Superconductivity in the Americium Metal as a Function of Pressure: Probing the Mott Transition

J.-C. Griveau, J. Rebizant, and G. H. Lander

European Commission, Joint Research Centre, Institute for Transuranium, Elements Postfach 2340, 76125 Karlsruhe, Germany

G. Kotliar

Center for Materials Theory, Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

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High-pressure measurements of the resistivity of americium metal are reported to 27 GPa and down to temperatures of 0.4 K. The unusual dependence of the superconducting temperature (T_c) on pressure is deduced. The critical field [$H_c(0)$ extrapolated to $T = 0$] increases dramatically from 0.05 to ~1 T as the pressure is increased, suggesting that the type of superconductivity is changing as pressure increases. At pressures of ~16 GPa the $5f$ electrons of Am are changing from localized to itinerant, and the crystal structure also transforms to a complex one. The role of a Mott-type transition in the development of the peak in T_c above 16 GPa is postulated.

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Americium is the first actinide element in which, at ambient pressures, the $5f$ electrons may be described as *localized* (as is found, for example, in most of the $4f$ rare-earth series) and thus do not participate in the bonding. Am^{3+} has an electronic ground state with a $J = 0$ singlet, so that (in Russell-Saunders coupling) $L = -S = 3$ and no magnetic moment exists. A similar conclusion is reached starting from the jj coupling scheme, Am^{3+} with six f electrons has a full $j = 5/2$ shell. This simple picture of Am metal, whereby six f electrons form an inert core, decoupled from the spd electrons that control the physical properties of the material, led to the prediction [1] in 1975 of superconductivity in Am, a prediction soon verified [2] showing $T_c = 0.79$ K. A decade ago equipment became available in the Institute of Transuranium Elements in Karlsruhe to measure the resistivity of active materials under pressure, and early work [3] showed that T_c rapidly increased with pressures in the GPa range. At that time the minimum temperature of the equipment was ~1.3 K, and no magnetic field was available to estimate H_c.

The interest in Am under pressure increased with the elegant experiments determining the crystal structures [4,5] as a function of pressure up to 100 GPa. In this pressure range, Am exhibits three phase transitions. The first between Am I (dhcp crystal structure) and Am II (fcc structure) involves only a small reduction in volume. The second phase transition occurs at 11 GPa with the development of Am III—an orthorhombic $Fddd$ structure, which is also found in the γ-Pu phase at high temperature. This transition involves a small contraction of ~2% in the volume of the unit cell. At 16 GPa a third phase transition occurs into the Am IV phase ($Pnma$ structure, close to that of α-uranium) with a 7% relative volume collapse.

As proposed in Ref. [1], at ambient pressure Am I can be described as a localized system in which the $5f$ electrons do not participate in the bonding. On the other hand, in Am IV the bulk modulus is substantially larger (~100 GPa) than in the other three preceding phases (~30 GPa), suggesting that the $5f$ electrons in this phase are fully delocalized and participate in the bonding [5]. Indeed, density functional calculations with the $5f$ electrons treated as core states give an equilibrium volume [6] close to that of Am I and obtained Am IV as the stable phase at high pressures [7]. These studies predict an abrupt Mott transition with a large volume collapse of the order of 25% to 30% on passing to Am IV.

The experiments of Refs. [4,5] raise the fundamental question of how the Mott transition (i.e., the evolution of the f electrons from the localized to the itinerant limit) takes place in Am metal. Am offers a perspective on the Mott phenomena complementary to the one obtained from Pu, its immediate neighbor in the periodic table. First, in all the phases of Pu, the f electrons are itinerant (even though in δ-Pu the f states are at the brink of localization [8,9]), whereas in Am the actual transition between a localized to an itinerant f electron is realized. Second, Pu has an open shell of f electrons, whereas Am, at least in the initial state, is closer to a full $j = 5/2$ shell.

