Fusion Curve of Cerium to 70 Kilobar and Phenomena Associated with Supercritical Behavior of fcc Cerium

A. JAYARAMAN

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey (Received 3 August 1964)

The fusion curve, the fcc-bcc transformation, and the γ -to- α Ce transformation have been investigated at high pressures. The fusion curve exhibits a broad minimum located at about 33 kbar and 662°C and has an initial slope of -4.7° /kbar. The fcc-bcc boundary has an initial slope of -1.4° /kbar and meets the fusion curve at a triple point near 26 kbar and 674°C. The γ -to- α Ce boundary was delineated by following the resistance discontinuity and has a slope of 26.5°/kbar. The discontinuous resistance drop associated with this transformation progressively diminishes at higher temperatures, and above 545°K the resistivity is a smooth function of pressure. The fusion-curve minimum is the result of a rapid density increase in the neighboring fcc Ce with pressure, due to a continuous transition from γ to α Ce $(4f \rightarrow 5d$ electronic promotion) along the extrapolated transition line, and reflects a P-V relationship in the solid typical of supercritical behavior. Thus the fusion as well as the resistivity data lend strong support to the termination of the γ -to- α Ce transformation at a critical point, first proposed by Ponyatovskii. The results of resistivity measurements suggest the coordinates 550°K and 17.5 kbar for the critical point.

INTRODUCTION

 $HE \gamma$ -to- α Ce transformation, discovered by Bridgman¹ at about 8 kbar during his room temperature compression and resistivity measurements, has been the subject of numerous investigations at high pressures²⁻⁵ as well as at low temperatures.⁶⁻⁸ Its uniqueness, in that the two forms are isostructural⁹ and involve the promotion of the 4f electron to the 5dstate,^{9,10} is now well established. Further, strong experimental evidence that the transformation may end in a critical point was presented by Beecroft and Swenson.¹¹ This suggestion has recently received additional support from high pressure x-ray diffraction studies at elevated temperatures by Davis and Adams.¹² Jamieson¹³ has proposed a thermodynamic model on the basis of which he predicts the termination of the γ -to- α Ce transformation at a critical point. It occurred to us that if the critical point exists. Ce might exhibit supercritical behavior which would become apparent either in the

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fusion curve or in the fcc-bcc boundary, whichever happens to be bordering the critical region.

In this paper, the fusion curve, the fcc-bcc transformation under pressure, and the results of resistance measurements on the γ -to- α Ce transition are reported. The fusion curve of Ce is indeed unique in that it has a rather broad minimum, the occurrence of which is connected with supercritical behavior of the neighboring solid.

EXPERIMENTAL

A piston cylinder device was used to generate pressures. Pressures to 45 kbar were attained using unsupported tungsten carbide pistons and higher pressures by the double staging technique.¹⁴ Friction corrections were made in the manner described earlier.¹⁴ The pressures are believed to be correct to ± 1 kbar up to 45 kbar and ± 2 kbar above 45 kbar. Samples were encapsulated in Nb containers. The purity of the sample was quoted as 99.5%. Melting points and the fcc-bcc transformation temperatures were determined by the method of differential thermal analysis. The thermal arrests associated with the melting as well as the fcc-bcc transition were very large and very sharp. Transformation temperatures were measured using Chromel-Alumel thermocouple, without correcting for the effect of pressure on the thermal emf, and are believed to be correct to $\pm 3^{\circ}$. The internally heated resistance technique¹⁵ was employed for resistivity measurements.

