

Electrical resistivity and magnetic susceptibility of β -cerium from 2 to 300 K*

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The electrical resistivity and magnetic susceptibility of allotropically pure β -Ce and γ -Ce and some two-phase ($\alpha + \beta$ or $\beta + \gamma$) samples, which were predominantly β -Ce, were measured from 2 to 300 K. Because β -Ce transforms to α -Ce between 15 and 50 K, several unusual experimental techniques were used to obtain reliable data. Our results show that the electrical resistivity of β -Ce remains unusually large, $> 50 \mu\Omega\text{cm}$ down to 40 K and below this temperature it drops an order of magnitude. The magnetic-susceptibility data show that β -Ce obeys the Curie-Weiss law down to near its Néel temperature, ~ 12.5 K. Low-field susceptibility data, < 800 Oe, show a Néel temperature at 12.5 K and that the magnetic susceptibility near the ordering temperatures decreases with increasing field. X-ray metallographic data indicate that when β -Ce transforms to α -Ce the initial growth occurs at the surface and grows inward. The unusual temperature dependence of the electrical resistivity of β -Ce could not be explained by several existing models (band-spin fluctuation or crystalline field) which have been used to explain large increases in the resistivity for other materials. However, a recently developed model based on Kondo scattering which is quenched by magnetic ordering appears to account for the observed results.

I. INTRODUCTION

Since the discovery of β -Ce by Trombe and Foex in 1943¹ there have been numerous investigations of the low-temperature properties of cerium, including the electrical resistivity and magnetic susceptibility. Unfortunately, all of these studies have been carried out on a mixture of two or three phases (α -, β -, and γ -Ce) depending upon the temperature and thermal treatment. Furthermore, it has been impossible to sort out the individual contributions that each phase makes to the total observed property. Thus little is known about these three phases except for their crystal structures and temperatures of transformation.

In the last few years substantial progress has been made in the preparation of essentially single-phase double hcp (dhcp) β -Ce,² and this has opened the way for a careful study of its properties—the low-temperature heat capacity,³ and the electrical resistivity and magnetic susceptibility (the subjects of this paper). The heat-capacity measurements showed a double-peak structure near 13 K and the authors thought that there may be two ordering temperatures, similar to neodymium where the ions having two different site symmetries in the dhcp structure order at different temperatures. By analogy, they predicted that the ions at the cubic sites of β -Ce order at 12.45 K and those at the hexagonal sites at 13.7 K. In the work reported here we have measured the electrical resistivity and magnetic susceptibility of β -Ce with special emphasis on the region below 60 K.

Both the electrical resistivity and magnetic sus-

ceptibility are powerful tools for studying cerium because they can be used to detect the presence of small amounts ($\sim 0.5\%$) of α - or γ -Ce in nearly pure β -Ce. These experimental methods have the advantage over metallographic and x-ray techniques in that they are bulk property measurements and not limited to the surface layers as are the latter two. However, the most meaningful results were obtained when all four techniques were used together.

Allotropically pure β cerium is obtained by a cooling-warming cycle (298 – 4.2 – 298 K) plus annealing (348 K) process.² The success of this method depends on the fact that β -Ce is the thermodynamically stable phase below 353 ± 5 K and that no α phase forms if β -Ce is cooled rapidly enough to 4.2 K. Our magnetic-susceptibility and electrical-resistivity measurements made on slow-cooled β -Ce specimens confirmed that the $\beta \rightarrow \alpha$ transformation occurs at ~ 50 K, and upon warming α -Ce transforms to a mixture of $\sim 20\%$ β and $\sim 80\%$ γ at ~ 180 K.⁴ It is noted that McHargue and co-workers^{4,5} also observed the formation of α -Ce from β -Ce below 75 K. X-ray and metallographic data also indicated that the initially pure β -Ce sample contained $\sim 5\%$ γ – 95% β at room temperature upon completion of a resistivity or magnetic-susceptibility run. The apparent contradiction of being able to prepare pure β -Ce and then to find that when slowly cooled it partially transforms to α -Ce, prompted us to examine the procedures involved. We concluded that the cool-down time was important. Since the transformation of $\beta \rightarrow \alpha$ involves not only an electronic change but also a

shift of atoms from the dhcp crystalline lattice to a fcc lattice, it was possible to cool the sample rapidly enough to suppress this atomic shift and thus inhibit the formation of α -Ce.

II. EXPERIMENTAL PROCEDURE

The three different cerium stocks used in our study were prepared at the Ames Laboratory. The purities of these samples are all greater than 99.8 at.% and are believed to be the highest-purity cerium samples ever used in electrical resistivity and magnetic-susceptibility investigations of any cerium allotrope. The analyses of these cerium stocks are given in Table I.

The preparation of a β -cerium sample takes about six weeks because of the involved cycling and heat treating procedure used. Initially, single-phase, strain-free γ -cerium samples are cycled between room temperature and 4.2 K 10 times, annealed for over a week at 348 K (75 °C), and then the process of thermal cycling and annealing is repeated four more times. Details of this method are described in a previous paper.²

A. Electrical-resistivity measurements

The electrical-resistivity measurements on slowly cooled or slowly warmed samples were made using a standard four-probe dc technique. The sample size was approximately $1.1 \times 1.1 \times 30$

mm³, weighing ~ 0.2 g. The sample current was 10 mA, and was stable to better than 1 part in 10^5 . The voltage drop across the sample was determined by a dc potentiometric technique with a sensitivity of 10^{-8} V. The relative precision of a resistance measurement was $\pm 0.02\%$. The absolute accuracy of the resistivity is limited by the geometrical factor determination to about $\pm 0.1\%$ and was obtained by 10 measurements of the sample cross section and 10 measurements of the spacing between the voltage probes. Temperatures from 2.7 to 300 K were obtained in a liquid-helium cryostat. The temperatures were measured by a calibrated Cu vs Constantan thermocouple from 40 to 300 K and by an Au-0.03-at.%-Fe vs Cu thermocouple from 2.7 to 40 K. Above 40 K the temperatures are accurate to ± 0.2 K and below 40 K are accurate to ± 0.04 K.

In order to determine the effects of cooling rates on the $\beta \rightarrow \alpha$ transformation, an apparatus was constructed to measure the electrical resistivity of a sample continuously while cooling the sample rapidly from room temperature to 4.2 K. This was accomplished by means of a standard four-probe dc apparatus where the sample voltage was displayed continuously on a XY plotter as a function of sample temperature. Cooling times varying from 5 to 90 min were obtained by adjusting the amount of He exchange gas present in the sample chamber, which was immersed in liquid He. De-

TABLE I. Chemical analyses of cerium stocks used. Impurity levels are in atomic ppm. The presence of 82 elements were analyzed for. For those elements not listed the impurity level was 1 ppm or less, except for Nb, Tc, and the rare gases which were not analyzed for.

