and the changes of the dipolar energy owing to the rf field are determined by

$$W_D=\frac{1}{\mathrm{Tr}\,\mathcal{H}_D^{(s)2}}\int_0^\infty dt\,\mathrm{Tr}\,e^{i\mathcal{H}_0t}\,[\mathcal{H}_D^{(s)},\mathcal{H}_{\mathrm{rf}}(t)]$$

$$\times e^{-i\mathcal{H}_0t}\,[\mathcal{H}_{\mathrm{rf}}(0),\mathcal{H}_D^{(s)}]$$

$$=\left(\frac{\mu_N H_1}{2}\right)^2\sum_{m=-s}^{s}(\Delta_{m-1}^{m}A_m^{-})^2\,G^{(1m)}_{\Delta_{m-1}^{m}}\quad . \tag{20c}$$

Here $G_\Delta^{(1m)}$ was defined in expression (16b).

The saturation matrix elements are similar to those which have been obtained in Provotorov's paper[9] but here the operators $\mathfrak{N}_m^+$ and $\mathfrak{N}_m^-$ are used instead of the total spin operators.

IV. CONCLUSION

The above derivation is limited to a weak quadrupole interactions and enables one to obtain the kinetic equations for the system of any spin. In addition, the formalism can be applied to any kind of quadrupole-interacting spin system with the appropriately defined energy-level population operators and with a suitable choice of the secular part of the dipolar energy. For instance, in the case of a pure quadrupole-interacting spin system, with the axially symmetric EFG tensor, the level population operators are the sum of the above defined

$$\mathfrak{N}_k=\mathfrak{N}_m+\mathfrak{N}_{-m}\ .$$

The secular part of the dipolar interaction is defined to be that part of the $\mathcal{H}_D$, which commutes with $\mathfrak{N}_k$. The coefficients in the kinetic equations are, then, the combination of the coefficients in the expressions (16) and (20).

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Electrical Resistivity of α-Cerium*

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Electrical-resistivity measurements have been made between 1.5 and 300 °K on α-cerium cooled while at pressures of 10 or 18 kbar. Two types of behavior were found: Cerium quenched from 300 to 77 °K showed the presence of a magnetic impurity, possibly clusters of β-cerium; and cerium which was slowly cooled from room temperature showed no evidence of magnetic behavior. Whereas the "magnetically impure" sample showed a strong $\rho\propto T^2$ dependence at low temperatures, the slowly cooled sample had $\rho\propto T^5$. It is suggested that the magnetic impurity present in previous studies may have prevented the observation of superconductivity in α-cerium.

I. INTRODUCTION

The use of high-pressure techniques has allowed a number of researchers to stabilize the α phase of cerium ("the collapsed fcc structure") to liquid-helium temperatures.[1–3] In the technique generally used a sample is loaded in a pressure clamp to about 10 kbar at room temperature, quenched into liquid nitrogen, and then measurements may be made. In fact, if the pressure is released with the clamp under liquid nitrogen, samples may be retained in the α phase at zero pressure and data at zero pressure may be obtained even below 4 °K. Recent property measurements have included magnetic susceptibility[2,3] and specific heat.[1] One result of these studies has been a picture of α-cerium with a valence around 3.7, having 0.3 4*f* electrons per atom in a high density of states, virtual level, 0.02 eV wide.[4] This model fits in well with the estimation of exchange enhancements to the Pauli susceptibility of about 5–10. The effect of pressure is to slightly decrease the *f*-level contribution. This model is based on the promotion of ~0.6 4*f* electrons into the conduction band during the $\gamma \rightarrow \alpha'$ transformation. However, positron-annihilation studies show that the valence does not change from $3 \rightarrow 4 - x$, where $x < 1$, during the transformation,[5] which is contrary to promotional models. Appropriate references to the various models used to explain the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \alpha'$ transformations and a full discussion thereof may be found in Ref. 5.

