Magnetochemistry of the Heaviest Elements. Part VIII. Metallic Plutonium.*

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The magnetic susceptibility of metallic plutonium has been measured up to 350° c. Indications of structure transitions were observed at 119°, 205° and about 300°. The susceptibility of two samples was almost independent of temperature and had the value $2{\cdot}52 \times 10^{-6}$ per g. at 20° for the purest sample. A third sample showed a marked decrease of susceptibility with increase of temperature.

The magnetic susceptibility of metallic plutonium was examined for two main reasons. First, phase changes in metallic systems are often accompanied by small, but abrupt, changes in the susceptibility–temperature curve and the observation of such a curve for plutonium should give information concerning any transition temperatures occurring within the temperature range investigated. Secondly, comparison of the shape of the susceptibility–temperature curve with similar curves for other metals might give information concerning the electronic state of plutonium.

Experimental

The magnetic susceptibilities were measured by use of the quartz torsion fibre microbalance described by Dawson and Lister (*J.*, 1950, 2177). Each sample was sealed in an argon atmosphere inside a Pyrex capillary. After the measurements had been completed, each sample tube

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was broken open at a scratch applied with a sharp edge of broken porcelain, the sample was removed, the two halves of the tube were sealed together, and the magnetic effect on the empty tube was determined. Measurements above room temperature were made by surrounding the sample tube with a non-inductively wound furnace and the temperatures were measured by two thermocouples protruding into the furnace tube, one above and one below the sample. The balance was calibrated by using ferrous ammonium sulphate for which the gram-susceptibility at 20° was taken as $32{\cdot}31 \times 10^{-6}$.

Four samples of plutonium obtained from three separate preparations were used. They were in the form of short lengths of extruded wire; details are given in the tables of results. Sample C is regarded as the purest.

Preliminary measurements on sample A indicated that an abrupt increase in the susceptibility at about 120° was reproducible on the heating curves provided that the sample was allowed to remain at room temperature for about 24 hr. between each set of measurements. Considerable hysteresis was observed; in fact, the change of susceptibility appeared to be not less than 60° lower on cooling than on heating. Cooling curves were not investigated in detail, and for samples B and C, heating curves only were observed with the exception that a single measurement on sample B indicated that the second change in susceptibility behaviour was at least 40° lower on cooling.

The complete heating curves on samples B and C were each extended over three days: first day, α-phase; second day, α → β-transition, β-phase; retained in beta-phase overnight, third day, β → γ-transition and higher temperatures.

The results are given in the Tables. The times quoted in the second columns are the intervals during which the sample temperatures were held constant at the values given in the first columns; the magnetic susceptibilities per g. (χ_g) are shown in the final columns.

*The magnetic susceptibility of plutonium.**

Temp.	*t*	$10^6\chi_g$	Temp.	*t*	$10^6\chi_g$	Temp.	*t*	$10^6\chi_g$	Temp.		$10^6\chi_g$
Sample A. Weight, 6·74 mg. Length 5 mm. Purity, 99·66% excluding oxygen (this sample had a rather thick yellow oxide coating).											
−183°	—	4·20	114°	1	2·62	135°	1	2·70	208°	1	2·66
− 72	—	2·75	116	1	2·65	156	1	2·68	234	0·5	2·57
+ 27	1	2·68	118	1·5	2·68	175	1	2·70	283	0·5	2·56
62	1	2·62	118	2·5	2·70	190	0·5	2·69	294	0·3	2·51
84	1	2·63	125	1	2·69	195	0·5	2·69	304	0·3	2·51
86	2	2·62	127	1	2·69	201	1	2·71	327	0·3	2·52
110	1	2·62	133	0·5	2·70						
Sample B. Weight, 19·84 mg. Length 2·8 mm. Purity, 99·8% excluding oxygen, but no appreciable oxidation visible.											
19	—	5·23	120	1	4·06	185	0·5	2·67	248	0·3	2·26
50·5	0·5	4·90	120	2	4·08	195	0·5	2·52	263	0·3	2·25
79	0·5	4·55	129	1	3·88	196	0·5	2·51	280	0·3	2·24
103	0·5	4·18	143	0·5	3·52	200	0·5	2·40	295	0·3	2·23
110·5	0·5	4·07	155	0·5	3·28	200	1	2·40	304	0·3	2·19
118	1	4·01	166	0·5	3·02	210	0·5	2·33	318	0·3	2·19
120	0·5	4·02	176	0·5	2·80	220	1	2·30	341	0·3	2·19
Sample C. Weight, 20·57 mg. Length 1·6 mm. Purity, 99·87% excluding oxygen (no appreciable oxidation visible).											
20	—	2·52	115·5	1·5	2·49	140	17	2·61	203	0·7	2·59
48	0·5	2·51	117·5	0·5	2·49	167	1	2·61	216·5	0·7	2·52
76·5	0·7	2·51	120	2	2·58	186	1	2·59	239	0·5	2·53
97	1·5	2·50	140	1	2·61	196	0·5	2·59	282	0·5	2·52
101	0·7	2·50									

* *t* = Heating time (hr.).