Impurity	Ce(1)	Ce(2)	Ce(3)	Impurity	Ce(1)	Ce(2)	Ce(3)
H	139	139	278	Ba	<10	<5	<0.3
Li	<20	...	<0.0007	La	34	4	9
C	152	887	47	Pr	5	<4	<1
N	90	500	100	Nd	8	<0.4	4
O	639	350	385	Sm	<0.07	<0.3	<0.4
F	111	103	192	Eu	<0.05	<0.08	<0.05
Na	10	2	0.04	Gd	<1.2	<0.9	6
Cl	8	6	0.7	Tb	<0.2	<0.5	<1
K	5	2	0.03	Dy	<0.1	<0.5	1
Ca	20	1	0.2	Ho	<0.3	<0.3	<1
Cr	15	0.2	3.4	Er	1.6	<0.5	5
Mn	<1	<0.1	0.75	Tm	<0.05	<0.06	<0.06
Fe	7.5	7.5	<1.3	Yb	<0.05	<0.2	<0.3
Co	<0.1	<0.02	0.04	Lu	9	3	0.9
Ni	3	0.5	3	Ta	7	2	6.0
Cu	3	0.4	2	Pt	<0.5	<0.5	4.0
Y	5	<5	<10				
					Ce(1)	Ce(2)	Ce(3)
Total magnetic rare earths (max.)					16.6	7.7	19.8
Total magnetic transition metal (max.)					26.6	8.3	8.5
Total impurity (max.)					1338	2047	1099
Cerium purity (at. %) (min.)					99.87	99.80	99.89

partures from a uniform temperature throughout the sample and thermal gradients in the measuring circuits limit the accuracy of the measured data to about $\pm 5\%$. The reproducibility, however, of several runs on the same sample is within $\pm 2\%$. The sample was heated by removing the apparatus from the liquid-He bath and allowing it to warm in the laboratory with a warming time of about 25 min.

B. Magnetic-susceptibility measurements

The magnetic susceptibilities of the slowly cooled or slowly warmed cerium samples were measured by using three different techniques—Faraday, Foner, and an ac mutual induction method. Both the Faraday and Foner measurements were made over a temperature range of 2–300 K, and the ac measurements from 2 to 60 K. The precision and accuracy in the measured susceptibility were: $\pm 0.5\%$ and $\pm 2\%$, respectively, for the Faraday magnetometer; $\pm 0.1\%$ and $\pm 0.5\%$, respectively, for the Foner magnetometer; $\pm 0.1\%$ and $\pm 3\%$, respectively, for the ac measurements. The temperatures were measured by using an Au–0.03-at.-%-Fe vs copper thermocouple from 1.5 to 20 K and a Cu vs Constantan thermocouple from 20 to 300 K in the Faraday and Foner magnetometers, and a germanium resistance thermometer in the mutual inductance apparatus. The sample sizes were: $1.5 \times 1.5 \times 5 \text{ mm}^3$, weighing $\sim 0.08 \text{ g}$ for the Faraday magnetometer; $3 \times 3 \times 5 \text{ mm}^3$, weighing $\sim 0.3 \text{ g}$ for the Foner magnetometer, and $2 \times 2 \times 20 \text{ mm}^3$, weighing $\sim 0.6 \text{ g}$ for the ac measurements. The Faraday measurements were made at fields varying from 4 to 19 kOe and the Foner measurements at 10 kOe. The ac susceptibility measurements were made at 33 Hz with a measuring field of about 0.1 Oe, but some data were obtained as a function of magnetic fields from 0.1 up to 800 Oe.

A special ac susceptibility apparatus was designed for measuring the magnetic susceptibility of a sample continuously while rapidly cooling the sample from room temperature to 4.2 K. Sample cooling times from 8 to 90 min were obtained by adjusting the amount of helium exchange gas in the sample chamber which was immersed in liquid helium. The sample temperature was determined by an Au–0.03-at.-%-Fe vs Cu thermocouple in contact with the sample. Susceptibilities were obtained by a mutual induction technique operating at 87 Hz with a measuring field of about 1 Oe. The sample susceptibility was displayed on an XY plotter as a function of sample temperature. The temperatures were determined with an accuracy of about $\pm 1\%$ and the susceptibility was accurate to about $\pm 5\%$.

III. RESULTS: ELECTRICAL RESISTIVITY

A. Equilibrium data—slow cooling

The electrical resistivity of initially allotropically pure β - and γ -Ce samples are shown in Fig. 1 when measurements are taken by slowly cooling down to liquid helium. It is seen that the room-temperature resistivity of β -Ce is $\sim 15 \mu\Omega \text{ cm}$ larger than that of γ -Ce; that both allotropic forms have nearly similar temperature dependences from 300 to 100 K upon cooling; that both β -Ce and γ -Ce transform to α -Ce at ~ 50 and $\sim 100 \text{ K}$, respectively; that both samples exhibit a large hysteresis when α -Ce transforms back to $(\gamma + \beta)$ -Ce at $\sim 180 \text{ K}$; and that the β -Ce, which has not transformed to α -Ce, orders at $\sim 13 \text{ K}$. Furthermore it is evident that upon completion of the resistivity measurements after one cycle the room-temperature resistivity is slightly less than the initial value for β -Ce and slightly more for γ -Ce. This is because of the fact that α -Ce transforms to a mixture of $\sim 80\%$ γ -Ce and 20% β -Ce upon warming.^{4,6} One, however, cannot use this change in resistivity to estimate the amount of β - or γ -Ce in a sample because the electrical resistivity of β -Ce is probably anisotropic as are the other noncubic rare-earth metals.⁷ Indeed, the resistivity of another β -Ce sample made from the Ce(3) stock had a room-temperature resistivity of $82.8 \mu\Omega \text{ cm}$, which compares with $89.0 \mu\Omega \text{ cm}$ for the sample shown in Fig. 1. It is possible that part of this difference

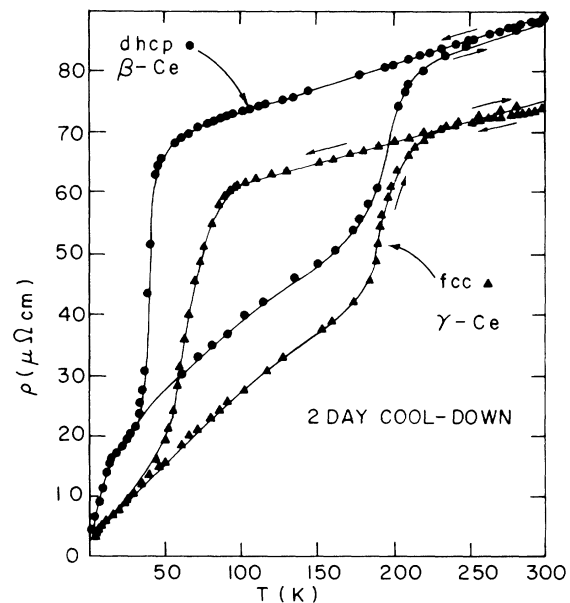


FIG. 1. Electrical resistivities of β -Ce, Ce(2), and γ -Ce, Ce(3), cooled down over a two-day period and warmed up over a $1\frac{1}{2}$ -day period.

could be due to impurities, which vary by a factor of two, see Table I, in the two cerium stocks and/or to slight differences in the γ -Ce concentrations in the samples [a (1–2)% variation is possible within the precision of the x-ray method used for determining the amounts of the two phases].

