PHYSICAL REVIEW B VOLUME 11, NUMBER 11 1 JUNE 1975

Heat capacity and magnetic susceptibility of single-phase α-cerium*

D. C. Koskimaki[†] and K. A. Gschneidner, Jr.

Ames Laboratory–United States Atomic Energy Commission and Department of Metallurgy, Iowa State University, Ames, Iowa 50010

(Received 20 January 1975)

The heat capacity of single-phase α-cerium has been measured from 1.6 to 22 K and the magnetic susceptibility from 1.6 to 150 K. The electronic-specific-heat constant was found to be 12.8 ± 0.2 mJ (g atom)$^{-1}$ K^{-2} and the Debye temperature at zero degrees was found to be 179 ± 2 K. The susceptibility results show a skewed *U* type of temperature behavior with minimum of 3.77×10^{-6} emu g^{-1} near 50 K and a rapid rise of about 20% below 20 K. The results are interpreted according to various models for the nature of α-cerium and the $\alpha \rightleftarrows \gamma$ transition.

INTRODUCTION

Pure cerium undergoes an isostructural transformation, $\gamma \to \alpha$, when subjected to increased pressure or reduced temperature.[1] This transition appears to be due to delocalization of the 4*f* electron in γ-cerium and is probably similar in mechanism to the electronic transition which occurs in several samarium and europium monochalcogenides.[2–5] During the transition to α-cerium, the specific volume decreases by nearly 16%,[1] the valence appears to increase from +3 to around +3.7,[6] and the Curie-Weiss magnetic moment disappears.[7] Since the phase boundary culminates in a critical point,[8] these changes can occur continuously or discontinuously.

The nature of α-cerium and the $\gamma \rightleftarrows \alpha$ transition have been the subject of controversy in recent years. Part of the controversy can be attributed to the difficulty in preparing and making measurements on single-phase α-cerium. The β (dhcp) phase is stable below 273 K, and a γ-cerium sample cooled directly from room temperature at zero pressure will always contain varying amounts of β-cerium at low temperatures. Only in the last few years have pressure methods been successfully used for the preparation of relatively pure α-cerium, and the resulting samples have been subjected to heat capacity,[9] magnetic susceptibility,[10] and resistivity[10–12] measurements at atmospheric pressure. However, even with pressure methods the resulting α-cerium in some of these studies has appeared to contain at least 1% β-cerium or more. Since β-cerium is an antiferromagnet below 12.5 K, the strong effects in the specific heat and susceptibility in the ordering region of β-cerium tend to mask the properties of α-cerium, even with small amounts of β-cerium. In the present work we have expended much effort perfecting our experimental techniques and have succeeded in obtaining very pure (> 99.5%) α-cerium. The description of our methods is presented elsewhere.[13] In this paper we report the results of our heat-capacity and magnetic-susceptibility measurements and interpret these results in light of various theories on the nature of α-cerium and the $\gamma \rightleftarrows \alpha$ transition.

EXPERIMENTAL PROCEDURE

The cerium used in this investigation was prepared at Ames Laboratory–U. S. AEC and has a purity of 99.8 at. % with respect to 76 elements. The analysis of this metal is given in Table I.

The method used to prepare close to 100% single-phase α-cerium was to apply 10-kbar pressure to pure γ-cerium at room temperature, reduce the temperature to 77 K while maintaining the pressure, release the pressure, transfer the sample to the heat-capacity or susceptibility apparatus at 77 K, and then take measurements being careful never to allow the sample to warm above about 180 K where the $\alpha \to \gamma$ transition begins to occur. More details can be found in another paper.[13]

Heat-capacity measurements were made on an adiabatic calorimeter accurate to about 2% below 3 K and about 1% between 3 and 20 K. Separate measurements were made on two cylindrical samples approximately 0.7 in. long and 0.353 in. in diameter.

The magnetic susceptibility was measured using a Faraday magnetometer with an absolute error of about 3% and a relative error of 1%. The sample was cylindrical with a diameter of 0.25 in. and a length of 0.2 in. More details on the apparatus[14] and handling of cerium can be found elsewhere.[13,15]

RESULTS

Heat capacity

Figure 1 illustrates the heat-capacity results for α-cerium.[16] Also shown are the results of Panousis and Gschneidner[9] (PG), which tend to be higher by approximately 25% depending on the temperature. Their results are corrected here for a

TABLE I. Chemical analysis of cerium used (impurity levels are in atomic ppm).

