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Resistivity and superconductivity of americium metal under pressure up to 25 GPa

P. Link* and D. Braithwaite**
Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe (Germany)

J. Wittig
Forschungszentrum Jülich, Institut für Festkörperforschung, D-52425 Jülich (Germany)

U. Benedict
European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe (Germany)

R.G. Haire
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6375 (USA)

Abstract

We report resistance data for americium metal under pressure up to 25 GPa and at temperatures down to 1.3 K. Samples of ^{243}Am with the double-hexagonal-closed-packed (d.h.c.p.) structure and also with the f.c.c. structure at ambient pressure were studied. The superconducting transition temperature of americium is shown to increase in both cases considerably with pressure, reaching a maximum value of 2.3 K at 6.6 GPa in the case of d.h.c.p. americium. The pressure variation of the superconducting critical temperature and the normal state properties of americium metal exhibit several anomalies, which are discussed with respect to phase transitions established by high pressure X-ray crystallography.

1. Introduction

Americium exists in a pivotal position in the actinide series of elements in that it lies at the transition point for elements normally displaying either itinerant or loacalized 5f electron states. Although the f electrons of americium are normally localized, which could suggest it would be magnetic, it is non-magnetic because of its 5f^6 ground state ($J=0$). The latter situation gave rise to the speculation that americium might be a superconductor [1, 2], which was later verified experimentally [3]. The application of pressure on americium has the potential to increase the overlap between its 5f shells, which would promote the transition from localized to delocalized f electrons. Theoretical approaches have predicted that this transition in americium would be accompanied by a dramatic volume collapse, of the order of 30% [4–6]. Several high pressure X-ray diffraction experiments have been performed [7–9], which show that under pressure the double-hexagonal-close-packed (d.h.c.p.) phase (Am I) transforms to the high temperature f.c.c. phase (Am II). Transitions to a third phase (Am III) and finally an orthorhombic structure (Am IV) [7–9] are reported to occur at higher pressures. The transition pressures given by different researchers vary noticeably and also the structures of the Am III and IV phases are not finally clarified (for a summary see Benedict [10]). The transition to the orthorhombic, α-U form (Am IV) at around 21 GPa [7] is accompanied by a volume collapse of only 6%, the biggest found so far. The resistance of americium has been studied at room temperature to pressures up to 12 GPa [11]; the resistance was found to increase slightly at low pressures and rose sharply as the highest pressures were approached.

We report here the high pressure resistance of the d.h.c.p. and f.c.c. forms of americium as a function of temperature down to 1.3 K and up to pressures of 25 GPa. The superconducting critical temperatures initially

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*Present address: Université de Genève, Section de Physique, DPMC, 24 quai Ernest Ansermet, CH 1211 Genève 4, Switzerland.

**On leave of absence from Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Grenoble, DRFMC–SPSMS, France.

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increased significantly with pressure; T_c and the resistance as a function of pressure were shown to exhibit several anomalies. The comparison of these two high pressure series of measurements leads us to the discussion of potential phase boundaries and a possible change in the nature of the 5f electrons in this metal.

2. Experimental details

2.1. Materials

Thin foils of americium metal (^{243}Am; $t_{1/2} = 7.38 \times 10^3$ years; specific heat, 5.8×10^{-3} W g^{-1}) in two crystal forms were prepared by controlled vapour deposition and subsequent annealing. X-ray diffraction analysis showed that each form was a single phase. One sample had the d.h.c.p. crystal structure ($a_0 = 0.3467(4)$ nm, $c_0 = 1.1240(8)$ nm), while the second crystal form was f.c.c. ($a_0 = 0.4849(5)$ nm). The ^{243}Am isotope was selected to minimize effects from self-heating due to radioactive decay.

2.2. Instrumentation

The experimental instrumentation has been described in detail [12–14]. Briefly, the americium sample together with a piece of Pb serving as an internal manometer [13] was placed in a pyrophyllite sealed cell compressed between two sintered diamond Bridgman anvils. As the pressure transmitting medium we used steatite to obtain quasi-hydrostatic pressures. The resistance of the sample and the Pb was measured with a four-probe d.c. method.