RESULTS

The phase diagram of Ce is presented in Fig. 1. The fusion curve as well as the fcc-bcc boundary have negative slopes, -4.7 and -1.4° /kbar, respectively, and meet at a triple point near 26 kbar and 674°C. Beyond the triple point the fusion curve continues

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FIG. 1. Phase diagram of cerium.

with the same trend and gradually reverses slope, exhibiting a *rather broad minimum* at about 33 kbar and 662° C. No thermal arrest other than that due to melting was detected in the neighborhood of the minimum. The intersections of the fusion curve and the fcc-bcc boundary on the temperatures axis are very close to the known melting and fcc-bcc transformation temperatures of Ce,¹⁶ 795 and 730°C, respectively, at atmospheric pressure. The volume change accompanying fcc-bcc transition and melting has been calculated, using the presently determined slope and published values¹⁶ for the heat of transition. The data are given in Table I.



FIG. 2. Pressure-resistance isotherms of fcc Ce. The resistancepressure curves were obtained on increasing pressures.

The boundary between γ and α Ce was delineated using the resistance discontinuity method. In these experiments temperature was held constant while the pressure on the sample was varied by slow compression. Transition pressures were read at the commencement of the discontinuous resistance drop. The data are plotted in Fig. 1. It may be noted that the γ -to- α Ce boundary when extrapolated intersects the melting curve at the minimum. The resistance versus pressure isotherms are shown in Fig. 2. These curves indicate that the magnitude of the vertical drop in resistance progressively diminishes with temperature. The isotherm for 598°K does not show any discontinuous resistance drop, and the resistivity of the sample smoothly varies with pressure. This behavior is reminiscent of the changes in the volume discontinuities noted by Beecroft and Swenson¹¹ at corresponding temperatures.

Not shown in Fig. 2 is the hysteresis associated with the reverse transformation. The hysteresis interval seems to vary with temperature, decreasing somewhat with increasing temperatures. At 300°K it is about 2 kbar; at 501°K it is probably less than 1 kbar.

TABLE I. Thermodynamic data.

Phase	dT/dP	ΔS	ΔV
boundary	°/kbar	eu	cm ³ /mole
bcc-liquid	-4.7	1.16ª	-0.228
fcc-bcc	-1.4	0.7ª	-0.037
γ - α Ce	26.5	1.89 (300°K)	2.1 (300°K)

^a Reference 22.

The presently determined slope for the γ -to- α Ce transition is 26.5°/kbar compared to 24°/kbar quoted by Beecroft and Swenson¹¹ and 25.5°/kbar by Davis and Adams.¹² For a volume change $\Delta V/V_P$ of 11% at the transition, calculated using the x-ray data of Lawson and Tang for α Ce and the lattice constant of γ Ce corrected for compressibility¹ and a slope of 26.5 kbar, the heat of transition at 300°K is calculated to be 568 cal per mole. Beecroft and Swenson¹¹ calculate 880 cal/mole and Gschneidner *et al.*⁷ 648 cal/mole at room temperature. The discrepancies appear to arise from the volume change assumed for the transition.

DISCUSSION

The fusion curve of Ce has certain unique features which are of importance in the elucidation of the highpressure-high-temperature properties of Ce. Of particular interest is the occurrence of a broad minimum and its significance.

The trajectory of a fusion curve in the *P*-*T* plane would be determined by the magnitude and sign of the volume change ΔV accompanying fusion, as well as by changes in the entropy of fusion. Conversely from the melting curve, using the Clapeyron equation (dT/dP) $= \Delta V/\Delta S$, it is possible to obtain qualitative informa-

¹⁶ The Rare Earths, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons, Inc., New York, 1961), p. 185.