In this Letter we experimentally address these issues and their impact on the superconductivity of Am. Measurements have been performed at the Institute for Transuranium Elements, Karlsruhe, on thin foils of americium metal (^{243}Am; $t_{1/2} = 7.38 \times 10^3$ yr) with the dhcp structure. Two samples (A and B) were extracted from the same batch as in Ref. [3]. The dimensions of samples A and B were, respectively, $\sim 600 \times 70 \times 30$ μm^3 and $550 \times 80 \times 30$ μm^3. The low amount of material (<100 μg) reduced the self-heating effect (6.3 mW/g) due to alpha decay. The resistance of the sample was measured by a four probe dc technique with the sample and a thin foil of lead (manometer) held in a pyrophyllite gasket and with a solid pressure-transmitting medium of steatite. The external

pressure device was a piston-cylinder system made of nonmagnetic CuBe, with the pressure generated by two 1.5 mm diameter anvils made of low-magnetic tungsten carbide and sintered diamonds [3]. We adapted a ^{3}He refrigerator to cool the pressure device to temperatures of 275 mK. Self-heating effects prevented cooling of the sample below ~400 mK. An external superconducting magnet allowed a maximum magnetic field of 0.6 T to be applied.

Figure 1 displays the resistance as a function of (T, p) for ^{243}Am up to $p_{max} = 27$ GPa and down to $T_{min} = 0.4$ K. Overall, the measurements reproduce well the behavior previously reported, but they are now extended to below 0.8 K, the ambient pressure T_c, and a small magnetic field can be applied (see below). We note that the residual resistivity ratio (RRR) of the present sample as presented in Fig. 1 is considerably better than those shown in Ref. [3].

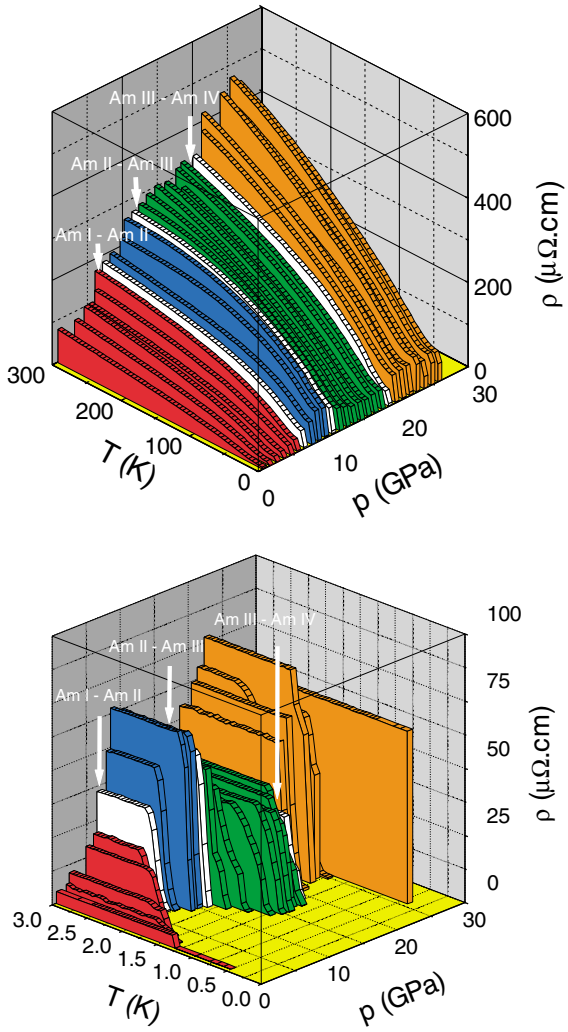

FIG. 1 (color). Overview of the resistivity data as a function of pressure and temperature. The phase boundaries (taken from Refs. [4,5]) are shown. The lower figure shows the same data but only up to a maximum of 3 K, to show clearly the superconducting region.

This better RRR, probably due to having a better grain structure in our sample, allows more quantitative deduction of the superconducting parameters.