Impurity	Conc.	Impurity	Conc.
H	139	Ag	<0.1
N	500	Cd	<0.2
O	350	In	<0.08
C	887	Sn	<1
F	103	Sb	<0.08
Li	•••	Te	<0.1
Be	<0.02	I	<0.1
B	<0.01	Cs	<0.05
Na	2	Ba	<5
Mg	0.4	Hf	<0.8
Al	0.1	Ta	2
Si	2	W	0.5
P	0.3	Re	<0.7
S	<0.5	Os	<2
Cl	6	Ir	<5
K	2	Pt	<0.5
Ca	1	Au	<0.2
Ti	0.5	Hg	0.1
V	<0.5	Tl	<0.1
Cr	0.2	Pb	<0.5
Mn	<0.1	Bi	<0.5
Fe	7.5	Th	0.1
Co	<0.02	U	<0.2
Ni	0.5	Sc	<0.5
Cu	0.4	Y	<5
Zn	0.08	La	4
Ga	•••	Pr	<4
Ge	<0.2	Nd	<0.4
As	<0.04	Sm	<0.3
Se	<0.06	Eu	<0.08
Br	<0.06	Gd	<0.9
Sr	•••	Tb	<0.5
Zr	<1	Dy	<0.5
Nb	•••	Ho	<0.3
Mo	<1	Er	<0.5
Ru	<1	Tm	<0.06
Rh	<0.2	Yb	<0.2
Pd	<0.1	Lu	3
Total magnetic-rare-earth impurities			7.7
Total magnetic-transition-metal impurities (Cr, Mn, Fe, Co, Ni)			8.3
Total amount of impurities (76 elements)			2047
Total nonmetallic impurities (15 elements)			1986
Total metallic impurities (61 elements)			61

copper plug in the sample holder which was inadvertently left out of the calculations. The present results given in Figs. 1 and 2 are the combined data obtained from two α-cerium samples. After the first sample was run, the disagreement between the earlier results of Panousis and Gschneidner was evident. Because of this a second sample was prepared from the same γ-cerium stock to verify the results obtained on the first sample.

The difference between the PG and the present results is believed to be due to about 6% β in the PG sample. The dashed line shown in Fig. 1 is an interpolation to 6% α, 94% β using the α-cerium data of the present investigation and the 91% β, 9% α data of Panousis and Gschneidner.[17] The data generally coincide with the interpolation, except in the region around 12.5 K, the antiferromagnetic ordering temperature of β-cerium. In this region the peak in the PG data is considerably broadened and generally shifted upward in temperature. This peak broadening possibly caused them to considerably underestimate the amount of β-cerium in their sample. Also, after the heat capacity of the copper plug is subtracted out of the PG data, the peak is more noticeable since this correction is larger above 13 K than it is below 13 K. The β-cerium probably formed during the drilling and tapping of their sample, which was not done to our sample. The broadening of the peak is probably due to the large amounts of deformation in the lattice resulting from the pressure method used for preparing the sample.

Panousis and Gschneidner[9] noted a rise below 5 K in their heat-capacity data for α-cerium (Fig. 2). This rise is not seen in the C/T-vs-T^2 plot (Fig. 2) of the present investigation. This difference may be due to the differences in the purities of the samples used in the two investigations. Their sample contained 30 atomic ppm iron and a total of 109 atomic ppm of the magnetic rare earths, which compares with 7.5 and 7.7 atomic ppm. respectively, in our sample (see Table I). A second possibility is that the rise in their data is part of a high-temperature tail of a magnetic-impurity ordering. Both Conway[18] and Lounasmaa[19] observed low-temperature peaks in their heat-capacity data for cerium phase mixtures, which could be due to the same causes.

Figure 3 illustrates the Debye temperature as a function of temperature. The value of Θ_D at zero degrees is 179 ± 2 K compared to 117 K for Panousis and Gschneidner[9] and 200 K for Phillips *et al.*,[20] which was obtained from measurements at 10 kbar.

