New Phase Boundary for Cerium

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(Received 18 August 1969)

The phase boundary for the high-pressure superconducting α' phase of cerium has been determined from 77 to 480°K from observations of the resistance anomaly which occurs at the $\alpha \to \alpha'$ transition. The observed transition pressure at 297°K is 55.8±0.5 kbar, varying linearly with temperature with $\partial P/\partial T = -34.9$ bar/deg. The change in the electronic properties of cerium as a function of pressure is discussed.

A RECENT room-temperature high-pressure x-ray study[1] of cerium has revealed that the superconducting phase[2] formed above 50 kbar is the result of a further collapse of the fcc phase, with a $\sim 4\%$ change in volume, following the well-known $\gamma \to \alpha$ transition at ~ 7 kbar. We have employed the resistance anomaly[2–4] which occurs at this transition to trace out the $\alpha - \alpha'$ phase boundary over the temperature range 77 to 480°K.

The sample ($3 \times 0.5 \times 0.03$ mm) of Johnson-Matthey 99.9% Ce was sandwiched between AgCl discs dusted with talc and mounted between Bridgman anvils.[5] Pressures were determined relative to a previous calibration against the resistance discontinuities of Bi (25.4, 26.8, and 88 kbar), Tl (36.7 kbar), and Ba (58.6 kbar). The potential drop across the specimen and a manganin resistance pressure gauge situated in the main hydraulic line to the press ram were displayed directly on an X-Y recorder. The resistance increase at the transition was reasonably sharp (~ 5 kbar wide at room temperature) and amounted to $\sim 6\%$ of the total resistance. It was found to be independent of temperature and did not exhibit the very large hysteresis or sluggishness reported by Wittig.[2] The room-temperature hysteresis was ~ 13 kbar, increasing at 77°K to ~ 25 kbar and decreasing to ~ 7 kbar at 480°K. The transition pressure was taken to be the midpoint of the resistance increase on the forward pressure cycle.

We find a transition pressure of 55.8±0.5 kbar at 297°K compared with previous values of 91,[3] 60–65,[4] and 50 kbar [2] from resistance measurements and 50 kbar from the x-ray measurements.[1] This variation in transition pressure is probably a result of differences in sample purity since it has been established[6] that, for example, the addition of Yb rapidly increases the transition pressure. The transition pressure was found to vary linearly with temperature between 77 and 480°K with $\partial P/\partial T = -34.9$ bar/deg.

In Fig. 1, we reproduce the phase diagram[7] for cerium including the newly determined $\alpha - \alpha'$ phase boundary. It should be noted that whereas there is very strong evidence[8–11] that the $\gamma - \alpha$ boundary terminates in a critical point in the vicinity of 600°K and 20 kbar, there is no indication that this will happen for the $\alpha - \alpha'$ boundary. It is also interesting to observe that, on extrapolation, the $\alpha - \alpha'$ boundary line intersects the minimum in the fusion curve at the same point as the extrapolated $\gamma - \alpha$ boundary line.

The $\gamma \to \alpha$ transition has been explained as the consequence of the transfer of an electron from a $4f$ state to a $5d$ state. It has been questioned whether there is a complete transfer of the $4f$ electron and various estimates have been made of the valence state of $\alpha -$Ce.[12] Heat-capacity measurements[13] taken on $\alpha -$Ce at 11 kbar have demonstrated the absence of local moments but the high density of states which was found suggests that a high degree of $4f$ character is present in the electron wave functions at the Fermi surface.

Beecroft and Swenson[8] have suggested that the degree of $4f$ character in the wave functions for the γ and α phases varies continuously along the phase boundary until at the critical point it is the same for both phases. Jayaraman[11] has pointed out that the initial negative slope of the fusion curve implies that the density is higher in the liquid than in the solid and he explains

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this by a collapse of the Ce atoms on melting due to a further reduction of their $4f$ character. He also remarks that a rapid increase in density in the solid is to be expected along the extrapolated line of the $\gamma-\alpha$ boundary, terminating at the minimum in the fusion curve, beyond which, presumably, the loss of $4f$ character is complete.

It would seem more appropriate therefore, to associate the $\gamma \rightarrow \alpha$ transition with a change in the magnetic character of the $4f$ electron[14] and the loss of the $4f$ character with the $\alpha \rightarrow \alpha'$ transition. This proposal is consistent with the absence of an increase in the number of conduction electrons at the $\gamma \rightarrow \alpha$ transition, as deduced from positron annihilation measurements.[15] It may be argued then that the absence of superconductivity in the α phase[13] is due to the strong $4f$ character associated with the cerium.

The absence of superconductivity in scandium and yttrium, elements isoelectronic with lanthanum and having very similar density of electron states at the Fermi level, led to the suggestion[16,17] that the superconductivity of La is anomalous in origin and associated with the proximity of the $4f$ electron states to the Fermi surface. The large positive pressure dependence of the superconducting transition temperature was considered[17] to be a further indication of an unusual superconductive mechanism for this element.

However, it now seems evident that $4f$ electron character, far from being a necessary factor, plays an adverse role in the occurrence of superconductivity in cerium. Thus, it would now appear more reasonable to assume that lanthanum is a superconductor in spite of any $4f$ character which may exist in its electron wave functions and it is the reduction of this $4f$ character which results in the increase of T_c under pressure. A similar viewpoint has been adopted by Ratto, Coqblin, and Galleain d'Agliano[18] in their model for the superconducting properties of La and Ce.

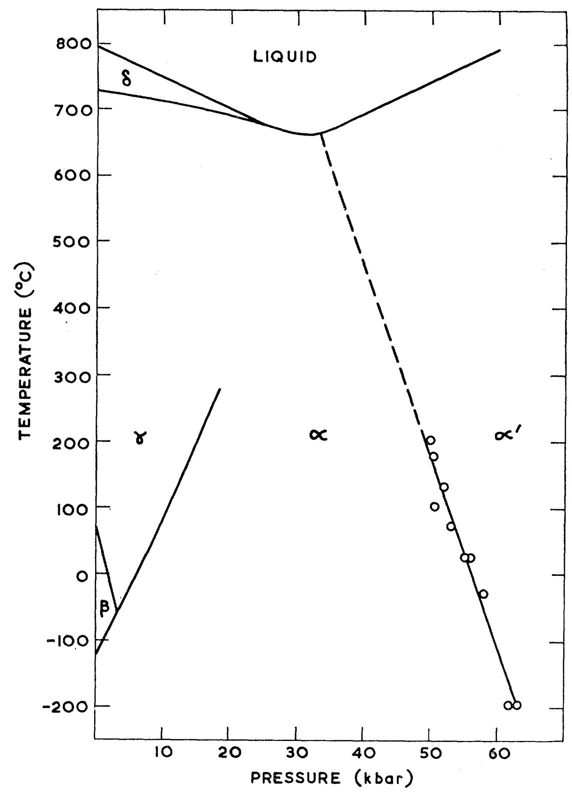

FIG. 1. Phase diagram for cerium.

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