The strong increase of resistivity as a function of increasing pressure [3,10] and temperature [3,11] have been noted before and appear as an intrinsic property of Am that is not observed in other (lighter) actinides. These observations suggest that the f electrons play an important role in the transport properties, strongly scattering the spd conduction electrons when they are localized, and contributing to the transport when they are itinerant.

Figure 2 shows T_c as a function of fractional volume shift $\Delta V/V_0$, where $\Delta V = V_0 - V(p)$, with V_0 the atomic volume at ambient pressure. The figure exhibits a rich behavior with two maxima, one near the Am I–Am II boundary and the second very sharp maximum within the Am IV phase. At the highest pressures, T_c decreases with pressure with a slope of -0.15 K/GPa (Fig. 2) and is extrapolated to disappear at around 55% of the initial volume (30 GPa). Both Am II and Am III remain superconductors at all temperatures, a point that was not established in the previous work. The inset shows measurements to determine critical field $H_c(T)$ at $\Delta V/V_0 = 0.39$, corresponding to 20.8 GPa. The width of the superconducting transition temperature ($\Delta T_c \sim 100$ mK) indicates good hydrostatic pressure conditions.

The first important result of our studies is the very sharp maximum in T_c as observed in Am IV just as the compressibility data [4,5] show that the bulk modulus has changed, a complicated α-uranium-like structure is adopted, and, according to all calculations, the $5f$ electrons

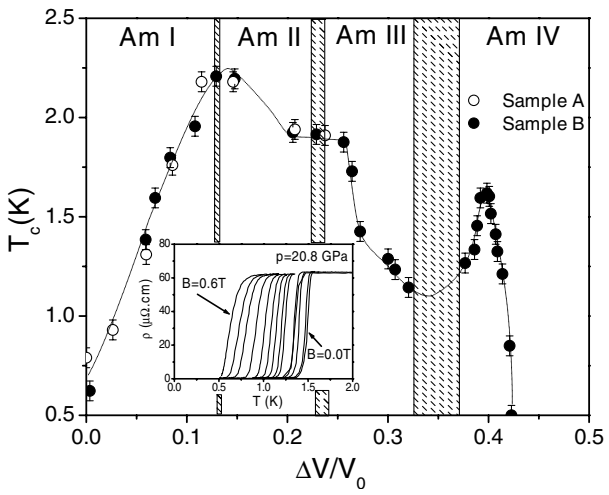

FIG. 2. The superconducting temperature T_c plotted as a function of fractional volume shift $\Delta V/V_0$, where $\Delta V = V_0 - V(p)$, with V_0 the atomic volume at ambient pressure. T_c is determined as the midheight of the transition. The inset shows the change of resistivity as a function of applied magnetic field at an atomic volume corresponding to the maximum within the Am IV phase. The shaded areas represent the transition between the different phases.

have become itinerant; i.e., the Mott transition has occurred. The maximum of T_c in the proximity to the Mott transition can be understood on very general grounds. At very large pressures, the transition temperature decreases since the f kinetic energy becomes large compared to the pairing interactions (i.e., the f density of states is reduced). At smaller pressures in the Am III phase, the decrease in pressure localizes the f electrons, which therefore cannot superconduct. These ideas have recently been supported by explicit dynamical mean field calculations [12]. Here these ideas are realized in an element. With decreasing pressure, the dramatic decrease in the bulk modulus when progressing from the Am IV to Am III phase is an experimental proof of the localization of the $5f$ electrons upon entering Am III.

Previous studies at ambient pressure [13] indicate Am is a type-I superconductor with a relatively high zero-temperature critical field $H_c(0) = 53$ mT compared to other BCS superconducting elements [14] considering its low T_c [15]. The pressure dependence of the upper critical fields measured here is surprising, with $H_c(0)$ increasing rapidly with pressure as shown in Fig. 3 and attaining a value of over 1 T at the maximum of T_c. This feature has already been observed in some elements at structural phase transitions (Ga), and a change of type of superconductivity is observed [16]. Since a critical field of 1 T would be most unusual for a type-I superconductor with $T_c = 2.3$ K, the following question must be raised: Does Am become a type-II superconductor under pressure?