The PG value of 117 K has no significance since it was derived from measurements on a two-phase sample. The other two values compare favorably especially when one considers the 179-K value was obtained from ambient-pressure measurements and the 200-K value at high pressure. Furthermore the increase in Θ_D with pressure is consistent with sonic measurements performed on α-cerium at room temperature and high pressure.[21] These authors[21] found that the Θ_D increased ~4 K per kbar, which compares with ~2 K per kbar for the difference between our Θ_D value and the 10-kbar value of Phillips *et al.* The 179-K value for the Debye temperature of α-cerium is also reasonable when compared with the Θ_D value for β-cerium (152 K),[22] especially in view of the fact that α is ~16% more dense than β.

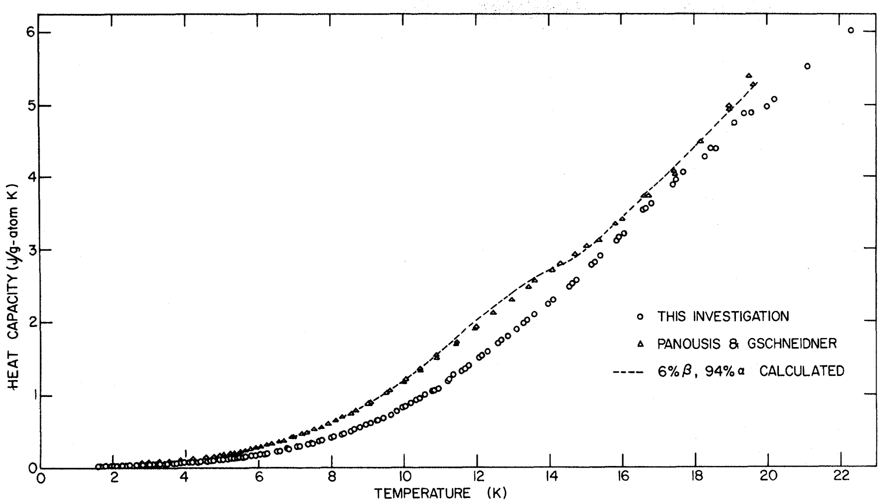

FIG. 1. Heat capacity of α-cerium. The present results, although not distinguished, are based on measurements made on two samples (see text).

The electronic-specific-heat constant γ is 12.8 ± 0.2 mJ (g atom)$^{-1}$ K^{-2}, which compares favorably with the values of 9.79 and 11.3 mJ (g atom)$^{-1}$ K^{-2} for Panousis and Gschneidner[9] and Phillips *et al.*,[20] respectively. Again, the PG value should be discarded since it was obtained from measurements on a two-phase sample. The difference between our value and the Phillips *et al.* value would suggest a decrease in the density of states at the Fermi surface of about 12% by increasing the pressure to 10 kbar. However, this difference might also be due to the difference in impurities in the two samples, especially if the Fermi level lies in a region of the band structure where the density of states changes rapidly with energy. Unfortunately Phillips and co-workers did not give a chemical analysis for their cerium sample.

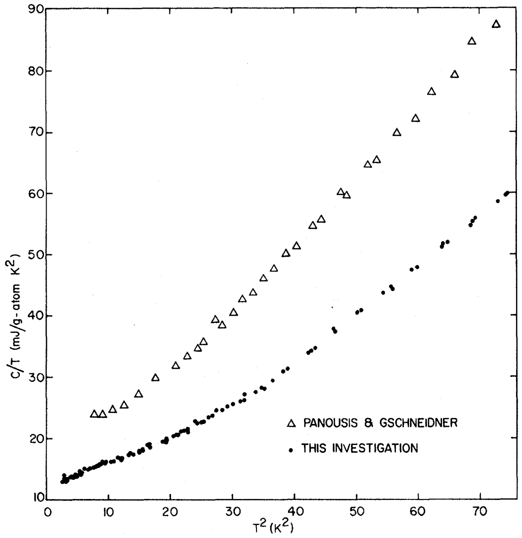

FIG. 2. C/T-vs-T^2 plot for α-cerium. The present results, although not distinguished, are based on measurements made on two samples (see text).