Cycling experiments show that the temperature at which the transformation starts, M_s , for the $\beta \rightarrow \alpha$ transformation shifts to higher temperatures as the number of cycles increases until M_s reaches the transformation temperature of the initially pure γ -Ce sample (see Fig. 2). Furthermore, the sharp $\beta \rightarrow \alpha$ transformation (~ 12 K wide) becomes increasingly broad with cycling (≥ 50 K wide on the fifth cycle), which is due to γ -Ce beginning to transform at ~ 100 K followed by the simultaneous transformation of γ - and β -Ce. It would appear that the M_s temperature is a good indicator of the phase purity of the initial β -Ce sample, however, we have made no attempt to establish a quantitative relationship.

The electrical resistivity near the Néel temperature of β -Ce was carefully examined to see if the ordering on the cubic and hexagonal sites could be

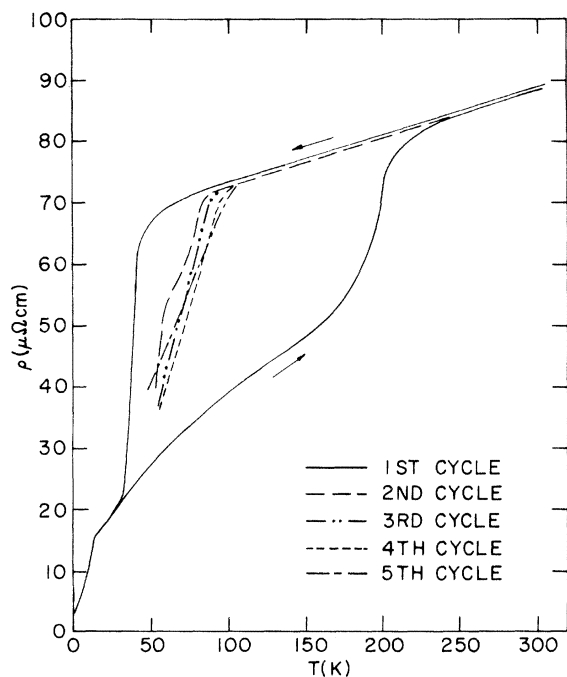


FIG. 2. Electrical resistivity of β -Ce, Ce(2), as a function of cycling. All data were taken on slowly cooled samples. On the second and succeeding cycles the resistivity was only measured down to 50 K and then the sample was warmed to room temperature, but no data were taken during the warming part of the cycle. The resistivity curve for the first cycle is the same as that shown in Fig. 1 for β -Ce.

observed to confirm the heat-capacity results.³ A single kink in the resistivity is clearly evident at 14.0 ± 0.1 K (Figs. 1 and 2). The significance of this kink will be discussed later.

B. Rapid cooling and heating data

Continuous electrical-resistivity measurements on β -Ce samples which were quenched from room temperature to 4.2 K were obtained to see if the $\beta \rightarrow \alpha$ transformations could be prevented. The results are shown in Fig. 3 along with that of a γ -Ce sample which was cooled in the same manner as the β -Ce sample. The large drop in resistivity of β -Ce (about one order of magnitude) below 20 K is surprising and completely unexpected. One might believe that this drop is due to the $\beta \rightarrow \alpha$ transformation, but as we will show this is not the case. First of all the heating curve shows only a small hysteresis, which is probably due to thermal gradients set up in the sample and measuring equipment during rapid cooling and heating. If α -Ce had formed, we would have expected to see the reverse transformation ($\alpha \rightarrow \beta$) occurring at about 180 K as occurs for γ -Ce (see Fig. 3). Second, the measurements were repeated seven times and at various cooling rates (up to 60 min for cooling from 298 to 4.2 K) and the results were reproducible within $\pm 2\%$ and no evidence was found for the $\beta \rightarrow \alpha$ transformation at 45 K. But when the cool-down time was increased to 90

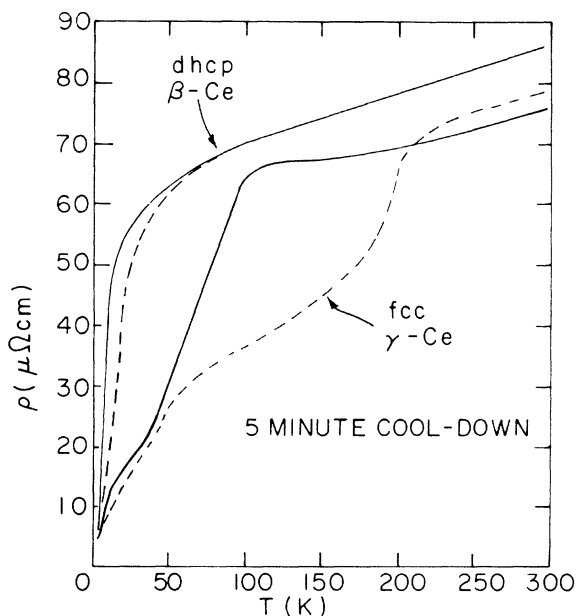


FIG. 3. Electrical resistivities of β -Ce, Ce(2), and γ -Ce, Ce(3), which were measured while rapidly cooling the sample from 298 to 4.2 K in 4–5 min. Solid line—cooling and dashed line—warming.

min, there was evidence for some of the β -Ce ($\sim 1\%$) transforming to α -Ce at 45K. As noted above if α -Ce had formed the $\beta \rightarrow \alpha$ transformation temperature would have increased to ~ 100 K (Fig. 2) due to the presence of γ -Ce which formed when the sample was warmed up in the previous cycle(s). Third, x-ray measurements taken on the sample before the first cycle and after the seventh cycle showed that the β -Ce concentration, if anything, increased by about 2%. Fourth, neutron diffraction measurements at 4.2 K on a rapidly cooled β -Ce sample confirmed that the sample was pure β -Ce within the limits of detection ($\sim 2\%$). Fifth, as will be shown shortly, the resistivity measurements themselves are most sensitive detectors for the presence or for the formation of α -Ce.

The other important observation is that above 50 K the resistivity of the rapidly cooled samples and that of the slow cooled samples have the same and unusual temperature dependence. Normally the resistivity of a metal at 50 K is $\frac{1}{10} - \frac{1}{5}$ of the room temperature resistivity,⁸ but as is evident in Figs. 1-3 ρ_{50} is not even $\frac{1}{2}$ of ρ_{300} (it is $\sim \frac{1}{1.3}$ of ρ_{300}). This point will be discussed later, since it is essential in understanding the nature of β -Ce.