Discussion

Fig. 1 shows several sharp breaks in the susceptibility–temperature curves. It seems reasonable to associate these changes with the interconversion of different allotropic modifications of the metal. The following table gives the temperatures at which the changes occur and compares them with figures recently quoted for the same transitions determined by other methods. The transition temperatures obtained in this investigation are consist-

ently lower; this may be due to the considerably longer time allowed at each temperature for equilibrium to be established, although heating rates of only 1—2° per min. were used in

Transition temperatures on heating curves (°C).

Transition	Sample	Thermomagnetic	Dilatometric (1)	Dilatometric (2)	Thermal analysis (2)	Electrical resistance (2)
$\alpha \rightarrow \beta$	A	116—118°	136°	135°	140°	135°
	B	118—120				
	C	118—120				
$\beta \rightarrow \gamma$	A	202—208	225	225	235	220
	B	197—200				
	C	204—214				
$\gamma \rightarrow \delta$	A	286—294	320	315	325	325
	B	296—303				
	C	—				

(1) Lord, *Nature*, 1954, **173**, 534. (2) Ball, Robertson, Marden, Lee, and Adams, *ibid.*, p. 535.

the other methods. It is known, however, that these transitions are rather sluggish; for sample B, for instance, the $\alpha \rightarrow \beta$-change required rather more than 2 hr. for completion. The considerable hysteresis effects noted in the Experimental section were also found by

FIG. 1. *The thermomagnetic behaviour of plutonium.*

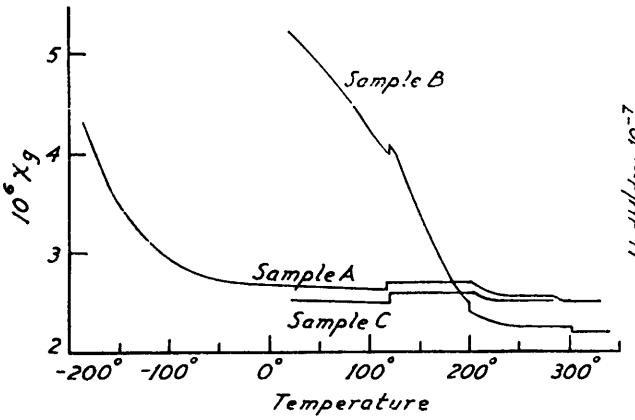
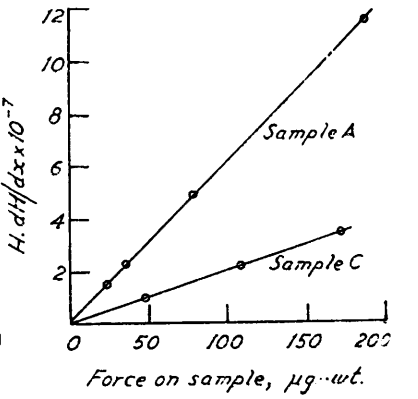


FIG. 2. *Test for ferromagnetic impurity.*



the other methods of investigation. A phase transition at about 475° reported by Ball *et al.* (*loc. cit.*) was not observed in the present investigation since the limit of operation of the balance was about 350°. The lack of results on sample C above 290° was due also to instability which developed in the balance at this point.

Samples A and C were in reasonable agreement in all respects; the slightly higher susceptibility of sample A may be due to the increased impurity, but is not likely to be due to the oxide coating since the susceptibility of plutonium dioxide is very close to that of the metal ($2{\cdot}69 \times 10^{-6}$ per g. at 27°, Dawson, *J.*, 1952, 1882). The susceptibility behaviour of these samples was almost independent of temperature and in this respect was similar to that of uranium (Bates and Hughes, *Proc. Phys. Soc.*, 1954, *B*, **67**, 28). Actually the α-phase showed a slight decrease of susceptibility with increasing temperature which could be predicted on Stoner's free-electron theory ("Magnetism and Matter," Methuen Co., London, 1934, Chap. XIV). Sample B, however, showed a very marked decrease of susceptibility with increasing temperature in both the α- and the β-phase, a type of behaviour found for the lanthanide metals where the susceptibility is due to the presence of ions containing screened unpaired *f*-electrons (*e.g.*, Klemm and Bommer, *Z. anorg. Chem.*, 1937, **231**, 138). The susceptibility at room temperature on a second sample from the same preparation as sample B was $5{\cdot}47 \times 10^{-6}$ per g., also much higher than for samples A and C. It is at present not possible to correlate the different thermomagnetic behaviour with variations of the known impurity contents and it is difficult to attribute it to any preferred orientation

effect. Sample C is believed to represent the nearest approach to the behaviour of pure plutonium metal.

The measurements reported in the tables were obtained by using a maximum field strength of *ca.* 2500 oersteds. It was not possible to extend the measurements to very high field strengths since this would overload the sensitive balance system; in the region 1000—6500 oersteds, however, there was no marked variation of susceptibility with field strength. As an illustration of this, the force acting on the samples in the magnetic field is plotted against $H.\mathrm{d}H/\mathrm{d}x$ in Fig. 2; appreciable amounts of ferromagnetic impurity would be expected to destroy the straight-line relation and to give rise to an intercept on the force axis at $H.\mathrm{d}H/\mathrm{d}x = 0$.

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