tion regarding the changes in the density of the solid or the liquid, as the case may be, provided ΔS does not vary appreciably with pressure. If there is no significant contribution to ΔV due to a rapid change in density of the liquid with pressure, then the fusion curve is determined principally by the density variation in the solid with pressure. In the case of the Ce the thermal arrest signals appear to have the same magnitude in the pressure range investigated, indicating that the latent heat of fusion and hence ΔS do not change appreciably with pressure. Assuming that there is no rapid density change in liquid Ce with pressure, we interpret the fusion curve in terms of density variation in the neighboring fcc Ce. Initially, the solid is less dense compared to the liquid, but this situation reverses at pressures above which the minimum occurs. The region of fcc Ce bordering the liquid lies in the phase diagram (see Fig. 1) above the postulated critical point for the γ -to- α Ce transition. If there were a critical point, this region of solid would be expected to show a smooth but somewhat rapid increase in density with pressure along the extrapolated γ -to- α Ce phase line, due to a continuous transition, analogous to the pressure-volume behavior of vapor-liquid systems above the critical temperature. The progressive change from negative to positive curvature of the fusion curve with a broad minimum reflects such an increase of density of the neighboring fcc Ce, which seems a truly supercritical behavior. Thus the P-V relationship of this solid lends strong support to the termination of the γ - α Ce phase boundary at a critical point.

Extrapolation of the observed discontinuous resistance change to zero magnitude would place the critical point for the γ -to- α Ce transition at about 550°K and 17.5 kbar. It would be seen from Fig. 2 that the isotherm for 545°K hardly shows any abrupt resistance drop. Beecroft and Swenson¹¹ show that the discontinuous volume change upon transition noted as a function of temperature would extrapolate to zero magnitude at about 630°K and 20 kbar. But these authors have commented that the extrapolation may not be very accurate due to uncertainties in locating the transition pressure at higher temperatures. Ponyatovskii³ found that at P = 18 kbar and T = 553°K the heat of transition vanished. The presently derived value for the critical point is in close agreement with the latter.

It has been pointed out¹⁷ that a critical point can exist only for phases between which the difference is of a purely quantitative nature and which do not differ in internal symmetry; the different crystalline modifications of a substance or a crystalline solid and liquid are ruled out. The γ -to- α Ce transformation, being isostructural and differing in the valence state of Ce atoms $(4f^1, 5d^1, 6S^2 \text{ and } 4f^0, 5d^2, 6S^2, \text{ respectively})$, apparently satisfies these conditions. Beecroft and Swenson¹¹ have speculated that the degree of 4f character in the wave functions of the two states approach each other along the equilibrium line with pressure and temperature until they merge for the two phases at the critical point. This would imply that the size of the Ce ion varies continuously depending on the extent of 4f-5d character. In support of this, they have quoted studies on alloys of Ce^{18,19} at zero pressure, which seem to indicate a continuous variation of the size of the Ce ion with composition and temperature, supposedly due to a continuous change in the valence state of Ce. According to Jamieson's¹³ model, the critical point for the γ -to- α Ce transition would occur when the degree of ionization $(4f \rightarrow 5d)$ which is a function of pressure and temperature is 50%. Beecroft and Swenson¹¹ have suggested that the influence of the γ -to- α Ce transformation on the equation of state would be felt along the extrapolated transition line well beyond the critical point. The equation of state of fcc Ce deduced from the fusion curve is in full accord with this suggestion.

The negative slopes of the fcc-bcc and the bcc-liquid phase boundaries of Ce indicate that the densities of the three phases are in the sequence fcc < bcc < liquid. Several instances where the bcc phase has a higher density relative to fcc are now known,15,20 and we discussed in an earlier publication¹⁴ how an effective coordination >12 can be realized in the bcc arrangement leading to such a circumstance. To account for the higher density of liquid Ce relative to the fcc and bcc phases, the Ce atoms in the liquid must have either a higher effective coordination (probably >13), or a smaller radius. Although the attainment of such high coordination in liquids has been discussed,²¹ we believe the latter circumstance is more probable and suggest that the atoms in liquid Ce have collapsed to a smaller size because of $4f \rightarrow 5d$ electron promotion, a phenomenon known to take place in fcc Ce.¹⁰

The occurrence of fusion curve minimum in Ce and maximum in the case of Cs,²³ Ba,²⁴ and Eu²⁵ reveal that the melting behavior of simple metallic elements could be complex. It appears that while a fusion curve maximum is due to a progressive increase in the density of the liquid, the minimum is related to an increase of density in the solid phase. When the solid is close packed, as it is with Ce, such a density increase would seem to require a progressive change in the size of the atom. The mechanism that provides this in the case

