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TITLE: MULTIPLE MARTENSITIC TRANSFORMATIONS, INCOMMENSURATE/ COMMENSURATE PHASES AND CHARGE-DENSITY-WAVE STATES IN PLUTONIUM METAL: THEIR CONSEQUENCES

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MULTIPLE MARTENSITIC TRANSFORMATIONS, INCOMMENSURATE/COMMENSURATE PHASES AND CHARGE-DENSITY-WAVE STATES IN PLUTONIUM METAL: THEIR CONSEQUENCES

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Simultaneous measurements of electrical resistivity, elongation and temperature have been made on a Pu metal specimen between -80K and 733K. This temperature range covers part of the α-phase range and up through a major portion of the δ-phase range.

Figure 1 shows two hysteresis loops suggestive of martensite-like transformations. The first loop which spans the $\alpha \rightleftarrows \beta$ phase transformation is like that seen with Au-49% Cd. The second loop which spans the $\gamma \rightleftarrows \delta$ transformation is like that seen with Fe-Ni (70:30) alloy, but inverted. These loops seen with Pu metal are thus like those of completely different transition element alloy systems.

Figure 1 shows that the β and γ phases seem to be electronically similar on warming because there is no apparent change in electrical resistivity on the warming cycle. Likewise the resistivity at the indicated $M_f(\delta \rightleftarrows \gamma)$ transformation (cooling) becomes that of the β phase seen on warming. This seems to indicate that the β phase is the product phase of the $\gamma \rightleftarrows \delta$ transformation.

An interpretation of Fig. 1 is that there is a thermal modification of the f-d-s electron distribution on warming from 80K to 733K and a reverse modification of the electron distribution on cooling back over the same temperature range but with a temperature delay in the crystal structure changes required.

Only one elongated hysteresis loop is seen on Fig. 2. This figure suggests that the indicated double martensitic transformation of Fig. 1 is smeared out on cooling into one continuous transformation between δ and α phases. This suggests the possibility of a direct δ to α phase transformation under the correct processing condition.

Regions I, II and III which are shown on Fig. 2 were first seen by Pascard [1]. He considered the transformations between these three regions to be martensitic. Region I appears to be the δ phase existing into a lower temperature range, while Region II can be interpreted as being a new

phase. The steps seen in Region III can be indicative of martensitic bursts.

Figure 2 also suggests that the β phase is the product phase of the $\gamma \rightleftarrows \delta$ reverse transformation. This figure also suggests that the γ phase seen on cooling may be a composite structure (incommensurate) involving the β phase and δ' phase. This is based on the assumption that the new phase of Region II is a reappearance of the δ' phase. A composite structure involving β and δ' phases could give the (incommensurate) Fddd space group structure [2] reported for γ phase Pu.

The magnetic susceptibility behavior of Pu metal, as a function of temperature, is shown on Fig. 3 [3]. We believe the results shown on this figure can account for the hysteresis loops shown on Figs. 1 and 2.

The increase in magnetic susceptibility between the α and β phases may be due to a slight localization of d electrons (d-s hybridization) as is seen with TiNi alloy on its transformation from $P2_1/m$ (α-Pu structure) martensite. The decreasing susceptibility through the γ and δ phases must be due to a continued (6d7s) $\rightarrow$ 5f electron promotion on continued warming.

The increasing magnetic susceptibility noted on warming through the δ' phase should be due to an inverse modification of the electronic structure, i.e., a 5f $\rightarrow$ (6d7s) promotion. The minimum in magnetic susceptibility must represent the minimum in (6d7s) electron population in Pu metal and possibly the lowest metal density.

Figure 3 suggests why fixed-rate cooling from the ϵ-Pu phase region gives such a greatly different hysteresis loop in physical properties than is seen with fixed-rate cooling from the δ phase, as shown on Figs. 1 and 2. We suggest that the beta-phase electronic structure (warming) does not appear in either case.

We suggest that publications of Johannson (1975) [4], Baptist et al (1982) [5] and Bonnelle et al (1975) [6] give the solution outlined above. Johannson [4] assumed that the broad (6d7s) band had a higher binding energy capability than a narrow 5f band. He gave the division of electrons between the conduction band and the 5f band for Pu as: $(6d7s)^3 5f^5$. Baptist et al [5] attributed to Skriver (1981), in a private communication, that the ground state of FCC Pu (δ phase) is $5f^{5+x}(6d7s)^{3-x}$. This suggests a (6d7s) $\rightarrow$ 5f promotion on warming from α through to δ phase. Bonnelle et al

[6] noted that the atomic volume contraction from the $\delta \rightarrow \epsilon \rightarrow$ liquid Pu must be accompanied by an inverse modification of the electronic structure, i.e., a 5f → 6d promotion.