Because of the radiotoxicity of americium, loading operations were carried out in a glove-box. The assembled press was then transferred in a sealed container to a liquid He cryostat, where the temperature was scanned from room temperature down to 1.3 K. The pressure was always increased while the cell was at room temperature. The resistance of the sample was measured over the entire temperature range during cooling and heating for each pressure.

3. Results

The most significant finding in this study was the considerable rise in the superconducting transition temperature for both the d.h.c.p. and f.c.c. forms of americium under pressure. First we report our results obtained with the d.h.c.p. form of americium. Although signs of superconductivity were not seen at normal pressure and at 1.5 GPa within the attainable temperature range (minimum temperature was 1.3 K), at 2.2 GPa the transition temperature had increased sufficiently to be measured. In Fig. 1 the T_c *vs.* p dependence of the d.h.c.p. americium is shown together with the transition widths. We have chosen to plot the onset and $R = 0$ temperatures as an indication of the transition width, as they have greater physical significance than the more conveniently used 10% and 90% temperatures. Several remarkable features are seen in this diagram. Under increasing pressure T_c initially increases with a slope of about 0.45 K GPa^{-1}, if the onset at normal pressure is taken at 0.79 K as reported [3]. T_c increases monotonically up to a value of 2.3 K at 6.5 GPa. It then decreases until a secondary maximum (or at least a clear shoulder) appears at about 10 GPa. T_c decreases steadily again dropping below our temperature limit of 1.3 K at 13 GPa. Surprisingly enough, the d.h.c.p. americium sample's T_c becomes measurable at 17 GPa again and rises to 1.6 K at 19 GPa. T_c decreases once again and no indication of the superconductivity was seen above 21 GPa. As seen from Fig. 1 the superconducting transition observed at 20 GPa exhibited a pronounced tail on the low temperature side. As the width of the transition generally reflects the magnitude of the slope dT_c/dp, one may tentatively infer that the superconductivity of americium disappears particularly steeply at this point.

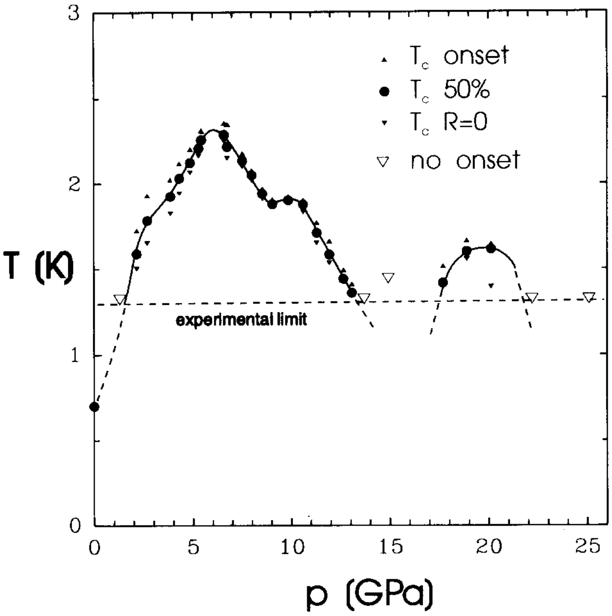

Fig. 1. Variation in the superconducting transition temperature T_c of d.h.c.p. americium with pressure. The different symbols show the onset, midpoint and zero resistance temperatures.

Figure 2 shows the critical temperature determined for the f.c.c. form of americium. We first observed the transition to superconductivity of the f.c.c. sample at a pressure of 4.7 GPa. The triangles represent the onset and $R = 0$ values of the transition and therefore the width of the transition. Taking into account the T_c value of 1.05 K at ambient pressure [3], T_c of the f.c.c. sample had to increase strongly to the maximal value of 1.83 K we observed at 4.7 GPa. At higher