C. Equilibrium and pseudoequilibrium data below 50 K

Because of the small hysteresis for β -Ce between 4 and 50 K (Fig. 3) and the lack of precision in the rapid cooling and heating experiments, we proceeded to obtain more reliable "equilibrium" data on β -Ce below 50 K. This was accomplished by quenching the β -Ce sample, which was mounted in the resistivity rig, down to 4.2 K and then further cooled to 2.8 K by pumping on the liquid-He bath. Resistivity data were then taken in the normal manner by establishing thermal equilibrium for each data point. The results are shown in Fig. 4 as the square points from 2.8 K to the point labeled B. At point B the sample began to transform ($\beta \rightarrow \alpha$) and followed the path shown in the insert of Fig. 4. As shown in our earlier note⁹ the equilibrium data taken between 2.8 and 15 K, lie approximately midway between the rapid cooling and rapid heating data shown in Fig. 3. As a result of several similar experiments it was found that at 14.0 K β -Ce does not transform to α -Ce over a 5 h period, but that at 14.8 K the transformation begins to occur within a few minutes. The most interesting feature of the low-temperature data is the anomalous rise in resistivity occurring between 2.8 and ~ 15 K (point B). This anomalous rise probably accounts for the kink observed in the resistivity of the β -Ce samples which contain some α -Ce, Figs. 1 and 2. As shown in Fig.

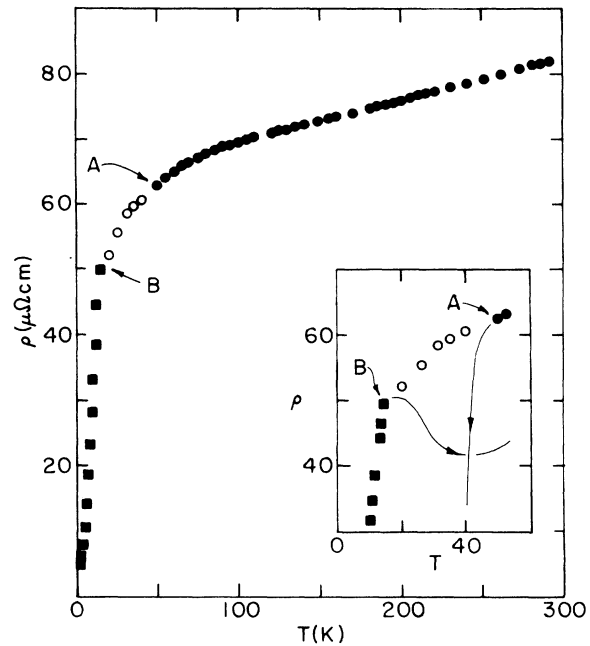


FIG. 4. Electrical resistivity data of β -Ce, Ce(3), taken by establishing thermal equilibrium for each data point (solid squares and circles). The open circles are pseudoequilibrium data points (see text for details).

4, upon slow cooling β -Ce begins to transform to α -Ce at 50 K, point A.

There is a narrow temperature range (~ 15 -50 K) over which it is impossible to obtain equilibrium resistivity data due to the $\beta \rightarrow \alpha$ transformation. Since it is desirable to have some electrical-resistivity results in this temperature range, a procedure was developed to obtain data under conditions as near to equilibrium as possible. In this case a β -Ce sample was quenched to 4.2 K to retain the dhcp structure and then was slowly warmed to 12 K. At this point the sample voltage probes were connected to a strip-chart recorder and the voltage was displayed as a function of time. The temperature was then raised abruptly in steps of 5 K and was maintained at each temperature for about 15 sec. By examining the sample voltage, at a set temperature, as a function of time it was observed that the sample resistivity decreased slowly ($\sim 0.5\%$ in 15 sec) in a linear fashion as the β -Ce transformed. By extrapolating the linear relationship to the time at which the sample passed through 15 K, resistivity values for pure β -Ce were inferred. It is believed that up to about 40 K the resistivity data thus obtained represent the true values for β -Ce to about 1%; above 40 K the sample began to transform too rapidly to make the procedure valid. The data obtained in this way are shown as open points in Fig. 4. It may be seen that

these data points provide a smooth link between the equilibrium data taken below 14 K and above 50 K, and lie between the cooling and heating curves shown for β -Ce in Fig. 3.

In Table II we have summarized the electrical-resistivity data for several cerium samples. Although the room-temperature resistivities for the two different β -Ce stocks differ by about 7%, their resistance ratios, ρ_{300}/ρ_2 , and M_s temperature are essentially the same. The resistance ratio for the β -Ce sample which does not undergo any transformation is slightly less than that for the sample which exhibits a partial transformation to α -Ce. This is consistent with the fact that the resistivity of α -Ce is about $2 \mu\Omega \text{ cm}$ at 2 K,^{10,11} and thus any α -Ce is expected to lower the resistivity of a Ce sample containing a mixture of β and α phases. This fact also explains why the resistivity ratio of the initially pure γ -Ce is higher than all the other samples—it contains much more α -Ce than any of the other specimens because all of the γ -Ce present in the sample transforms to α -Ce.^{4,5}

IV. RESULTS: MAGNETIC SUSCEPTIBILITY

A. High-field studies

The first magnetic-susceptibility measurements on β -Ce using the Faraday magnetometer were performed about six months before the electrical-resistivity experiments were started. Because of the design of this apparatus data could not be taken during cooling between liquid-nitrogen and liquid-helium temperatures, and this was unfortunate since the $\beta \rightarrow \alpha$ transformation could not be observed. On heating, however, it was obvious that α -Ce had formed because (i) the magnetic susceptibility was displaced by a constant factor from the cooling data over the range 90–180 K, and (ii) at ~ 190 K the susceptibility showed an observable change indicating α -Ce was transforming to $\gamma + \beta$, such that above 200 K the cooling and heating data lie on top of each other. Later measurements

TABLE II. Summary of electrical resistivities of some cerium samples.

Polymorph	Cerium stock	ρ_{300} ($\mu\Omega \text{ cm}$)	ρ_2 ($\mu\Omega \text{ cm}$)	M_s	
				$\beta \rightarrow \alpha$ (K)	ρ_{300}/ρ_2
β	Ce(2)	89.2	4.1	45	21.7
β	Ce(3)	82.8	3.8	45	21.8
β	Ce(3)	82.8	4.1 ^a	•••	20.3
γ	Ce(3)	74.4	2.6	100	28.6

^a Low-temperature data obtained by quenching to 4.2 K to prevent $\beta \rightarrow \alpha$ transformation.

using the Foner magnetometer showed that β -Ce begins to transform to α -Ce at ~ 50 K. In all other respects the Foner and Faraday results are identical.