This value for the electronic-specific-heat constant [12.8 mJ (g atom)$^{-1}$ K^{-2}] is the highest known γ value for pure metals (excluding values reported for the magnetically ordering trasnsition and rare-earth metals and Pu).[23] The γ value for α-cerium is 20–30% higher than the values for Sc, Y, α-La, and Lu, and 3.5 times larger than that of Th.[23]

Magnetic susceptibility

Figures 4 and 5 show the results for the magnetic susceptibility versus temperature for α-cerium.[15] For purposes of comparison the results of Grimberg *et al.*[10] and the results of MacPherson *et al.*[7] at 10-kbar pressure are also shown in Fig. 4. Our results show a skewed *U*-shaped temperature dependence for the susceptibility with a minimum of 3.77×10^{-6} emu g^{-1} around 50 K. The absence of any noticeable break in the χ-vs-T curve at 12.5 indicates that no β phase is present in our α-cerium sample.

The 10-kbar data for α-cerium as shown in Fig. 4 suggest a minimum at 110 K, but within experimental error the susceptibility from 70 to

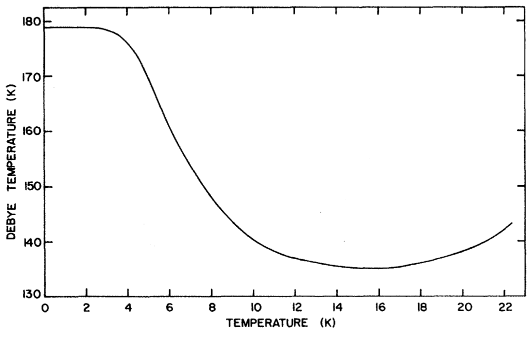

FIG. 3. Debye temperature as a function of temperature.

300 K could also be considered to be constant (see original paper by MacPherson *et al.*[7]). Our zero-pressure data show an increase above 50 K at a rate of 4.6×10^{-9} emu $g^{-1}K^{-1}$. The data extrapolate to a room-temperature value of 4.8×10^{-6} emu g^{-1} (6.7×10^{-4} emu $mole^{-1}$), which is the same value obtained when the high-pressure room-temperature data of MacPherson *et al.* are extrapolated to zero pressure. The data of Grimberg *et al.*[10] might exhibit a minimum, but unfortunately their measurements do not extend to sufficiently high temperatures to show this.

All three investigations show a strong temperature dependence, below 20 K for our data and below 50 K for the other two results. Both Grimberg *et al.* and MacPherson *et al.* found that their susceptibility measurements exhibited a field dependence due to magnetic impurities—the corrected curves are given in Fig. 4. In contrast to this behavior no field dependence was observed in our α-cerium specimen at 1.79 or 4.0 K in fields from 8.4 to 13.5 kOe (i.e., the susceptibility was constant within ± 0.3% at 1.79 and ± 0.5% at 4 K, well within the precision of our measurements). Furthermore, a calculation of contributions to the susceptibility from paramagnetic impurities based on our chemical analysis yields at most 0.2×10^{-6} emu g^{-1} at 2 K, which accounts for only one-fifth of the excess susceptibility at this temperature.

One other feature in our data needs explanation. The minimum susceptibility of 3.77×10^{-6} emu g^{-1} is 4.5 times the Pauli contribution predicted from our electronic-specific-heat constant. This discrepancy has also been noted by MacPherson *et al.* and by Grimberg *et al.*

DISCUSSION

The unusual temperature dependence of the susceptibility of α-cerium is evident in Fig. 5, where it is compared to the susceptibility of other paramagnetic metals.[24] Of these metals only α-Mn, Pd, and Sc, in addition to α-cerium, show any unusual temperature dependence. In the case of α-Mn the maximum and minimum are due to antiferromagnetic ordering at ~100 K. The temperature dependence of Pd is opposite that of α-cerium and Sc. Scandium, like α-cerium, exhibits a rapid rise below about 20 K, but does not go through a minimum and an increase in the susceptibility with increasing temperature at higher temperatures. Thus, any explanations for the temperature dependence of the magnetic susceptibilities of Mn, Pd, and Sc probably are not applicable to α-cerium.

