Investigation of the Electronic Structure of α'-Cerium by Angular-Correlation Studies of Positron-Annihilation Radiation*

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The electronic structures of the γ, α, and α' phases of cerium metal were investigated by measurement of the angular correlation of positron-annihilation radiation at pressures up to 90 kbar. The observed increase in the width of the angular correlation with increasing pressure was small and consistent with the assumption that the number of free electrons per atom is essentially the same, presumably three, in all three phases. The changes in width were much smaller than predicted by the promotional model which assumes that the $4f$ electron is promoted to the conduction band as cerium is compressed. It is therefore concluded that the promotional model does not provide a satisfactory explanation of the high-pressure behavior of cerium metal.

I. INTRODUCTION

A number of the anomalous properties of cerium metal have their origins in the spatial and energetic proximity of the $4f$ electron to the conduction electrons. However, the details of the interaction which produces these properties are only rudimentarily understood. This is particularly true in the case of the α' phase of cerium which exists only at very high pressures and is consequently amenable to study by only a limited number of experimental techniques. The positron-annihilation method is one of the few applicable methods for electronic-structure investigations at high pressures; in the present work the angular correlations of positron-annihilation radiation for the γ, α, and α' phases of cerium metal are examined as a function of pressure in an effort to contribute to the understanding of the electronic structure of the α' phase.

It is apparent from the phase diagram alone, shown in Fig. 1,[1-4] that cerium is a most unusual metal. Two features of the phase diagram to note are that (i) cerium has five distinct solid phases, which is an unusually large number for an elemental metal. (ii) The first-order γ-α transition does not involve a change in structure; both phases are fcc and the γ-α phase boundary terminates at a critical point similar to a liquid-gas critical point.[4,5] In the present work the behavior of the high-pressure α' phase, which is quite different from that of the other phases, is of primary interest. Both the β and γ phases are stable at room temperature because of the hysteresis of the β-γ transition.[1] The following is a brief review of the behavior of a sample of γ-cerium as it is compressed isothermally at room temperature to form α-cerium and, subsequently, α'-cerium.

Structure. An annealed sample of cerium at atmospheric pressure and room temperature will be in the γ phase which is fcc with a lattice parameter of 5.16 Å.[6] The compressibility of γ-cerium is moderate.[4] At 7 kbar cerium transforms to the α phase which is also fcc with a lattice parameter of 4.85 Å.[4,6] α-cerium is very compressible and has a lattice parameter of 4.73 Å at 49 kbar, just prior to the $\alpha \rightarrow \alpha'$ transition.[6] At 55 kbar cerium transforms to the α' phase which is also close packed, either fcc with a lattice parameter of 4.66 Å,[6] or hcp.[7] α'-cerium is nearly incompressible below 100 kbar.[6]

Resistivity. The $\gamma \rightarrow \alpha$ transition is accompanied by a drop in the resistivity of approximately 50%. The resistivity continues to drop as α-cerium is compressed. At the $\alpha \rightarrow \alpha'$ transition the resistivity increases by approximately 30%.[8]

Hall effect. The Hall coefficients for the γ and α phases are both positive. The value for the α phase is approximately one-fourth that of the γ phase.[9] The Hall coefficient of α'-cerium has not

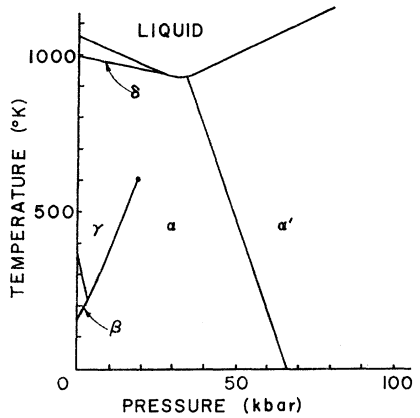

FIG. 1. Phase diagram for cerium (after Refs. 1–4).

been measured.

Magnetic properties. The γ phase of cerium is magnetic with a magnetic moment and susceptibility consistent with a singly occupied $4f$ level.[10,11] The α phase has a much smaller susceptibility and may be regarded as a paramagnetic metal.[11] However, superconductivity has not been found in α-cerium.[12,13] The magnetic behavior of α'-cerium remains to be investigated experimentally; however, the existence of superconductivity in α'-cerium implies that it may be regarded as nonmagnetic.[8]

Positron annihilation. The positron is strongly repelled by the atomic cores and it therefore annihilates principally with the conduction electrons and outer core electrons of a metal. Because of this both the lifetime of a positron in a metal and the angular correlation of its annihilation radiation are very sensitive to the density of the conduction electrons. The changes which are observed in the positron lifetime and angular correlation upon the transformation of γ-cerium to the α phase are small and are consistent with the assumption that there are three free electrons per atom in both phases. The changes are far too small to be consistent with any significant change in valence at the $\gamma \rightarrow \alpha$ transition.[14]