To obtain correct low-temperature data without interfering fcc phases we used the same cooling procedures as described above for the electrical-resistivity measurements. The first experiments were to measure the magnetic susceptibility continuously while rapidly cooling both β - and γ -Ce samples using an ac magnetic-susceptibility technique. For the γ -Ce sample these results show: the $\gamma \rightarrow \alpha$ transformation upon cooling at 90–100 K; the antiferromagnetic ordering of the β -Ce fraction which forms when γ -Ce is cooled below^{4,5} 273 K; the reverse transformation $\alpha \rightarrow \beta + \gamma$ at 180 K; and the large hysteresis associated with the formation of α -Ce. In contrast, for the β -Ce sample no evidence is found for the formation of α -Ce and the susceptibility associated with antiferromagnetic ordering of β -Ce is ~ 3 times as large as that observed for the originally pure γ -Ce sample.

In the next experiment a sample of β -Ce was quenched to 4.2 K and then measurements were made on the Foner magnetometer by allowing the sample to reach thermal equilibrium as each data point was taken upon warming. These measurements show a sharp peak at 12.6 K in the susceptibility which indicates antiferromagnetic ordering. The results of all of these experiments are summarized in Fig. 5 and the derived constants are given in Table III. Within experimental error the results obtained on Ce(1) with the Faraday magnetometer are the same as those obtained on Ce(3) with the Foner magnetometer. As can be seen, the

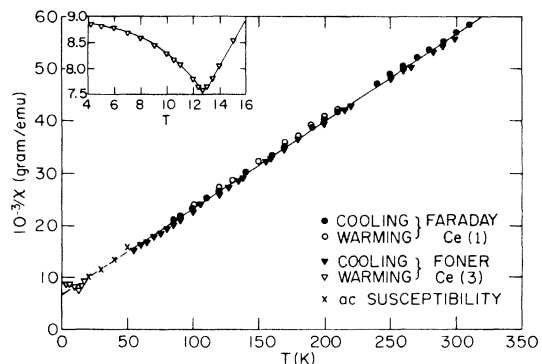


FIG. 5. Reciprocal of the magnetic susceptibility of β -Ce [combined results obtained from samples Ce(1), (2) and (3)] taken by establishing thermal equilibrium for each data point (Foner and Faraday results). The ac susceptibility data shown here are values averaged from the rapidly cooled and warmed results. The insert shows the details near the Néel temperature.

TABLE III. Summary of the magnetic-susceptibility measurements.

Polymorph	Cerium stock	Effective moment (μ_B)	Paramagnetic Curie temp. ($^{\circ}\text{K}$)	Remarks
β	Ce(1)	2.62	-44	Faraday magnetometer
β	Ce(3)	2.60	-38	Foner magnetometer
$\beta+\gamma$...	2.57	-42	Bates <i>et al.</i> (Ref. 12)
$\beta+\gamma$...	2.49	-38	After 102 cycles—Lock (Ref. 13)
γ	...	2.52	-50	Colvin <i>et al.</i> (Ref. 14)
γ	...	2.41	-9	Burr and Ehara (Ref. 15)

high-temperature (>50 K) data follow a linear relationship on the χ^{-1} -vs- T plot which shows that β -Ce obeys Curie-Weiss law. The slope of the Curie-Weiss relation indicates that β -Ce has an effective moment, p , of $2.61\mu_B$ per atom which compares favorably with the expected value of $g[J(J+1)]^{1/2} = 2.54\mu_B$ for the $^2F_{7/2}$ level. The theoretical value of p does not represent the true value, however, since effects of the $^2F_{7/2}$ level and temperature-independent paramagnetic contributions are neglected, and these would all tend to give a lower slope and a higher experimental value of p .

These high-field and neutron-diffraction data confirmed the magnetic ordering in β -Ce at 12.7 K in agreement with the earlier neutron diffraction⁵ and susceptibility¹³ measurements. In the region between 12 and 15 K the measurements were closely spaced in an effort to resolve the two ordering temperatures observed in the heat-capacity data for β -Ce. Two ordering temperatures were not detectable. However, these ordering temperatures may be too close together to be easily detected by Faraday or Foner measurements. For example, if the two ordering temperatures of Nd were less than 3 K apart, they could not be resolved by susceptibility measurements.¹³ Furthermore, the heat-capacity data which showed the double peak character of the antiferromagnetic transition differ from the Faraday and Foner measurements in that the heat-capacity data were taken in zero applied field. Hence a more thorough study was undertaken at low applied magnetic fields and these are described below.

B. Low-field studies

The low-field differential susceptibility of β -Ce near the magnetic ordering temperature is shown in Fig. 6. The data, which were obtained on a sample which was quenched to 4.2 K, are consistent with the high-field results and also show only one peak. Probably the most startling feature of these ac susceptibility measurements is the sen-

sitivity to small applied magnetic fields. As shown in Fig. 6 a field as small as 201 Oe will depress the susceptibility at the peak by several percent, almost down to the Foner susceptibility values measured at 10 kOe. This same behavior occurs in all the samples we have measured and the results are independent of magnetic field history. If there are two different transformation temperatures as suggested by the specific-heat results, then the effect of the higher temperature trans-

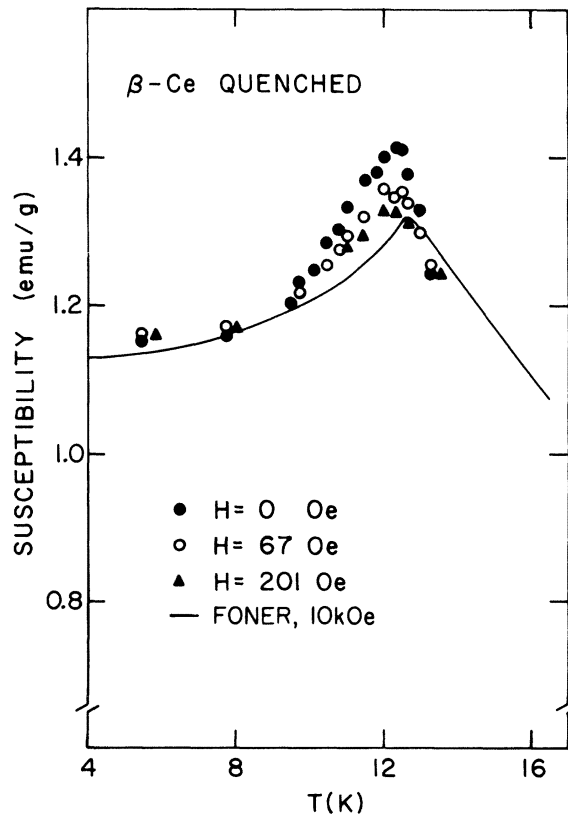


FIG. 6. ac susceptibility of β -Ce, Ce(3), near the magnetic ordering temperature as a function of field. Also shown are the Foner susceptibility data measured at 10 kOe.