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of Ce is definitely related to the $4f \rightarrow 5d$ electronic promotion. The Cs transition at 40 kbar²³ is regarded as electronic in nature $(6s \rightarrow 5d)$,²⁵ but the fusion curve does not show the kind of minimum observed in the case of Ce. In this case however the solid-solid boundary does not end before intersecting the melting curve. It seems therefore that the presence of an electronic transformation and its ending at a critical point are the requirements for the occurrence of fusion curve minimum. If this is the case, Ce might be a unique example.

It may be pointed out that the rapidly increasing

density of liquid Cs in the region of 30-45 kbar²³ is presumably connected with a progressive change in the size of Cs atoms in the liquid due to 6S-5d electron promotion. Since Cs II appears to be fcc,²⁶ this view would be in line with the proposed explanation for the higher density of liquid Ce compared to fcc Ce.

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²⁶ H. T. Hall, J. D. Barnett, and L. Merrill (private communication).

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Surface Dependence of Ferromagnetic Relaxation*

George R. Jones

Harry Diamond Laboratories, Washington, D. C. (Received 18 July 1963; revised manuscript received 24 August 1964)

A twofold investigation is made of ferromagnetic relaxation in yttrium iron garnet. First, a semiclassical spin-wave theory is developed to calculate the linewidth contribution by surface irregularities. The uniformprecession-mode ferromagnetic resonance is coupled to the degenerate spin waves by magnetic dipolar fields associated with the irregularity of the surface. The dipolar field is derived from the irregular surface boundary conditions and the fields associated with the uniform precession mode. Both the time-dependent and static fields were found to perturb the linewidth of the general case of ferromagnetic resonance. Second, the surface irregularities were measured with an interference microscope and a vertical illuminator microscope so that the calculated linewidths could be compared with observed linewidth for adequately described surfaces. For samples in which Fourier analysis of the surface was possible, the total observed linewidths of 0.5-3.0 Oe were in good agreement with predictions. Total linewidths corresponding to coarser surfaces were observed in the range 5-7 Oe. These were in agreement with predictions only to an order of magnitude. The following conclusions are based on the good agreement of the experimental and theoretical linewidths: (1) Degenerate spin-wave coupling is an adequate explanation of the surface-dependent linewidths; (2) dipolar magnetic fields associated with the irregular surface couples the resonant mode to the spin-waves; (3) classical spin-wave theory is useful in the description of this line broadening.

I. INTRODUCTION

HE source of the linewidth for the uniform pre-cessional mode in nonconducting ferromagnetic materials has been the subject of several excellent theoretical investigations.¹⁻³ These investigations deal with specific mechanisms by which energy in the uniform precessional mode is transferred into degenerate higher order magnetic disturbances (spin waves) or into the phonon spectrum of the material.

Clogston, Suhl, Walker, and Anderson¹ considered the scattering of energy into degenerate spin waves by irregularities in the magnetic lattice of a material. This theory is particularly useful in the case of ferrites, since these materials have intrinsic magnetic irregularities associated with their inverted spinel structure.

The ferrite linewidths predicted with this theory are in fair agreement with observations. Callen² treated the problem in a more formal manner. He established a connection between the parameters in a phenomenological equation of motion describing the behavior of the magnetic system and the parameters of a more fundamental form such as transition probabilities involving spinwaves and phonons. This result was then applied to the special mechanism of Clogston et al. in considering coupling of the uniform mode to degenerate spin waves alone. The results were "very similar."

Both treatments deal with scattering of energy from the uniform precessional mode associated with bulk properties of the material. The surface of the material enters the problem only through the effect of static demagnetization⁴ and the effect on the degenerate spin wave manifold. No specifically surface-dependent properties such as roughness are considered. In ferrite materials, where the Clogston mechanism is dominant, surface imperfections are relatively unimportant. The

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