Although it is generally accepted that the interaction of the $4f$ and conduction-electron levels gives rise to the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \alpha'$ transitions, none of the several models which have been proposed provides an explanation of the full range of observed phenomena. The promotional model, which assumes that the $4f$ electron is promoted to the conduction band as cerium is compressed or cooled, was the first model put forth to explain the behavior of cerium.[15,16] Currently the most cited version of the promotional model is based on the hypothesis that the transfer of the $4f$ electron to the conduction band at the $\gamma \rightarrow \alpha$ transition is only partial, leaving sufficient magnetic character to inhibit superconductivity in α-cerium.[17] The $4f$ character is assumed to continue to diminish as the α phase is compressed and to disappear at the $\alpha \rightarrow \alpha'$ transition.[6] α'-cerium would thus be a true tetravalent metal and would be expected to be superconducting as was found. Recently Ramirez and Falicov[18] have proposed a modification of the promotional model which exhibits the critical behavior found for the $\gamma \rightarrow \alpha$ transition. They suggest that the $4f$ level lies slightly above the conduction band at absolute zero and is populated by thermal activation as the temperature increases. They did not attempt to explain the $\alpha \rightarrow \alpha'$ transition. Another model which has been used to explain the behavior of cerium involves compensation of the spin of the $4f$ electron by the conduction electrons.[19–21] The basic premise of this model is that the spin of the $4f$ electron is compensated, in varying degrees in the various phases, by the spin of the conduction electrons as they scatter resonantly from the $4f$ electron. The $4f$ spin would be essentially uncompensated in the γ phase, partially compensated in the α phase, and fully compensated in the α' phase. The compensation is thought of as occurring in a manner similar to that which occurs when the conduction electrons of a metal scatter from dilute magnetic impurities.[22] A third model is based on the suggestion that $4f$ state undergoes a transition from a highly localized atomic core state in the γ phase to a delocalized $4f$ band in the α and α' phases as the overlap of the $4f$ states increases upon compression.[14] The transition would thus be similar to a Mott transition. The $\gamma \rightarrow \alpha$ transition would occur as the $4f$ electron underwent a transition to a delocalized state and the $\alpha \rightarrow \alpha'$ transition would be the result of the $4f$ electron losing its magnetic character entirely as the result of increased overlap. In view of the fact that the overlap of the $4f$ states should be quite small even in the α' phase, this hypothesis does not seem to be a likely one. In addition, the augmented-plane-wave (APW) calculations of Mukhopadhyay and Majumdar[23] indicate that the width of such a band would only be about 0.02 Ry. Nevertheless, there is little substantial experimental or theoretical evidence which directly rules out this hypothesis. Since the behavior of the various allotropic phases of cerium cannot be consistently explained by any other model at present, it would be premature to reject it.

The present paper extends measurements of the angular correlation of positron-annihilation radiation in cerium to the α' phase at pressures up to 90 kbar as a specific test of the promotional model of the $\alpha \rightarrow \alpha'$ transition.

II. EXPERIMENTAL PROCEDURE

A Bridgman opposed-anvil high-pressure cell, shown in Fig. 2, was used to pressurize the sample. The tungsten carbide anvils were $\frac{1}{2}$ in. in diam and the Isomica gasket was 0.015 in. thick. The sample–positron-source assembly consisted of two disks of cerium, each $\frac{1}{4}$ in. in diam and 0.007 in. thick, with a 30-mCi cobalt-58 positron source plated on a 0.00025-in. copper foil sandwiched in

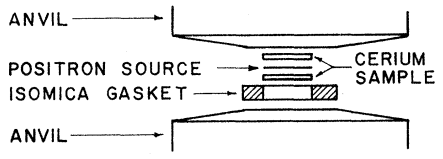

FIG. 2. High-pressure cell.

between. The cerium was obtained from the Research Chemicals Co. in the form of rolled sheets of 99.9% nominal purity. The sheets were further rolled to the desired thickness, vacuum annealed at 450 °C for two days, then slowly cooled to room temperature. This procedure insured that the sample was in the γ phase at the beginning of the experiment.[1] The sample faces were cleaned with fine abrasive paper, mounted with the source in the pressure cell, and immediately pressurized to 3 kbar to prevent oxidation of the sample. Inspection of the sample upon completion of the experiment showed that only minor oxidation of the sample occurred. The cell was calibrated using the bismuth resistance discontinuities occurring at 25.4, 26.8, and 88 kbar. The cerium resistance discontinuity accompanying the $\alpha \rightarrow \alpha'$ transition was found to occur at approximately 55 kbar, in general agreement with recent determinations of the α-α' phase boundary.[3,6] The cerium sample used for the resistance measurements was cut from the same sheet as the angular-correlation sample.

The angular correlations were measured using a standard long-slit apparatus of $\frac{1}{2}$-mrad angular resolution.[24] A coincidence circuit resolving time of 12 nsec was used to minimize the accidental coincidence rate. Measurements were made at $\frac{1}{4}$-mrad steps over the region of interest. The number of counts recorded at the peak position was in excess of 10 000 for all of the measured angular correlations.