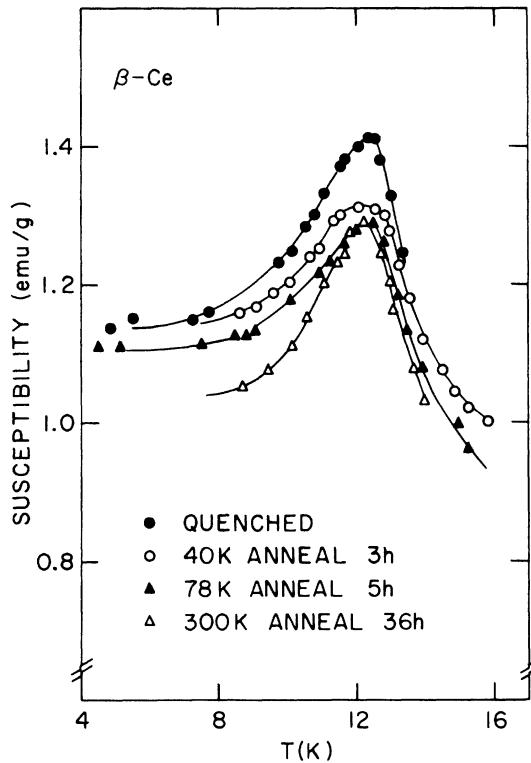


FIG. 7. Effect of various annealing treatments on the susceptibility of β -Ce, Ce(3). Only the "quenched" sample was pure β -Ce, the other curves are for a sample consisting of a mixture of α - and β -Ce phases (see text).

formation does not change the magnetic susceptibility enough to be seen in these differential susceptibility measurements.

When the β -Ce sample was warmed above 20 K the transformation to α -Ce is apparent in that the susceptibility bridge becomes very noisy and the magnitude of the susceptibility decreases. After the β -Ce sample was annealed for three hours at 40 K the susceptibility had diminished by about 8% as shown by the open circles in Fig. 7. Further thermal treatments—annealing at 78 K for 5 h and at 300 K for 36 h—did not change the magnitude of the peak, but did change its general shape. In all three runs in which the sample was annealed, the sample consisted of a mixture of α - and β -Ce [probably (90–95)% β -Ce].

V. RESULTS: METALLOGRAPHIC STUDIES

The microstructure of one of the β -Ce samples which had undergone a partial transformation to α -Ce during a magnetic-susceptibility run was examined. The sample was polished, anodized, and observed under polarized light using the procedure of McHargue and Yakel⁴ (Fig. 8). As is



FIG. 8. Micrographs of a β -Ce sample which had partly transformed to α -Ce between 15 and 50 K. The arrows indicate two γ -Ce regions which transformed from α -Ce at ~ 180 K and which under three different orientations of polarized light remain constantly dark, while the predominant β -Ce area exhibits varying light intensity. The sample was anodized with KOH.

seen in Fig. 8 whole martensite plates of one particular orientation have transformed to α -Ce at low temperature (15–50 K) and they transformed to γ -Ce upon warming (180–200 K). In contrast, the γ -Ce phase in samples which have been thermally cycled between room temperature and liquid-helium temperature a few times exists as small pockets between the β martensite plate—giving a much different appearing microstructure (for example, see the photomicrographs given in Rashid and Altstetter¹⁶ or Koch and McHargue¹⁷). This clearly indicates that in our earliest β -Ce magnetic susceptibility studies the α -Ce detected by the α - γ transformation during warming at 180–200 K was not due to the presence of γ -Ce, in our initial specimen, but rather to the β - α transformation occurring below 90 K upon cooling.

Another experiment was carried out because of the inconsistency between our earlier heat-capacity results, which suggested that the heat-capacity sample consisted of 99% β -Ce or better, and the resistivity and magnetic-susceptibility data which suggested that (5–10)% α -Ce forms in these samples. The heat-capacity sample was quite massive (39.4 g) compared to the samples used in this study (≤ 0.6 g). This suggested that α -Ce forms near the surface of the sample and does not penetrate into the interior because of strains set up in the material as β -Ce transforms to α -Ce. To verify this hypothesis, a flat β -Ce plate ($1.27 \times 5 \times 15$ mm³) was cooled down slowly in the same manner as for a resistivity or susceptibility run. After warming to room temperature the sample was examined by x rays and determined to have formed 8% α -Ce between 15 and 50 K. The surface was slowly etched away in ~ 0.1 -mm steps and x-ray patterns were taken after each reduction in thickness. These results showed that the α -Ce content, $(8 \pm 1)\%$, remained constant down to a

depth of 0.2–0.3 mm. At depths below 0.3 mm no detectable evidence was found for the formation of α -Ce. Using these values (i.e., 8% α -Ce is formed in the outer 0.3-mm skin of a sample) we calculated that 68% of the total volume of the β -Ce sample used for the Faraday study contained 8% α -Ce while the remainder contained no α -Ce, giving an overall composition of 5.5% α -Ce in this sample. This agrees quite well with the bulk magnetic-susceptibility data which indicated 6% α -Ce was present in the sample used for a Faraday measurements.

VI. DISCUSSION

A. Electrical resistivity

The electrical resistivity of β -Ce is quite unusual in that it has a weak temperature dependence at high temperatures and drops by an order of magnitude below about 40 K. Furthermore, β -Ce orders antiferromagnetically at ~ 13 K, and this ordering appears to have no large effect on the resistivity near 13 K. For a simple ordinary antiferromagnet one would expect the measured resistivity ρ_T to be given by

$$\rho_T = \rho_0 + \rho_{ph} + \rho_{mag}, \quad (1)$$

where ρ_0 is the residual resistivity, ρ_{ph} the normal phonon contribution, and ρ_{mag} the ordinary spin disorder contribution. The latter term is proportional to

$$\rho_{mag} \propto (g-1)^2 J(J+1) \quad (2)$$

or

$$\rho_{mag} \propto S(S+1), \quad (3)$$

depending on the form of the interaction Hamiltonian. From a plot of the known spin disorder values for the light lanthanide metals versus either $J(J+1)$ or $S(S+1)$ we obtain a value of $\rho_{mag} \approx 2 \mu\Omega$ cm for β -Ce. Thus, the resistivity of β -Ce should be similar to that of a nonmagnetic dhcp material such as α -La with the addition of a small $2\text{-}\mu\Omega$ cm anomaly at the ordering temperatures. Clearly, the precipitous $60\text{-}\mu\Omega$ cm anomaly observed in β -Ce is unusual and requires further consideration.