The above described physical properties of Pu metal phases suggest the behavior of transition element alloys or intermetallics, but with 5f bands superimposed on the (6d-7s) bands and hybridized with them.

We further suggest that a time lag between thermal hybridization of (f)-d-s electrons and thermal dehybridization of (f)-d-s electrons may be responsible for martensite-like transformations in many transition element metals and their alloys on compounds. The effect may be to give incommensurate and commensurate charge-density-wave states (or phases). Such effects have been reported for TiNi(X) alloys in their martensitic transformations [7].

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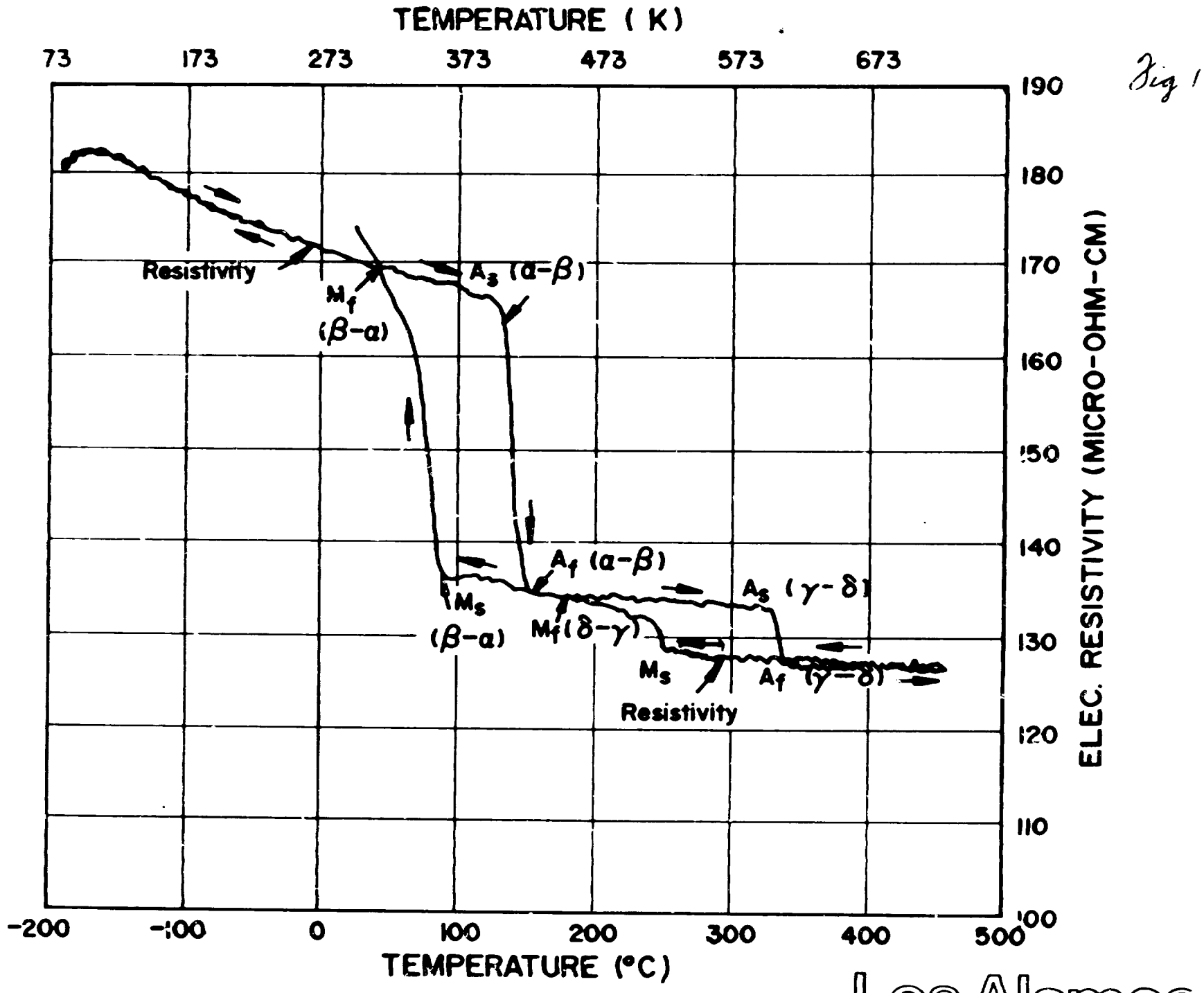

