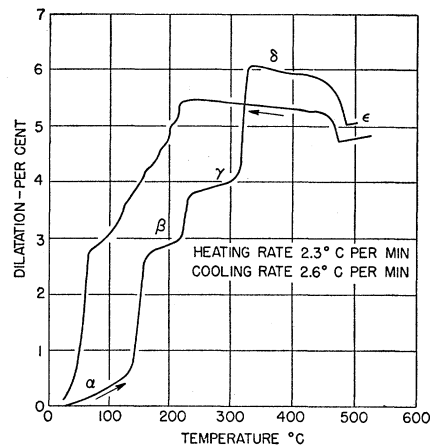


FIG. 1. Dilatation of plutonium metal (slightly impure) on heating and cooling.

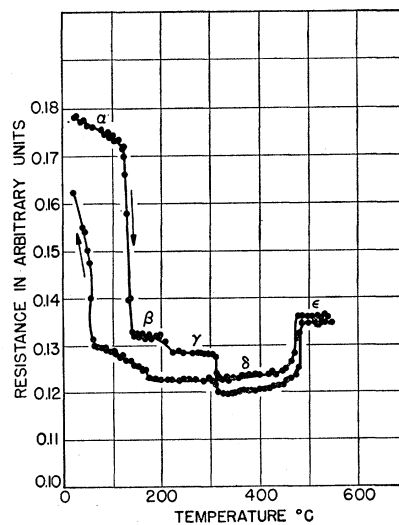


FIG. 2. Change of electrical resistance of plutonium metal on heating and cooling.

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
α	below 117°C	Orthorhombic, like uranium (doubtful)	19.8	55×10^{-6}	150 (25°)	-29.7×10^{-4}
β	117 to 200°C	Unknown (complex)	17.8	35×10^{-6}	110 (200°)	ca 0
γ	200 to 300°C	Unknown (complex)	...	36×10^{-6}	110 (300°)	ca 0
δ	300 to 475°C	Face-centered-cubic	16.0	-21×10^{-6}	102 (400°)	$+1.5 \times 10^{-4}$
ϵ	475 to 637°C	Body-centered-cubic	16.4	4×10^{-6}	120 (500°)	ca 0
liquid	above $637 \pm 5^\circ\text{C}$

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 α and δ phases. The electrical resistivity of all phases is high—that of the α phase exceeding all other “metallic” elements at room temperature. The temperature coefficient of resistance of α is negative and the thermal expansivity extremely high. The *negative* expansion coefficient of the δ phase, which is face-centered-cubic in structure, is without parallel among the elements.

Some further details are given in another paper.¹ 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.

¹ 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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(Received March 24, 1954)

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,¹ who tried to combine two normal elements on either side of a group into a superconducting phase, and he thus discovered Au₂Bi. Later on, however, it became evident that the superconductivity in Au₂Bi had nothing to do with averaging over a superconducting group of elements in the periodic system. Au₂Bi 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. Raub² 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,² 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.³ 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.⁴ 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 Mo₃Ir. This composition will shift the ratio again closer to the favorable value of Tc, and we did find in fact the transition temperature for Mo₃Ir at 8.8°K.

The optimum value for the valence electron/atom ratio had been found to be slightly below 5.⁴ 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.

¹ de Haas, van Aubel, and Voogel, *Leiden Comm. No. 197a,c* (1929).

² E. Raub, *Z. Metallkunde*, **45**, 23 (1954).

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

⁴ 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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(Received March 29, 1954)

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-