1. Determination of ρ_{anom}

Since the resistivity anomaly in β -Ce is not a simple spin disorder phenomenon, we must examine the anomalous resistivity ρ_{anom} . In order to determine ρ_{anom} the normal-resistivity contributions, $\rho_0 + \rho_{ph}$, must be removed from the total resistivity. With some confidence we assume that ρ_{ph} is the same as that of dhcp α -La, which has

recently been measured by Spedding and co-workers.¹⁸ The resultant anomalous resistivity of β -Ce ($\rho_{anom} = \rho_{\beta\text{-Ce}} - \rho_{\alpha\text{-La}}$) is shown in Fig. 9 as the curve labeled "dhcp La". The curves for ρ_{anom} which were obtained by using the observed ρ_{ph} contributions of hcp Y,¹⁹ and hcp Lu,²⁰ are virtually identical; the ρ_{anom} for either is labeled "Y" in Fig. 9. Also shown in Fig. 9 are curves derived from the ρ_{ph} contributions of dhcp La as published by Krizek²¹ (labeled "Krizek La") and from the Spedding *et al.*¹⁸ results for a La sample (labeled "Mixed La") containing 90% β (fcc) and 10% α (dhcp). There are several important observations to be made: (i) the low-temperature side of the resistivity peak is relatively insensitive to the choice of ρ_{ph} ; (ii) the resistivity peak shifts from 37 K to about 55 K depending on the choice of ρ_{ph} ; and (iii) the high-temperature slope of ρ_{anom} is approximately the same for dhcp La and Y, and it is about the same for mixed La and Krizek's La results. The curve labeled Y shown in Fig. 9 to depict the Y and Lu cases is not the proper curve for ρ_{anom} since no correction was applied to account for their higher Debye temperature, 276 K,²² and 196 K,²³ respectively, as compared to 152 K for β -Ce. When this correction is made the curve labeled "Y" shifts towards the "dhcp La" curve.

The paper of Krizek²¹ presented La data that were presumed to be for the dhcp phase but details concerning the nature of the sample were not included, and on the basis of the results of

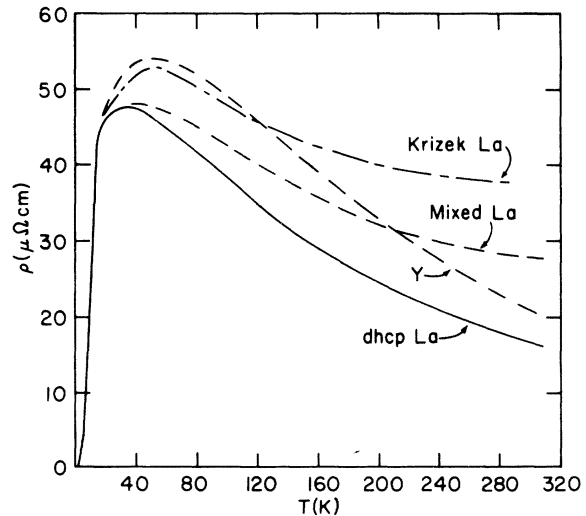


FIG. 9. Anomalous part of the resistivity of β -Ce as determined by subtracting the phonon and residual resistivity from the measured β -Ce electrical resistivity. The various curves are obtained by assuming different values for the phonon contribution to the resistivity, see text for further discussion.

Spedding and co-workers¹⁸ it appears that the Krizek La may have consisted of a mixture of β and α phases. We conclude that the best curve of ρ_{anom} for β -Ce is derived from the dhcp La data because they are isostructural and have the same number of valence electrons (3), and they have very similar properties except for those associated with the 4*f* electron of β -Ce.

A more serious problem in deriving ρ_{anom} is the question of preferred orientation in these dhcp metals, which undoubtedly have significantly different resistivities parallel and perpendicular to the basal plane. An x-ray texture analysis was made to determine whether or not preferred orientation existed in these samples. Unfortunately the large grain size of the samples does not permit us to unequivocally state that there is no preferred orientation in our samples. The x-ray patterns suggest that if there is any preferred orientation it is probably less than 10%. Neutron-diffraction examination of several different β -Ce samples also confirmed the absence of any gross preferred orientation (> 10%).

2. Existing models

A resistance anomaly similar to that shown in Fig. 9 for β -Ce has been found to occur in Np and Pu,^{8,24,25} and is generally attributed to the scattering of conduction electrons by spin fluctuations in a narrow but delocalized 5*f* band.^{24,25} In particular the band-spin-fluctuation model of Jullien *et al.*²⁵ has been shown to account rather nicely for the resistivity behavior of these actinide metals and some of their compounds. However, their model requires a constant band susceptibility. This term is not observed in the case of β -Ce, which obeys the Curie-Weiss law, and thus, their model is not applicable to β -Ce.

Several crystalline field (CF) theories have been proposed to explain large changes of resistivity in CeAl₂,^{26,27} CeAl₃,^{27,30} and²⁸⁻³⁰ Ce_{1-x}M_xAl₃ (*M* = La, Y, Th). Fortunately, our inelastic-neutron-scattering experiments at 77 and 298 K have permitted us to determine the crystalline field splittings in β -Ce to be 98 and 113 K for the Ce ions at the hexagonal sites and 206 K for the Ce ions at the cubic sites. Furthermore our heat-capacity results on β -Ce are consistent with these measured levels.^{3,31} Using these values for the CF levels we have calculated CF resistivity as a function of temperature using the various CF theories to see if they can explain the ρ_{anom} curve shown in Fig. 10. The calculation of Rao and Wallace²⁶ is based on a first-order Born approximation and the resultant CF resistivity versus temperature dependence is similar to curve A shown in Fig. 10

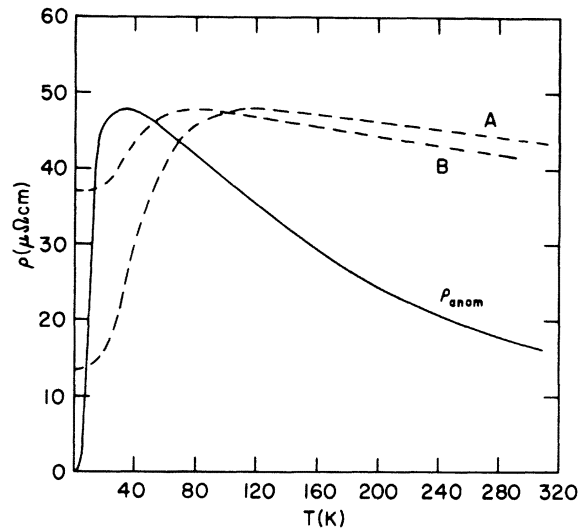


FIG. 10. Calculated crystalline field resistivities using the Kondo sideband model (Refs. 28–30). Curve A is calculated from the known crystalline field energy levels assuming that $J_x = \frac{3}{2}$ is the lowest doublet, $J_x = \frac{1}{2}$ is the first excited doublet and $J_x = \frac{5}{2}$ is the highest doublet. Similar curves are obtained for $J_x = \frac{5}{2} < \frac{3}{2} < \frac{1}{2}$ and $J_x = \frac{1}{2} < \frac{3}{2} < \frac{5}{2}$. Curve B is obtained when $J_x = \frac{3}{2} < \frac{1}{2} < \frac{5}{2}$. The curve labeled ρ_{anom} is the same as that labeled “dhcp La” in Fig. 9. The calculated curves were scaled such that the calculated maxima are the same as that of ρ_{anom} .

with a plateau being reached at approximately the temperature equivalent to the separation between the ground level and the first excited state (i.e., ~100 K). Cornut and Coqblin²⁷ performed a third-order perturbation calculation and the resultant CF resistivity-versus-temperature curve shows a rise from a nonzero value at 0 K to a peak at ~100 K (the separation between the ground and first excited level). Maranzana and co-workers²⁸⁻³⁰ carried out a second-order *s-f* exchange calculation known as the “Kondo sideband” model. The results of these calculations are shown in Fig. 10. Thus it is seen that three CF models are not capable of explaining ρ_{anom} for β -Ce for the known CF level splitting because the calculated CF resistivities show a maximum or the start of a plateau region at about 100 K, which is more than twice as high as the temperature of the observed peak.