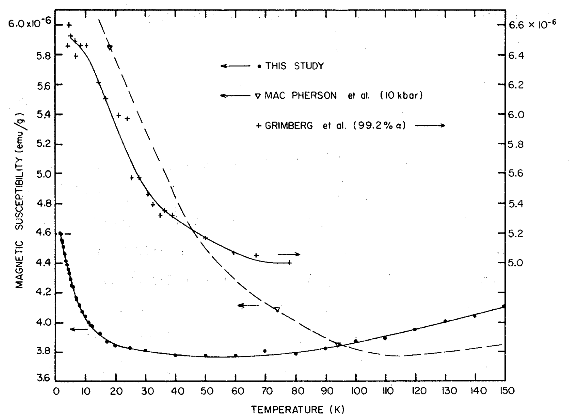

FIG. 4. Magnetic susceptibility of α-cerium. Note the shift in scale for the data of Grimberg *et al.*

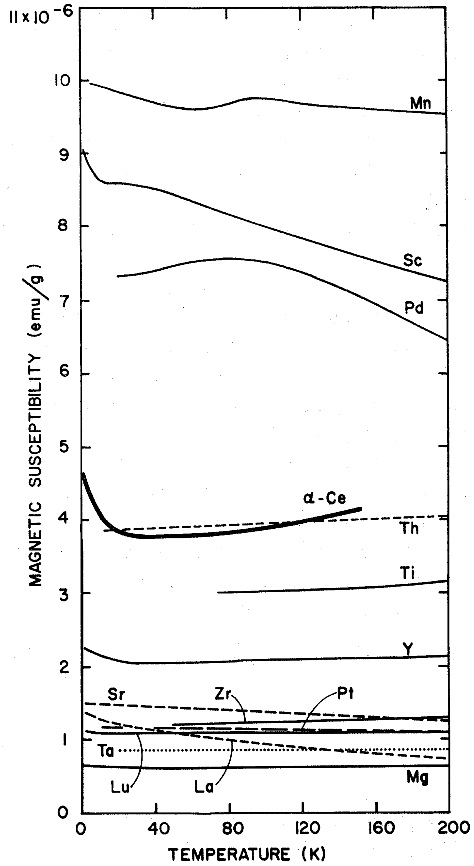

FIG. 5. Comparison of the magnetic susceptibility of α-cerium with other paramagnetic metals.

There are several models for the mechanism of the $\gamma\rightarrow\alpha$ transition and the nature of α-cerium but none of these adequately explain all of the features mentioned above. Zachariasen[25] and Pauling[26] first proposed that during the transition a $4f$ electron in the γ phase is transferred or promoted to the $5d6s$ conduction band. Several subsequent models have been based on this idea; however, most authors believe only a fraction (~0.7 at 1 atm) of the $4f$ electron is transferred during the $\gamma\rightarrow\alpha$ transformation.[6] The high observed electronic-specific-heat constant for α-cerium is consistent with a partially filled $4f$ band. If there were no electrons in the $4f$ band then an electronic-specific-heat constant of the size of that of thorium would be expected, and from what was noted above the α-cerium value is ~3.5 times larger than that of thorium.

Coqblin and Blandin[27] have proposed a promotional-type model based on Anderson's description of localized magnetic impurities in the Hartree-Fock approximation.[28] Their model predicts that the $4f$ level is broadened by resonance with the conduction band into a virtual bound level lying about 0.15 eV above the Fermi level in α-cerium. Part of the low-energy tail of the $4f$ peak would lie below the Fermi level, and the extra $4f$ contribution to the density of states would explain the high electronic-specific-heat constant, magnetic susceptibility, and the nonintegral valence of α-cerium. More specifically the high susceptibility would be due to an exchange enhancement such that the total susceptibility would be given by