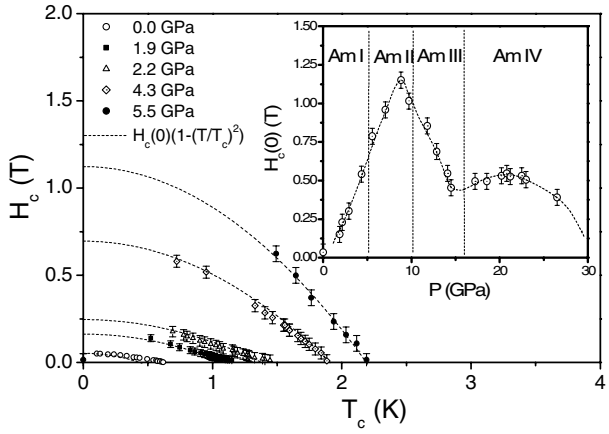

FIG. 3. The critical field $H_c(T)$ for various pressures with the extrapolations to $H_c(0)$. The inset shows the extrapolated critical field to $T = 0$, $H_c(0)$, as a function of pressure. Note that the $H_c(0)$ has been deduced with the empirical $H_c(0) \times (1 - t^2)$ law with $t = T/T_c(p)$. The dependence of this extrapolation will change depending on the type of superconductivity assumed. Assuming Am as the type II superconductor and using the Werthamer-Helfand-Hohenberg approximation [22] to determine the orbital critical field $H_{c2}(0)$ leads to similar values. Therefore, the exact value of $H_c(0)$ [or $H_{c2}(0)$] is not crucial; whatever form is used $H_c(0)$ [or $H_{c2}(0)$] increases dramatically as a function of pressure.

This point may be addressed by calculating the mean-free path l and the coherence length ξ_0 from resistivity and critical field measurements and determining if the material changes from a clean metal superconductor (in the "clean limit," $l \gg \xi_0$) to a "dirty superconductor" ($l \ll \xi_0$). Considering the relation between l and ρ [17], we assume Am has three delocalized spd electrons for all pressures in this region. For ξ_0, we assume either type-I or type-II superconductivity. Type-I superconductivity implies relations between $T_c(p)$, the unit cell volume under pressure, and $H_c(0)$ [18] only. For type II, $H_c(0)$ is assimilated into H_{c2}, and we extract the intermediate parameter ξ_{GL} [19]. ξ_0 is finally determined according to the "clean" or "dirty limit" scenario with $l(p)$ considered in addition [18,19]. l, ξ_{GL}, and ξ_0 estimated according to the type-II dirty limit scenario are presented in Fig. 4. We can also deduce the Sommerfeld coefficient γ [18,19].

At the highest pressures (where the superconductivity is of type II in the dirty limit) the value is derived to be modest ($\gamma \sim 60$ mJ mol^{-1} K^{-2}). Am IV at these high pressures (>20 GPa) is a metal with itinerant $5f$ and spd electrons spread out over a large energy near E_F, so this modest