3. Kondo model

Since the above mentioned models cannot account for the large change in the resistivity of β -Ce, we have analyzed ρ_{anom} and found that the high-temperature portion, above 40 K, could be fit to the theory of Matho and Béal-Monod³² for Kondo scattering. It then occurred to us that this scattering might be suppressed by the internal field associ-

ated with magnetic ordering thus giving rise to the observed resistivity drop. This problem has recently been analyzed in more detail by Liu and co-workers³³ who developed a model to explain the observed temperature dependence of ρ_{anom} . They concluded that β -Ce shows a Kondo resistivity anomaly at $T > 80$ K. Below 80 K the resistivity has a temperature dependence that is accounted for by use of a mean-field calculation of the internal field in an antiferromagnet, and for T just above $T_N \sim 12.5$ K by use of a two-spin cluster model.

As a check on this interpretation, we performed magnetoresistivity measurements³⁴ on β -Ce and a negative magnetoresistivity typical of field suppression of Kondo scattering was observed as expected.

In Fig. 11 we summarize the results of using the model of Liu *et al.*³³ to fit the four ρ_{anom} curves given in Fig. 9. The fit to the "dhcp La" curve is very good and yielded reasonable fitting parameters as they have shown. Attempts to fit the other curves of Fig. 9 have not been as convincing. Fitting parameters required for the "Y" curve are similar to those of "dhcp La" with a somewhat larger overall resistivity and with a d - f admixing interaction of $2I = 0.070$ eV, which is twice as large as that required for "dhcp La." The fit to the curve labeled "Krizek La" also yields fitting parameters which are reasonable (a smaller overall resistivity and $2I = 0.055$ eV). All of the curves are fit by the Liu *et al.* model with parameters that vary within a factor of 2. Apparently the overall conclusions of this paper are relatively independent of the specific choice of phonon resistivity. We feel, however, that the use of dhcp La for ρ_{ph} is the most appropriate choice.

As seen in Fig. 1, the electrical resistivity of γ -Ce above ~ 100 K is still rather large and its temperature variation is essentially parallel to that of β -Ce. This suggests that γ -Ce also exhibits Kondo scattering which is destroyed when γ -Ce transforms to α -Ce.

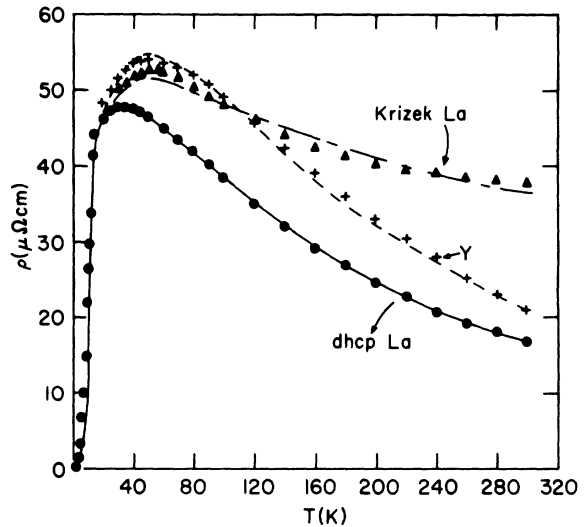


FIG. 11. Various curves for ρ_{anom} as fit by the model of Liu *et al.* (Ref. 33). The values of the fitting parameters $\rho_0(1 + a \ln T_F)$, $\rho_0 a$, and $2I$ are: for the dhcp La curve— $132.0 \mu\Omega$ cm, $20.2 \mu\Omega$ cm, 0.034 eV; for the Y curve— $191 \mu\Omega$ cm, 0.070 eV; and for the Krizek La curve— $105 \mu\Omega$ cm, $12 \mu\Omega$ cm, 0.055 eV. The solid or dashed lines are the theoretical fits and the dots, crosses and triangles are the experimental data taken from Fig. 9. The curve labeled "dhcp La" is felt to be the correct choice for ρ_{anom} .

B. Magnetic susceptibility

The high-field magnetic susceptibility behavior of β -Ce is simple and completely expected. The low-field studies, however, are interesting and unusual in that the susceptibility near the Néel temperature is very sensitive to the applied field (see Fig. 6). Similar behaviors are observed in α -Nd,³⁵ and α -Sm,³⁶ except these effects are seen at much higher fields. In the absence of single crystal measurements, especially neutron scattering experiments, there is little one can say about the field dependence of the magnetic moments on the

TABLE IV. Summary of some magnetic properties of β -Ce, α -Nd, and α -Sm.

Metal	Structure	Néel temperatures (K)		ΔT_N (K)	Spin-flip field of cubic sites (kOe)	Ref.
		Lower (cubic)	Upper (hex)			
β -Ce	dhcp	12.45	13.7	1.25	?	3
α -Nd	dhcp	7.5	19.2	11.7	35	35
α -Sm	α -Sm ^a	14	109	95	265	36
α -Sm	α -Sm ^a	15	106	91	...	37

^a A nine layer hexagonal structure (66.7% hcp-33.3% fcc).

various sites in β -Ce. One would expect these behaviors to be complex, similar to that observed in Nd,³⁵ and Sm.³⁶ The order of magnitude change in the difference between the ordering temperatures of the cubic and hexagonal sites, Table IV,

as one proceeds from Ce to Nd to Sm suggests that the difference in the exchange field and in the magnetocrystalline anisotropy associated with two sites decreases with decreasing atomic number and that it is almost zero in β -Ce.

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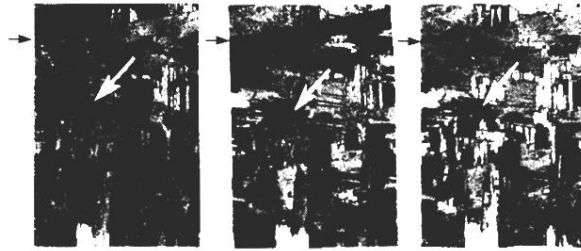


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