$$\chi = 2\mu_B^2[n_f(E_F)S + n_s(E_F)], \tag{1}$$

where

$$S = \frac{1}{1 - \bar{U}n_f(E_F)}\,. \tag{2}$$

Here $n_f(E_F)$ and $n_s(E_F)$ are the densities of states at the Fermi level due to the f electrons and the conduction electrons, respectively, $\bar{U}$ is an average value of the effective exchange integral of the f electrons, and S is the exchange enhancement factor. A calculation of the factor S is strongly dependent on how the total density of states at the Fermi level is apportioned between $n_f(E_F)$ and $n_s(E_F)$. Our electronic-specific-heat constant leads to a total density of states at the Fermi level of 2.72 states eV^{-1} atom^{-1}. The contribution from the conduction electrons has been calculated by Mukhopadhyay and Gyorffy[29] to be 0.75 states eV^{-1} atom^{-1}, which leads to an exchange enhancement factor of 5.8. Alternately if one assumes the s-d conduction-electron density of states in α-Ce is the same as that in α-La (fcc) but modified to take into account the 16% volume decrease, then one obtains from the experimental density of states[30] a value for $n_s(E_F)$ of 2.07 states eV^{-1} atom^{-1}, which leads to an enhancement factor of 15.7. Grimberg and Schinkel[31] have estimated a value of S as high as 37. The possibility of high exchange enhancements have led to the search for a T^2 term in the curve fitting the low-temperature resistivity of α-cerium.[11,12,32] Such a term should result from scattering of s electrons by the spin fluctuations of the f electrons. Katzman and Mydosh[32] have found such a term in the equation fitting their resistivity measurements but others[11,12] have failed to find a T^2 term except as would be expected from small amounts of β-cerium and impurities present in their samples. If the existence of a large exchange enhancement can be accepted, then the model by Coqblin and Blandin[27] could provide one explanation for the increase in susceptibility above 50 K. Coqblin has proposed that the decrease in susceptibility with increasing pressure[7] is the result of the $4f$ peak moving upward with pressure giving a decreasing $n_f(E_F)$. The same argument could apply to changes in temperature. The $4f$ peak would move downward with increasing temperature giving an increasing $n_f(E_F)$ and an increasing susceptibility.

Another model based on the promotion idea is that of Ramirez and Falicov.[33] In their model the f states in cerium lie in a very narrow, highly correlated band slightly above the Fermi level. They include in their calculations an interaction energy between f electrons and conduction electrons along with the more familiar electron and hole thermal excitation energies and various electronic entropy terms. Their resultant free-energy expression is minimized showing that the number of f electrons varies discontinuously as a function of temperature and pressure. By assuming a linear relationship between the energy of the $4f$ level and pressure, they can also predict a critical point. However, owing to some simplifying assumptions the model predicts that α-cerium should become tetravalent at low temperatures in disagreement with experiment. By including the effect of hybridization of the localized $4f$ states with the conduction band, Alascio, Lopez, and Olmedo[34,35] have refined the theory to predict nonintegral valences for α-cerium. They predict the susceptibility due to the $4f$ electrons in α-cerium to be of the form

$$\chi_f = \frac{\mu_B^2 g^2 J(J+1)}{3T_0}n, \tag{3}$$

where $g^2J(J+1) = 2.54$, the Curie moment expected for a $4f^1$ configuration, n is the occupancy of the $4f$ level, and T_0 is the energy of the $4f$ level relative to the Fermi level. The occupancy n is approximately related to T_0 by

$$n \approx \frac{2J+1}{\pi}\frac{\Gamma}{T_0}, \tag{4}$$

where Γ is the width of the $4f$ states. Using values of Γ and T_0 given by Alascio *et al.*,[34] Eq. (3) tends to underestimate χ_f by about one-half. However, since the f level is assumed to move downward with increasing temperature the theory could qualitatively predict our observed susceptibility increase above 50 K. As in the theory by Coqblin and Blandin, the reason for the shift in the f level is not given.

A third theory based on the promotional idea is the interconfigurational-fluctuation (ICF) model of Hirst.[36] According to Hirst, integral values of the

4*f* occupation have a stability due to Hund's-rule correlations. If mixing between the 4*f* electrons and conduction electrons is sufficiently strong, the Hund's-rule correlations can be overcome and an ICF state is set up in which the valence on individual ions in the crystal fluctuates between integral values with lifetimes on the order of 10^{-13} sec. The susceptibility of the ICF state would be of the form

$$\chi(T)=\frac{\langle\mu_{\mathrm{eff}}\rangle^2}{3k_B(T+T_f)}, \tag{5}$$

where $\langle\mu_{\mathrm{eff}}\rangle$ is the weighted average of the effective Curie moments of the pure configurational states and T_f is a temperature which reflects the strength of the conduction-electron–*f*-electron mixing. For α-cerium the $4f^1$ configuration has a Curie moment $2.54\mu_B$ while the $4f^0$ configuration lacks a moment. If the fraction of 4*f* configurations is assumed to be 0.3 then by our calculations T_f would be about 540 K (0.046 eV) at 50 K. Insofar as Hirst did not calculate a temperature dependence for the fraction of $4f^1$ configurations, Eq. (5) does not predict our observed susceptibility increase above 50 K. Again, one could visualize the increase in susceptibility above 50 K as an increase in the fraction of $4f^1$ configurations due to a downward shift in the *f* level relative to the Fermi level.