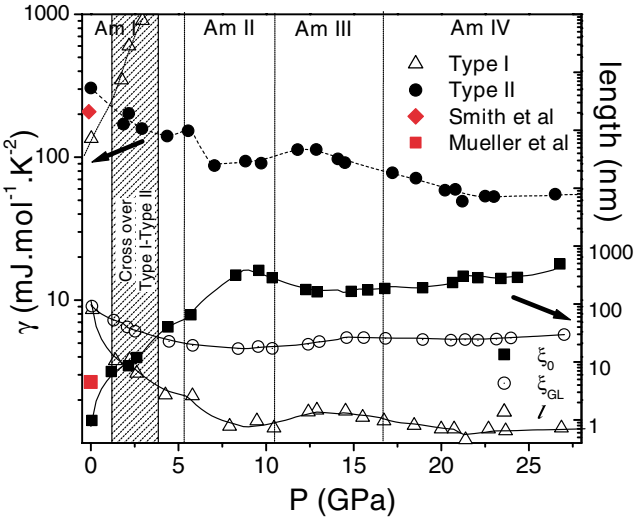

FIG. 4 (color). Upper curves: (Sommerfeld) coefficients deduced from the superconducting properties. Open triangles (circles) assuming type-I (type-II) superconductivity. The solid diamond is derived in Ref. [13] from the superconducting properties. The solid square is the value obtained in Ref. [13,20] by direct specific-heat measurements. The lower curves show the mean-free path (l) (open triangles) and the coherence lengths (ξ_0, ξ_{GL}) as deduced assuming (1) BCS (solid squares) in the clean limit and (2) Ginzburg-Landau in the dirty limit (solid circles). The drastic decrease of l with pressure (2 orders of magnitude) is directly related to the huge increase of resistivity at low temperature ($l \sim 1/\rho$ in the free electron approximation [17]). This implies an important scattering process that leads to an increase of magnetic penetration depth (λ_L) and a decrease of superconducting coherence length (ξ_0), and therefore to a possible change in the type of superconductivity [18].

specific heat is credible. At the Am III phase ($p < 16$ GPa) the $5f$ states move through E_F on their way to localization. The coefficient therefore increases when approaching the Am III–Am IV boundary. As the pressure is further reduced into Am II and then Am I, the Sommerfeld coefficient appears to increase further; however, this is not a reasonable result, indicating that the hypothesis of type II superconductivity is no longer correct. At the lowest pressures the form of the superconductivity becomes difficult to characterize, a point already emphasized by Smith *et al.* in their earlier work on this system [13]. The open triangles show our deduction of γ assuming type-I superconductivity. This is in good agreement with the value of 200 mJ mol^{-1} K^{-2} (solid diamonds) given in Ref. [13] as deduced also from the superconducting properties. On the other hand, these values are in sharp disagreement with the value of $\sim$3 mJ mol^{-1} K^{-2} deduced from specific-heat experiments [13,20] (solid squares). At low pressure the mean-free path becomes shorter than the coherence length (inset of Fig. 4), which is another indication that there is a change from type I (or some complicated) superconductivity at low pressures to type II at higher pressures. The precise physics of the superconductivity in the low-pressure range remains poorly defined.

A major challenge is to understand a broad maximum (Fig. 2) in T_c as a function of pressure in the range of pressures corresponding to Am I and Am II, when the $5f$ states are still localized. At zero pressure, Am metal is well described by an inert atomic occupied $5f^6$ configuration at each lattice site and an itinerant spd band containing three electrons. As pressure is applied, the energy of another configuration approaches the Fermi level, and begins to be admixed into the ground state, a fact that can account for the increase in room temperature resistivity, and the maximum of T_c, which in a mixed valence fluctuation mechanism occurs when the configurations $5f^6$ and $5f^5sd^1$ (or $5f^6sd^1$ and $5f^7$ at the Fermi level) become degenerate. These ideas were proposed in connection with $CeCu_2Si_2$ [21].

Across this total pressure range (up to 27 GPa) there is no sign of any transition to ordered magnetism, as judged by an anomaly in the resistivity, in contrast to the predictions of Söderlind *et al.* [6]. It would be interesting to perform specific-heat experiments of Am at low temperature and with modest pressures, as the exact form of the superconductivity at low pressures is not well established.

With elements such as americium the difficulty of manipulating the material has discouraged much experimental work. On the other hand, the extreme simplicity of the half-filled $j = 5/2$ shell of localized $5f$ electrons in ambient-pressure americium and the change as a function of pressure would appear to be a textbook example of the Mott transition. Indeed, theory has predicted a volume collapse of between 25% and 30% [6,7]. This is clearly far too simple. The structural study [4,5] shows that the volume changes are small, at most 7% between Am III and Am IV. Despite this, there is a very sharp increase in T_c as a function of pressure (see Fig. 2) that we attribute directly to the Mott transition when the $5f$ states pass through the Fermi level.

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