The low-temperature specific heat of α-cerium shows the pressence of a contribution to the specific heat in addition to the electron and phonon terms.[1] Impurity ordering is not a likely cause of the excess specific-heat contribution. The temperature dependence of the excess specific heat appears to be qualitatively similar to that found in spin-fluctuation systems, that is, proportional to $T^2 \ln T$.[6] Examination of earlier specific-heat data also reveals evidence for the additional contribution,[7] although it was not recognized at the time. Furthermore, the magnetic susceptibility of α-cerium at 10-kbar pressure shows it to have a large room-temperature value (between 5.5 and 6.6×10^{-4} emu/g atom), constant from 90 to 300 °K.[2,3] These values may be compared to the respective value for palladium $\chi_{300} = 5.3 \times 10^{-4}$ emu/g atom and with an exchange enhancement also near 10.[8] Thus, it seems possible that there might be conduction-electron-paramagnon scattering[9] in highly exchange-enhanced α-cerium due to the 4*f* virtual bound states at the Fermi level.

Schindler and Rice[10] obtained an expression for the *s*-electron spin-flip-scattering contribution to the electrical resistivity ρ_{sp},

$$\rho_{sp} = \alpha (T/\Theta_s)^2 [J_2(\Theta_s/T) - (T/\Theta_s)^3 J_5(\Theta_s/T)] , \qquad (1)$$

where Θ_s defines a characteristic spin-density-fluctuation temperature, α is a constant, and the *J*'s are the standard Block–Gruneisen integrals. The value of α/Θ_s^2 is proportional to the square of the exchange enhancement factor, $S = \chi/\chi_0$. Thus for a highly exchange-enhanced metal at low temperatures, $\rho - \rho_0 \propto T^2$ as the first term in Eq. (1) is dominant and overrides the normal T^5 term due to electron-phonon scattering. The low-temperature electrical resistivities of Pd and Pd-Ni alloys yielded $\rho \propto T^2$ and the composition dependence of α/Θ_s^2 is in good agreement with the model when local exchange-enhancement effects are considered.[11]

Thus, this study was undertaken to determine if a spin-fluctuation contribution could be observed in the electrical resistivity of α-cerium as had been suggested by Coqblin.[4b] Although experimental uncertainties prevented a comparison of the results with the very low ρ_{sp} found for pure Pd, it seems definite that ρ_{sp} for α-cerium is no larger than for palladium containing ≥ 0.5-at.% Ni.[10] A consequence of this study was the observation that experimental methods used previously to stabilize α-cerium to low temperatures introduce a magnetic impurity, viz., faulted planes of Ce atoms which can act as magnetic scattering centers (the β structure, hcp, is known to order antiferromagnetically). The implications of the latter fact will also be discussed.

II. EXPERIMENTAL

A sheet sample of $3.4 \times 0.78 \times 0.23$ mm was cut from an ingot of cerium (99.9%) obtained from United Mineral and Chemical Co. Four platinum leads were spot welded onto the sample, before it was annealed at 600 °K for 4 h. The sample was loaded into a Be-Cu clamp device with BN and Teflon-pressure-transmitting parts. The sample was fully contained in the Teflon. The clamp was pressurized to 10 kbar, quenched into liquid nitrogen, and quickly loaded into the liquid-helium cryostat which was precooled to 77 °K. This is the same method used by other authors to obtain "pure" α-cerium.[1-3] Three sets of measurements were taken with the sample warmed to room temperature and requenched in liquid nitrogen for each set of data. For temperatures below 4.2 °K, liquid helium was condensed in the sample chamber and the sample was cooled by pumping on the helium. Data were taken at 0.1–0.2 °K intervals using a Honeywell six-dial potentiometer with a Keithly 14-nV null detector as the galvanometer. Constant direct current was obtained with a PAR constant-current source. Calibrated Ge resistance thermometers were used below 4.2 °K. Above 4.2 °K, the sample chamber contained He gas and data were taken with an automated digital system[12] as the temperature was raised with a heater at 0.3 °K/min. Calibrated AuFe and AuCo thermocouples were used above 4.2 °K, with their results weighted and averaged between 10 and 15 °K. All pressures reported are nominal values determined by the room-temperature dimensions and the applied force.