A fourth model for the $\gamma\rightarrow\alpha$ transition is the possibility that the 4*f* shell delocalizes into a 4*f* band similar to the delocalization which occurs in a Mott transition. Johansson[37] has recently written a paper strongly arguing in favor of this idea. In α-cerium the 4*f* band would overlap the Fermi level such that a fractional number of electrons (near 0.7) would occupy the band. To account for the high susceptibility in α-cerium it is necessary to invoke the exchange-enhancement idea. However, it is difficult to predict a mechanism leading to the observed temperature dependence of the susceptibility.

None of the above models predicts the low-temperature rise in the susceptibility below 20 K. As previously mentioned, only about one-fifth of the low-temperature rise could be due to paramagnetic impurities. There are several other possible contributions. The α-cerium sample, by nature of the method used to prepare it, is highly deformed and may contain γ-like atoms at points of high local deformation in the lattice or on grain boundaries. The α-cerium atoms which are neighbors of magnetic impurity atoms (γ-like atoms) may experience a susceptibility enhancement. Finally, there may be some kind of an intrinsic effect in the α-cerium itself. For example, Edelstein[38] has predicted a $T^{-1/2}$ dependence of the susceptibility of α-cerium based on a possible similarity of α-cerium to spin-compensated systems exhibiting a Kondo effect. Although no Kondo effect has been seen in pure α-cerium, one of the possible consequences of the model proposed by Coqblin and Blandin[27] is spin compensation of the conduction electrons with the *f* electrons. However, if the $T^{-1/2}$ dependence exists it is masked by other contributions to the susceptibility and cannot be shown explicitly in our data.

ACKNOWLEDGMENTS

We wish to acknowledge P. E. Palmer for preparing the γ-cerium metal starting material, O. D. McMasters for his assistance in carrying out some of the computations, and M. S. Anderson for helping on the pressure-cooling runs to obtain α-cerium from γ-cerium. Also the efforts of Mass Spectrometric, Vacuum Fusion, and Wet Chemical Services Groups of the Ames Laboratory in supplying a complete quantitative analysis of the cerium starting material are deeply appreciated.

---

*Prepared for the U. S. Atomic Energy Commission, under Contract No. W-7405-eng-82.

†Present address: Armco Steel Corp., Armco Research Center, Middletown, Ohio 45042.

[1] K. A. Gschneidner, Jr., R. O. Elliott, and R. R. MacDonald, J. Phys. Chem. Solids 23, 555 (1962); also see earlier references cited therein.

[2] A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 368 (1970); 25, 1430 (1970).

[3] M. B. Maple and D. Wohlleben, Phys. Rev. Lett. 27, 511 (1971).

[4] A. Jayaraman, Phys. Rev. Lett. 29, 1674 (1972).

[5] A. Jayaraman, E. Bucher, P.D. Dernier, and L. D. Longinotti, Phys. Rev. Lett. 31, 700 (1973).

[6] K. A. Gschneidner, Jr. and R. Smoluchowski, J. Less-Common Metals 5, 374 (1963).

[7] M. R. MacPherson, G. E. Everett, D. Wohlleben, and M. B. Maple, Phys. Rev. Lett. 26, 20 (1971).

[8] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 15, 234 (1960).

[9] N. T. Panousis and K. A. Gschneidner, Jr., Solid State Commun. 8, 1779 (1970).

[10] A. J. T. Grimberg, C. J. Schinkel, and A. P. L. M. Zandee, Solid State Commun. 11, 1579 (1972).

[11] M. Nicholas-Francillon and D. Jerome, Solid State Commun. 12, 523 (1973).

[12] M. B. Brodsky and R. J. Friddle, Phys. Rev. B 7, 3255 (1973).

[13] D. C. Koskimaki, K. A. Gschneidner, Jr., and N. T. Panousis, J. Cryst. Growth 22, 225 (1974).

[14] F. H. Spedding and J. J. Croat, J. Chem. Phys. 58, 5514 (1973).

[15] D. C. Koskimaki, Ph. D. thesis, U.S. AEC Report No. IS-T-605 (Iowa State University, Ames, 1973) (unpublished).