Fig 1

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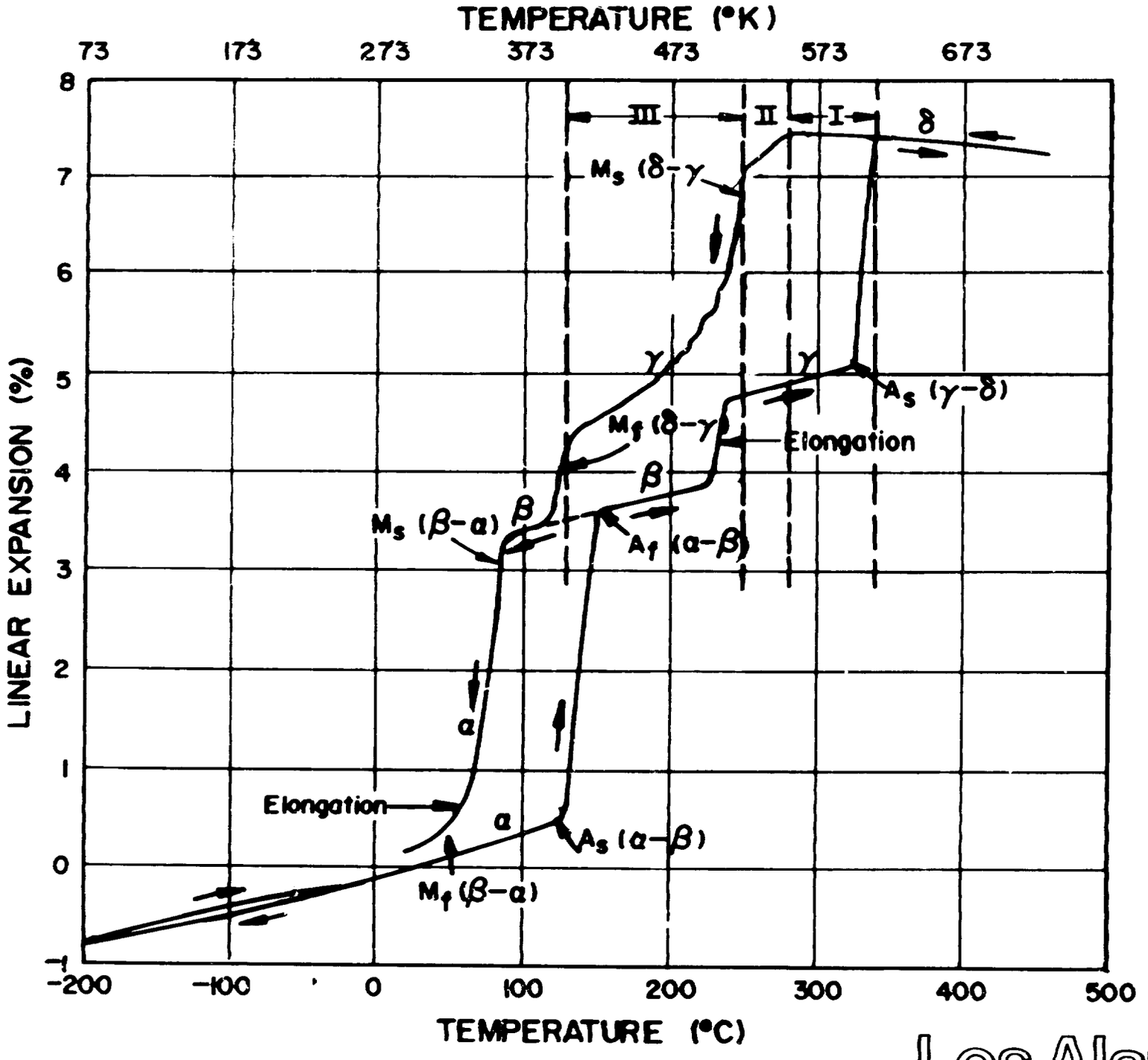

Fig. 2

Fig 3