As is seen in Fig. 1(a), the resistivity at 10 kbar showed the desired T^2 dependence below $T \sim 5$ °K, and linear T dependence above $T \sim 43$ °K. However, as Fig. 1(b) shows, the resistivity abruptly changes at about 230 °K. This behavior was found in each run, with the "transition" temperature different for runs 1 and 2 at 260 and 230 °K, respectively. (Run 3 was not taken above 80 °K.) As will be discussed further, it was concluded that the fast cooling from room temperature to 77 °K strained the sample. In view of the low stacking-fault energy for cerium,[13] local areas of high-defect concentration could be formed on the microscopic scale. If, for example, these allow Ce atoms to locally look like small pieces

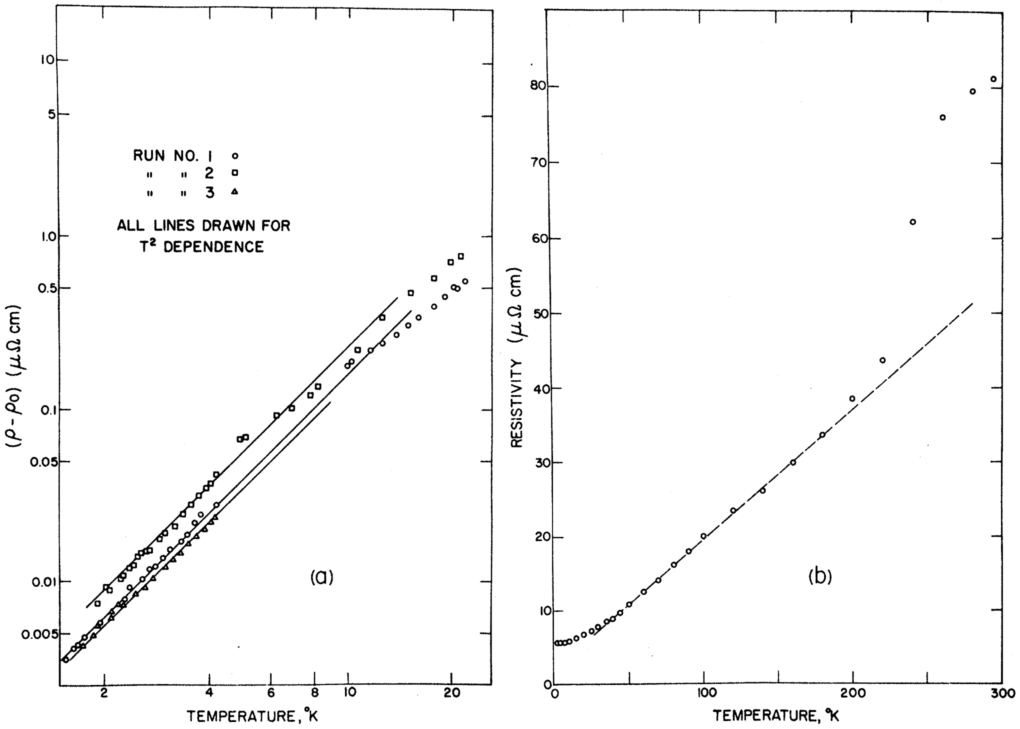

FIG. 1. Resistivity temperature curves for α-cerium at 10 kbar quenched into liquid nitrogen; (a) log-log plot of the data at low temperatues, and (b) over-all curve for run 2.

of the antiferromagnetic β-cerium,[14] we would have magnetic impurity clusters (not due to chemical impurities).

In order to test the hypothesis of the previous paragraph, a second sample of Ce from the same ingot was prepared and loaded into a different clamp made of hardened steel (A.I.S.I. type A2). This sample was pressurized to 18 kbar, slowly cooled to 77 °K (~0.3 °K/min) in the Dewar, and data were taken as before between 77 and 300 °K. No abrupt transition was found. The sample was recooled slowly and measurements were made from 4.2 to 1.5 °K, 4.2 to 90 °K, and 90 to 300 °K. The results of the 90–300°K run were nearly identical to the first run from 77 to 300 °K. Measurements were also made between 1.3 and 80 °K at 12 and 0 kbar, with the pressure released each time while the clamp assembly was under liquid nitrogen. The clamp was then repressurized to 10 kbar to allow direct comparison to the data of Fig. 1.

III. RESULTS

In addition to the T^2 dependence of the resistivity data of Fig. 1, it should be noted that the magnitude of this spin scattering is different for each run. The difference, plus the different transition temperature for runs 1 and 2, are clearly not a property of the pure bulk metal, nor of the chemical impurities, which are present in each run. However, these differences are likely due to slight differences in the details of the three quenching experiments. Such differences could easily change the magnitude of any strains or strain-induced phenomena.