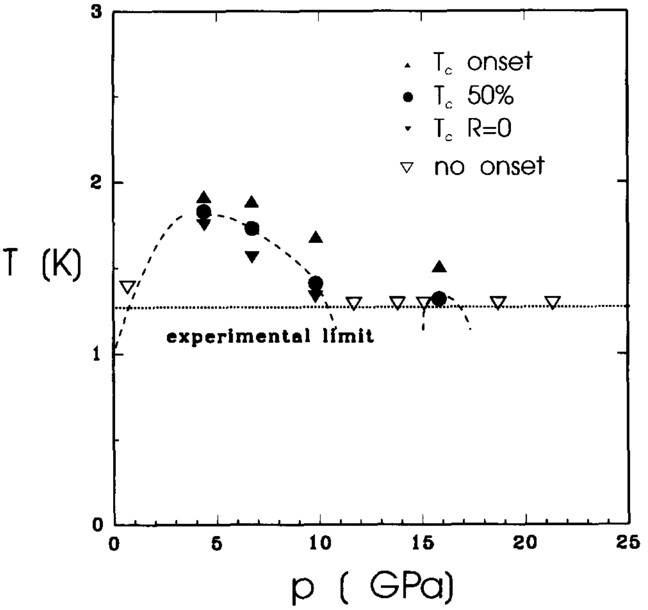

Fig. 2. Variation in the superconducting transition temperature T_c of f.c.c. americium with pressure. The different symbols show the onset, midpoint and zero resistance temperatures.

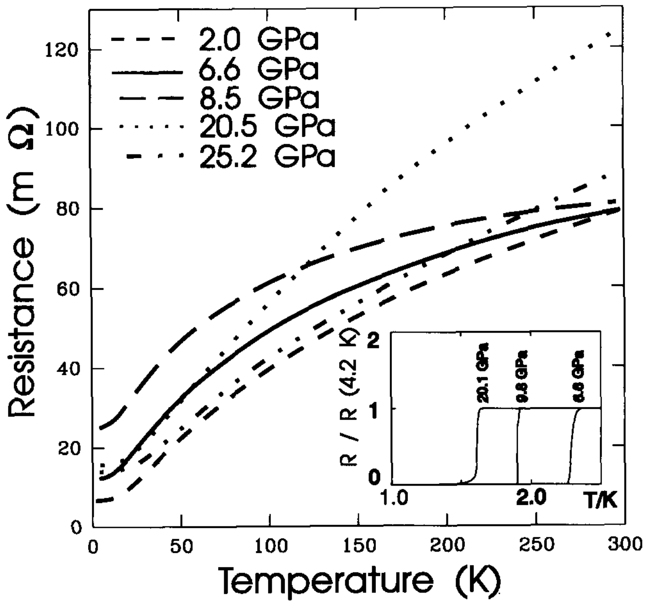

Fig. 3. Resistance *vs.* temperature curves for d.h.c.p. americium at selected pressures. The superconducting transitions for three pressures are also shown, representing the sharpest transition (9.8 GPa), the broadest transition (20 GPa) and the highest T_c (6.6 GPa).

pressures T_c decreases and becomes undetectable around 10 GPa, to reappear at 16 GPa and to disappear again for the highest pressures.

Figure 3 shows resistance *vs.* temperature curves for the d.h.c.p. form of americium; transitions are also shown. The superconducting transition of americium was sharp and, with a slow scanning of the temperature, totally reversible. The lowest pressure resistance curves agree very well with previous, normal pressure measurements on thin samples [15]. In Fig. 4(a) we show a compiled diagram of the resistance of d.h.c.p. americium *vs.* pressure and temperature. A broad maximum in the low temperature resistance occurring at pressures between 6.6 GPa and 10 GPa is one and a sharp peak at 20 GPa, most pronounced at higher temperatures, another remarkable feature exhibited by this view. The ratio between the resistance at 273 K and 4.2 K is considerably smaller in the f.c.c. sample, probably because of the different preparation procedure. At our lowest pressure measurement of 0.7 GPa we find a ratio $R(273\ \mathrm{K})/R(4.2\ \mathrm{K})$ of around 5, while the d.h.c.p. sample had a ratio of 15. The resistance *vs.* pressure curves of the f.c.c. sample are w-shaped (Fig. 4(b)). For pressures above 10 GPa, they exhibit a similar shape to those of the d.h.c.p. sample shown in Fig. 4(a). The resistance of the f.c.c. sample decreases first to a minimum around 4.5 GPa and increases then to a maximum at 9 GPa for ambient temperature. At low temperatures the maximum is shifted to lower pressures. Further, the resistance decreases again to a minimum around 15 GPa. Finally there is a pronounced maximum around 18 GPa.