[16] The experimental heat-capacity data may be obtained by ordering NAPS Document No. 02403, ASIS National

Auxiliary Publications Service, CCM Information Corp., 305 E. 46th St., New York, N. Y. 10017; remitting $2.00 for microfiche or $5.00 for photocopies; or from K. A. Gschneidner, Jr., Ames Laboratory, Iowa State University, Ames, Iowa 50010 (free).

[17] N. T. Panousis and K. A. Gschneidner, Jr., Phys. Rev. B 5, 4767 (1972).

[18] M. M. Conway, Ph. D. thesis, U.S. AEC Report No. LBL-827 (University of California, 1972) (unpublished).

[19] O. V. Lounasmaa, Phys. Rev. 133, A502 (1964).

[20] N. E. Phillips, J. C. Ho, and T. F. Smith, Phys. Lett. A 27, 49 (1968).

[21] F. F. Vornov, L. F. Vereshchagin, and V. A. Goncharova, Dokl. Akad. Nauk SSSR 135, 1104 (1960) [Sov. Phys.-Doklady 135, 1280 (1960)].

[22] D. C. Koskimaki and K. A. Gschneidner, Jr., Phys. Rev. B 10, 2055 (1974).

[23] The electronic-specific-heat constants were obtained from the following sources: K. A. Gschneidner, Jr., Solid State Phys. 16, 275 (1964); N. E. Phillips, Crit. Rev. Solid State Sci. 2, 467 (1972); K. A. Gschneidner, Jr., Rev. Chim. Miner. 10, 157 (1973)—Lu; and K. A. Gschneidner, Jr., in *Scandium—Its Occurrence, Chemistry, Physics, Metallurgy, Biology and Technology*, (Academic, New York, to be published), Chap. 5.

[24] The paramagnetic data were taken from the following sources: F. E. Hoare and J. C. Matthews, Proc. R. Soc. A 212, 137 (1952)—Pd, Pt; C. J. Kriessman and H. B. Callen, Phys. Rev. 94, 837 (1954)—Ti, Zr; F. E. Hoare, J. S. Kouvelites, J. C. Matthews, and J. Preston, Proc. Phys. Soc. Lond. B 67, 728 (1954)—Ta; R. Kohlhass and W. D. Weiss, Z. Naturforsch. A 24, 287 (1969)—Mn; H. U. Åström and K. Svensson, Phys. Scr. 1, 66 (1970)—Mg; J. D. Greiner and J. F. Smith, Phys. Rev. B 4, 3275 (1971)—Th; F. H. Spedding and J. J. Croat, J. Chem. Phys. 58, 5514 (1973); 59, 2451 (1973)—Sc and Y, La and Lu, respectively; and R.-R. Birnschein and T. Heumann, J. Less-Common Metals 37, 293 (1974)—Sr.

[25] W. H. Zachariasen, quoted by A. W. Lawson and T. Tang, Phys. Rev. 76, 301 (1949).

[26] L. Pauling, quoted by A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. 18, 145 (1950).

[27] B. Coqblin and A. Blandin, Adv. Phys. 17, 281 (1968); B. Coqblin, J. Phys. Suppl. 32, C1-599 (1971).

[28] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[29] G. Mukhopadhyay and B. L. Gyorffy, J. Phys. F 3, 1373 (1973).

[30] H. W. Myron and S. H. Liu, Phys. Rev. B 1, 2414 (1970).

[31] A. J. T. Grimberg and C. J. Schinkel, Solid State Commun. 13, 193 (1973).

[32] H. Katzman and J. A. Mydosh, Phys. Rev. Lett. 29, 998 (1972).

[33] R. Ramirez and L. M. Falicov, Phys. Rev. B 3, 2425 (1971).

[34] B. Alascio, A. Lopez, and C. F. E. Olmedo, J. Phys. F 3, 1324 (1973).

[35] C. F. E. Olmedo, A. Lopez, and B. Alascio, Solid State Commun. 12, 1239 (1973).

[36] L. L. Hirst, J. Phys. Chem. Solids 35, 1285 (1974); Phys. Kondens. Mater. 11, 255 (1970).

[37] B. Johansson, Philos. Mag. 30, 469 (1974); and also FOA 4 Report C 4588-A2, 1974 (unpublished).

[38] A. S. Edelstein, Phys. Rev. Lett. 20, 1348 (1968); Solid State Commun. 8, 1849 (1970).