Figures 2–4 show the results for samples cooled slowly at 18 kbar. As is seen in Fig. 2, the resistivity-temperature curve from 1.6 to 300 °K varies smoothly with no apparent break near 250 °K. In Fig. 3, plots of the low-temperature data show the marked differences between the sample quenched to 77 °K and the slowly cooled sample. Although it appears that the slope of each slow-cooled sample is essentially zero at the lowest temperatures, the scatter in the data due to an unfavorable sample geometry are large enough to prevent this conclusion from being reached unequivocally. For example, the dashed lines show that temperature variation of the magnitude found in pure Pd[10] could be hidden in the scatter. However, it is seen that the present data do show less temperature dependence than is found in Pd–0.5-at.% Ni. An upper limit $\alpha/\Theta_s^2 \leq 40\times10^{-6}$ $\mu\Omega\,\mathrm{cm}/°\mathrm{K}^2$ may be set for the slow-cooled cerium.

Figure 4 shows that the resistivities at 0 and 18 kbar follow $\rho \propto T^5$ at temperatures in the range 10–30 °K. Again, the scatter and the very small temperature variation tend to mask the behavior at lower temperatures. The data in Fig. 2, above 160 °K, form a perfect straight line. The resistivity ratio for the sample slowly cooled at 18 kbar is 16.4, not indicative of a high-purity level, which

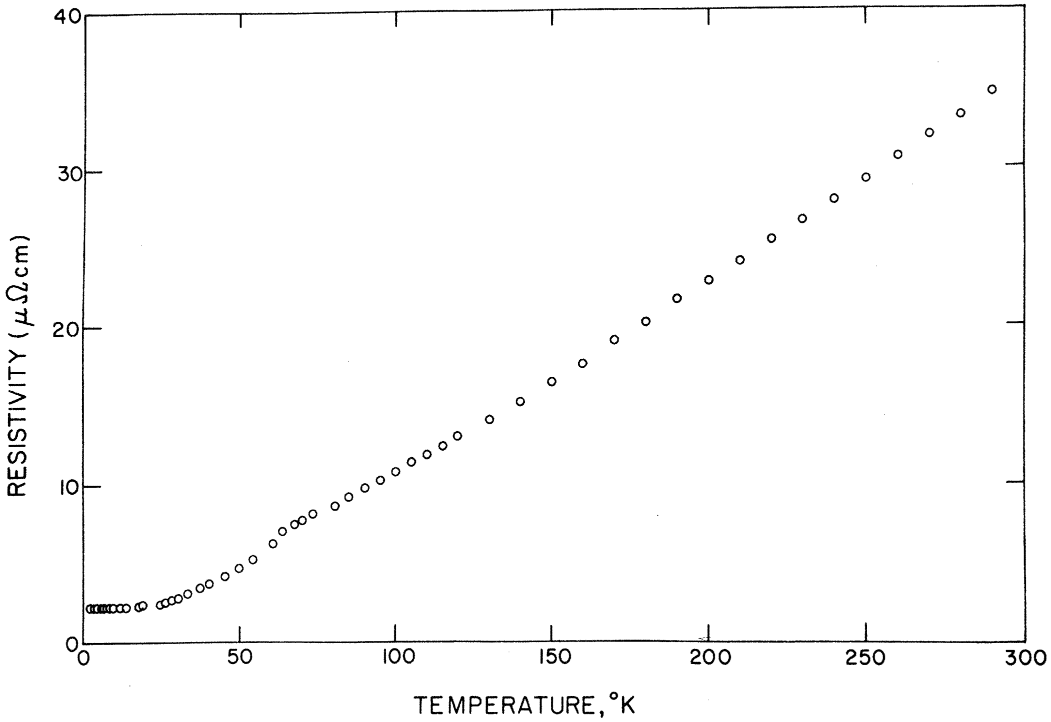

FIG. 2. Resistivity-temperature curve for α-cerium at 18 kbar cooled slowly from room temperature. The offset at 60–80 °K is due to an air leak in the sample chamber, which gave erroneous temperature readings.