4. Discussion

Comparing Figs. 4(a) and 4(b) for the d.h.c.p. and f.c.c. americium respectively, the main differences appear at low pressures, where the phase transition Am I–Am II should not occur in the case of f.c.c. americium. In the neighbourhood of 20 GPa we find for both a pronounced maximum, which we attribute to the phase transition to the Am IV phase. The difference of 2 GPa in the absolute pressure of this maximum (Fig. 4) might be due to experimental uncertainties such as the pressure gradient in the cell, although this is more than the usual error.

The differences appearing in the low pressure region may help us to distinguish the phase boundaries Am I–Am II and Am II–Am III. From the *R–T–p* diagram of f.c.c. americium (Fig. 4(b)) we see at constant temperature that the initial slope of the resistance *vs.* pressure is inverted, compared with d.h.c.p. Furthermore we find a maximum in the resistance, which obviously shifts from around 6.5 GPa at low temperatures to about 9 GPa at ambient temperature. Tentatively one may attribute this feature to the trace of the Am II–Am III transition. Thus it appears that the maximum at low temperatures in the case of d.h.c.p. americium (Fig. 4(a)) is a mixture of two superimposed effects, *i.e.* phase transitions. We finally suggest a transition pressure of around 6 GPa for the Am I–Am II transition at all temperatures below 300 K. This agrees with the tran-