III. RESULTS AND DISCUSSION

The angular correlations for γ-, α-, and α'-cerium, measured at 3, 30, and 90 kbar, respectively, are shown in Fig. 3. For clarity, smooth curves were fitted to the angular correlations and the individual data points were omitted. The angular correlation for α'-cerium was also measured at 65, 72, and 80 kbar; no significant difference was found between these and the 90-kbar angular correlation. The γ- and α-phase angular correlations are in agreement with those of previous investigations.[14] Also shown in Fig. 3 are the locations of θ_F, the angle corresponding to the free-electron-model Fermi-surface radius, for the various phases. The values of θ_F for the γ and α phases were calculated for an assumed valence of three while the value for the α' phase was calculated for both an assumed valence of three and an assumed valence of four.

Metals which are close to free-electron-like, potassium for example,[25] have angular correlations which are essentially parabolic at angles less than θ_F; at θ_F a sharp change in slope occurs, and beyond θ_F the angular correlation is approximately Gaussian.[26] The angular correlations measured for cerium do not show a sharp break at θ_F because the electronic structure of cerium deviates from a free-electron-like structure. Consequently, the valence can not be determined exactly. All three angular correlations are, however, in better agreement with trivalency than tetravalency. Although the electronic structure of cerium deviates from a free-electron-like structure, the free-electron model is still a reasonable first approximation. In such cases the change in width of the angular correlation in the region near θ_F is easily measurable and, therefore, the change in valence can be determined even though the value of the absolute valence cannot be measured accurately.[14] The free-electron model predicts that the angular correlation for α'-cerium should be 0.57 mrad wider than that for γ-cerium in the region near θ_F if both phases have the same valence and 1.16 mrad wider if the valence of α'-cerium is one greater than that of γ-cerium. The measured result is 0.40 $\pm$ 0.05 mrad. This indicates that the valence of α'-cerium is essentially the same as that of γ-cerium. As it is generally accepted that the valence of γ-cerium is three or very close to three,[17] it may be concluded that α'-cerium has three electrons per atom in states that are free-electron-like and the $4f$ electron remains in a state that is $4f$-like. The results of this investigation of the electronic structure of α'-cerium are not consistent with the promotional model. However, the results do not provide a basis for choice among the nonpromotional models involving a change in the $4f$ state. The strong positron-ion repulsion

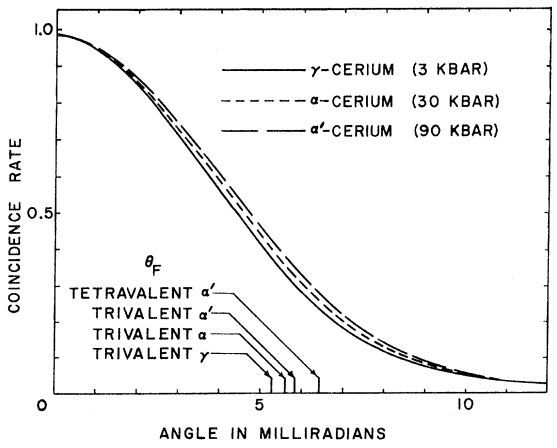

FIG. 3. Angular correlations of positron-annihilation radiation for γ-, α-, and α'-cerium at 3, 30, and 90 kbar, respectively. The values for θ_F were calculated using the free-electron model for the assumed valences shown. The counting rate is in arbitrary units and all three angular correlations are normalized to the same value at zero angle.

reduces the rate at which positrons annihilate with the $4f$ electron to the point that a change in the $4f$ state cannot be observed by the angular-correlation method.

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Interstitial Diffusion of Copper in Lead at Pressures up to 56 kbar*†

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The diffusion of copper in lead has been investigated using radioactive-tracer and sectioning techniques. The measured diffusion coefficients span the hydrostatic pressure range 0–56 kbar and temperature range 218–530 °C. The activation energy and volume at the melting temperature and atmospheric pressure are, respectively, $\Delta H = 5.6 \pm 0.5$ kcal/mole and $\Delta V/V_0 = 0.04 \pm 0.03$. The pressure and temperature coefficients of the activation volume, although quite uncertain, were also determined. The small activation energy and volume indicate that copper diffuses in lead primarily by the interstitial mechanism.

I. INTRODUCTION

Recently there has been renewed interest in the relatively rapid diffusion of the noble metals in lead. A number of models have been proposed to explain this rapid migration of atoms, but more experimental data are needed to determine which, if any, of these models is correct. This work completes a set of high-pressure studies of the noble metals in lead. These metals, gold, silver, and copper, are very similar in electronic structure. Each is characterized by an inert-gas electron core in addition to a filled d shell and one s electron. The differences in their diffusivities in lead may be attributed primarily to size effects and to minor differences in binding.

Interestingly, one of the first reported investigations of solid-state diffusion involved the diffusion of the noble metal gold in lead. Roberts-Austen[1] found that gold atoms migrate rapidly in lead even at temperatures as low as 200 °C. Hevesy[2] measured lead self-diffusion and found that it was orders of magnitude slower than the diffusion of gold in lead. Seith and co-workers[3–5]