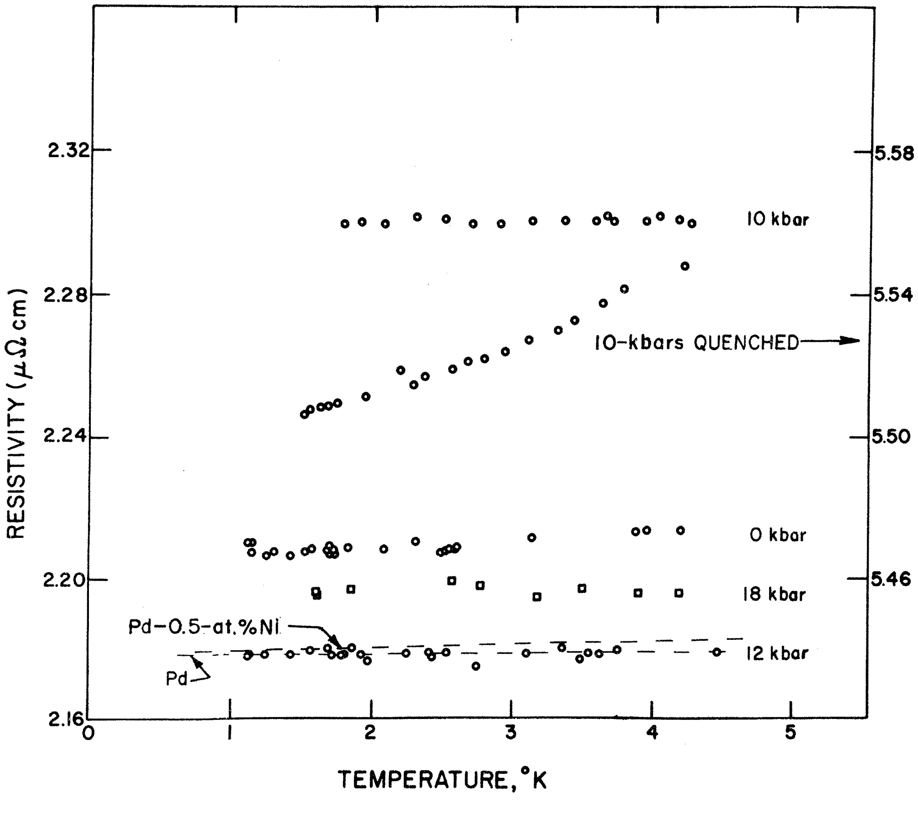

FIG. 3. Low-temperature resistivity data for slow-cooled α-cerium, compared to quenched α-cerium, Pd, and Pd–0.5-at.% Ni from Ref. 10.

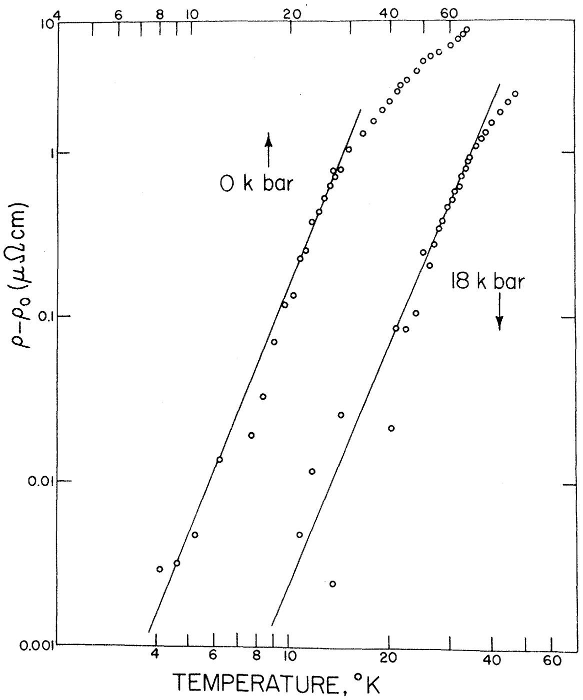

FIG. 4. Log-log plot of the resistivity-temperature data for slow-cooled α-cerium at 0 and 18 kbar.

is in keeping with the presence of 0.1 wt% of total impurities. Some of the impurity scattering could also include a small amount due to the strain-induced effects. The variation of the resistivity with pressure at 4.2 °K is not simple. This is likely due to small strain-induced effects as a result of the several unloadings and loadings of pressure at 77 °K.