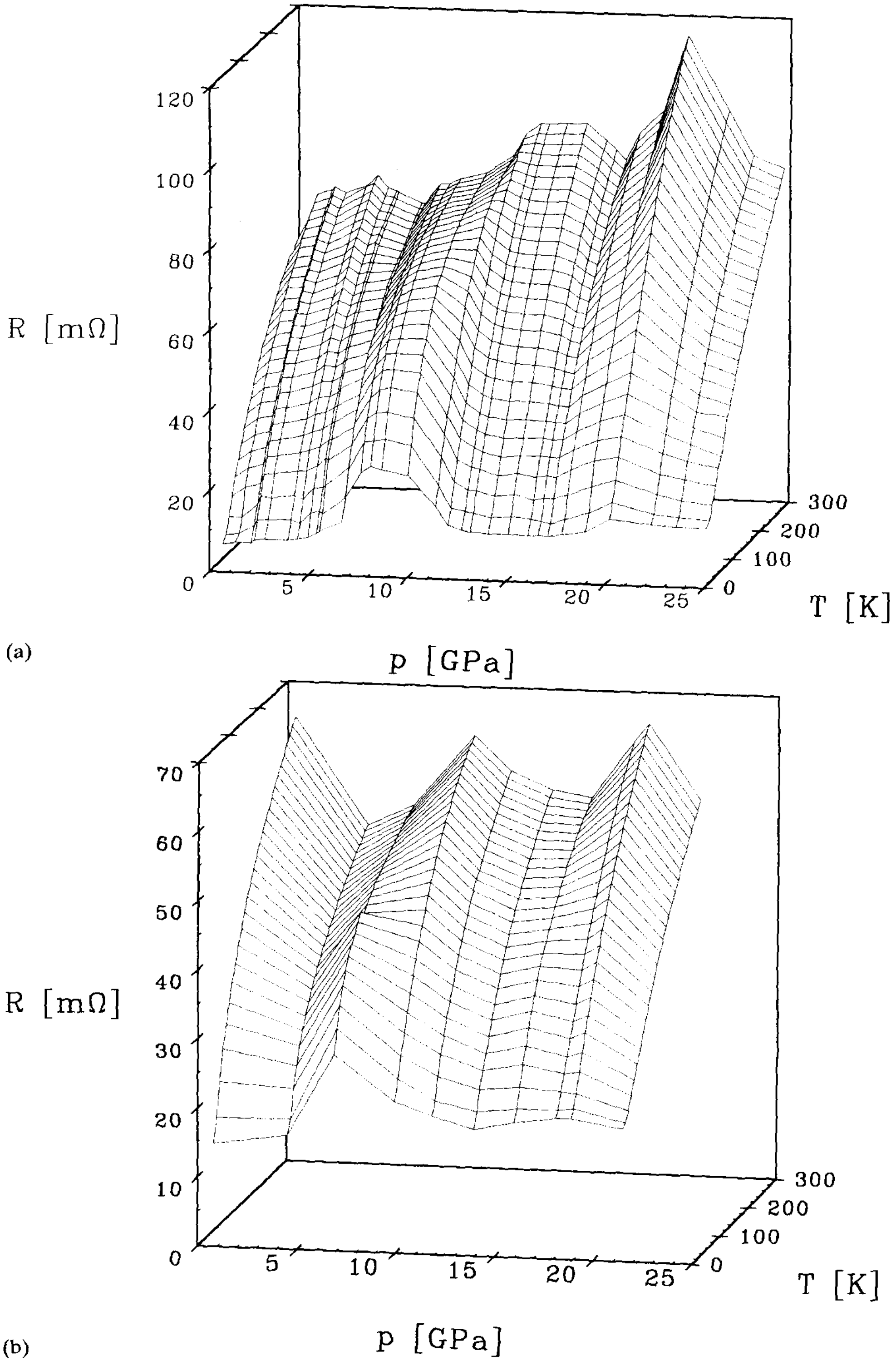

Fig. 4. Resistance *vs.* pressure and temperature for (a) d.h.c.p. americium and (b) f.c.c. americium. The isobaric lines represent the pressures where the measurements were made. The isothermal lines are guidelines for the eye.

sition pressure given by Akella *et al.* [8] at room temperature. For the transition from Am II to Am III we take the phase boundary as derived from Fig. 4(b).

These phase transitions are also reflected in the variation in the critical temperatures (Figs. 1 and 2). In the case of d.h.c.p. americium we find a maximum in T_c around 6 GPa, the pressure where, according to our analysis, the Am I–Am II transition takes place. The strong initial increase in T_c with pressure is reminiscent of the behaviour of lanthanum [16]. To stress the similarity of americium with lanthanum further, we mention that lanthanum undergoes a d.h.c.p.-to-f.c.c. phase transition at 2.8 GPa also. Contrary to the behaviour of lanthanum, where T_c discontinuously rises by roughly 1 K at the phase transition, for americium we find the phase transition marked by a maximum in T_c. The shoulder around 9 GPa might be assignable to the Am II–Am III transition. Finally the drop of T_c at 20 GPa we consider to be caused by the Am III–Am IV transition. This phase transition was previously associated with the onset of the itinerancy of the 5f electrons [7]. We believe our measurements provide some, admittedly faint, support for this notion. The sharp drop in the superconducting critical temperature above 20 GPa may be taken as a sign of a "magnetic behaviour", when the $5f^6$ configuration starts breaking up. Further investigation of $T_c(p)$ dependence in this pressure region is of considerable interest, but clearly outside of the present experimental possibilities.

A comparison of Figs. 1 and 2 shows that the T_c data for the f.c.c. americium are appreciably lower than the T_c values of the d.h.c.p. americium although there is considerable qualitative agreement. One can also see from Fig. 2 that in the case of the f.c.c. americium the transitions are generally broader than those of the d.h.c.p. americium. We tend to attribute this finding to the different sample treatment during the preparation, as already seen in the residual resistance ratio. Nevertheless we are able to deduce from our data that the critical temperature has a maximum around 5 GPa, disappears and has at high pressures a second relative maximum before it finally disappears. This behaviour is in general similar to that of d.h.c.p. americium and for more detailed conclusions more data are necessary.

5. Summary

We have shown that the superconducting T_c of americium exhibits fascinating features when pressure is applied. Also, important new, although indirect, evidence for the delocalization of the 5f electrons at the Am III to IV transition is provided. Our results seem to support the X-ray data as to the different phases of americium and provide some new information on the low temperature part of the phase diagram, although some uncertainties still remain. We hope that these results will stimulate further work on this highly interesting transuranium element.

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