IV. DISCUSSION

A. Magnetic Impurity

It seems fairly clear from Figs. 1 and 3 that α-cerium prepared by quenching to 77 °K contains a magnetic impurity. Its presence is shown by the low-temperature T^2 dependence and the much larger residual resistivity, 5.5 vs 2.2 $\mu\Omega$cm for slowly cooled cerium. Otte and Chessin[13] have shown that deformation of α-cerium can lead to extrinsic stacking faults of the *ABACABAC*$\cdots$ type hcp sequence. The *ABABAB*$\cdots$ hcp, β-cerium structure is known to be antiferromagnetic below 12.5 °K, with local-moment behavior at higher temperatures.[14] Thus, in local regions where stacking faults exist, there are cerium atoms arranged similarly as in β-cerium. These regions may be thought of as β clusters (one displaced Ce atom plus its coordinated 12 atoms). Although the local defect structure actually formed in the quenched samples might not be "β-like", the known magnetic behavior of β-cerium makes it a likely choice.

Grimberg *et al.*[3] have already attributed the temperature-dependent susceptibility of α-cerium below 80 °K to the retention of 1–2% β-cerium at high pressures in their work and in Ref. 2. The same must be true of the specific-heat work.[1] The resistivity ratio $\rho_{80}/\rho_{1.2}=2.4$ of one of Grimberg's samples may be compared to a ratio of 2.9 for the data of Fig. 1, which is indicative of ~1% retained β, here also.

The "transition" at 230 °K in Fig. 1 is probably due to the retained β phase also. It is not clear, however, what transformations are taking place. The magnitude of the change, an increase of ~30 $\mu\Omega$cm, could be attributed to a transformation of about 80% of the sample to γ-cerium. The mechanism of how ~1% metastable β phase triggers a transformation of about 80% of the sample to metastable γ is not understood. However, it is well known that the transformations in cerium are influenced by strains.[14]

It is tempting to consider the positive $d\rho/dT$ at low temperatures on the basis of spin fluctuations due to dissolved magnetic impurities, such as in Rh(Fe)[15] or Pd(Pu).[16] However, it is likely that the "β" impurity regions must be considered as clusters, since it is the defect atom plus its nearest neighbors which can have a structure like β-cerium.

B. "Simple" α-Cerium

This discussion pertains to the data taken on the slowly cooled sample. The resistivity-temperature behavior is that of a simple transition metal. There is a room-temperature resistivity of 36.1 $\mu\Omega$cm, T^5 behavior at low temperatures and $T^{1.0}$ behavior at temperatures above the Debye temperature, 117 °K. The room-temperature value may be compared to other non-*f*-electron metals Zr (43 $\mu\Omega$cm),[17] Ti(49 $\mu\Omega$cm),[17] Y(62 $\mu\Omega$cm),[18] Lu(62 $\mu\Omega$ cm),[19] and Th(15.8 $\mu\Omega$ cm).[20]

Thus, on this basis, we would conclude that if α-cerium contains 4*f* electrons (one full electron, or fractional) then the *f* electrons are hybridized into bands. As mentioned before, the specific heat and susceptibility data lead to the conclusion of α-cerium being highly exchange enhanced. Although the data are probably based on "magnetically impure" Ce, this conclusion could still be correct. Thus, the fact that we cannot see the $\rho\propto T^2$ dependence at low temperatures in "pure" Ce does not preclude its presence. However, if the conclusion that cooling strains can cause some β-like regions due to stacking faults is correct, it may be impossible to ever prove the presence of spin-fluctuation resistivity. Any T^2 dependence which might be observed could be attributed to the presence of the magnetic defect impurity and not to spin fluctuations.

C. Superconductive α-Cerium

Wittig[21] has shown that pressures higher than 50 kbar cause transformation to a further collapsed fcc structure, α',[22] which becomes a superconductor at about 1.7 °K.[21] It had been supposed that this transformation removes the last vestiges of the $4f$ electron. He further proposes that α-cerium should also be superconducting. The present work suggests that superconductivity has not been observed because of the usual presence of the 1–2% magnetic impurity. Thus, it may be possible to observe a superconducting transition in α-cerium by further high-pressure experiments with slow-cooling, and still lower temperatures. Naturally the chances of success would be further enhanced by use of true hydrostatic pressure. However, the positron-annihilation experiments show that γ, α, and α' phases all have a valence of 3 and not 4.[5] Thus the possibility of f-band behavior, raised by Blandin *et al.*[23] and Gustafson *et al.*[5] must be considered, and α-cerium may not be a superconductor because the $\alpha' \rightarrow \alpha$ transformation could be connected with a band-structure shift leading to a highly exchange-enhanced metal such as Pd.

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