

Specific Heat of Cerium and Europium Metals between 0.4 and 4°K*

O. V. LOUNASMAA†

Argonne National Laboratory, Argonne, Illinois

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The specific heats of cerium and europium metals have been measured between 0.4 and 4°K in a He³ cryostat. For cerium, two experiments were made with samples consisting of 62 and 39% of the α phase (fcc), the balance being β cerium (hex). Due to a pronounced peak at 12.5°K the specific heat is quite large already at 4°K. A previously unknown flat anomaly in C_p was found around 0.8°K. By combining the present measurements with those of Parkinson and Roberts (3% of α cerium) and by assuming $C_L=0.612T^3$ and $C_B=10.5T$ (specific heats always given in mJ/mole°K) for the lattice and electronic specific heats of the trivalent β phase an analysis gave $C_p=x(0.50T^3+21T)+(1-x)(0.612T^3+10.5T+C_M)$. Here x is the fraction of α cerium in the sample and C_M is the magnetic specific heat of the β phase. C_B is thus about twice as large for the quadrivalent α phase as for β cerium. In the former modification $C_M=0$ because there is no magnetic $4f$ electron. Since all of the stable isotopes of cerium are even-even nuclei the nuclear specific heat $C_N=0$.

Below 1.2°K the specific heat of europium can be represented with 0.8% maximum deviation from experimental points by $C_p=27.96T^3+6.18T+2.333T^{-2}$. Above 1.2°K the temperature dependence of C_M gradually becomes less than T^3 and the results no longer can be expressed as a simple power law. This points to an anomaly in C_M , centered probably somewhere between 4 and 10°K. As averages of two least-squares analyses we adopt $C_B=(5.8\pm 1.0)T$, $C_N=(2.36\pm 0.07)T^{-2}$. C_B is thus in between the values $\sim 10.5T$ and $2.9T$ observed for many trivalent lanthanides and divalent ytterbium, respectively. Europium metal appears to be divalent and the ground state of Eu²⁺ ions is $^8S_{7/2}$. Since the orbital angular momentum of the $4f$ electrons is zero in an S state, C_N is rather small. The effective magnetic field at europium nuclei becomes $H_{\text{eff}}=260\pm 4$ kG in excellent agreement with $H_{\text{eff}}=264\pm 8$ kG deduced recently by Barrett and Shirley from Mössbauer measurements. Another interpretation of the experimental results, suggesting that europium at low temperatures might be a mixture of di- and trivalent phases, is also briefly discussed.

I. INTRODUCTION

THE specific heat C_p of cerium and europium metals has been measured in a He³ cryostat. For cerium, our data cover the temperature interval from 0.38 to 4.0°K; for europium, the experimental range is from 0.36 to 4.0°K. These two rare earths oxidize rapidly when exposed to air and they are very hygroscopic. Special and rather elaborate procedures, in contrast to other rare earths, were thus necessary for handling these metals.

The specific heat of cerium has previously been measured by Parkinson, Simon, and Spedding¹ from 1.5 to 180°K, and by Parkinson and Roberts² between 1.5 and 20°K. In these experiments, heat capacity peaks were found at 12.5 and 160°K and it was further established that the height of the low-temperature anomaly depends on the thermal history of the sample. On the basis of these and other types of measurements it is known that cerium at low temperatures has two stable crystallographic modifications, a fcc phase (α cerium), and a hexagonal phase (β cerium). The relative amounts of these two phases in a given sample depend on many factors as will be discussed briefly later. The peak in C_p at 12.5°K is caused by β cerium only.

The present heat capacity measurements on cerium were undertaken for further studying these very interesting phenomena and especially for extending the C_p data towards lower temperatures. The stable isotopes of this element are all even-even nuclei, and thus the nuclear specific heat C_N , very pronounced below 1°K for most rare earths, is identically = 0 for cerium. It was, therefore, hoped that the electronic specific heat C_B , caused by the conduction electrons, could be evaluated for the two crystallographic modifications of this metal.

No earlier measurements have been reported on the specific heat of europium. In contrast to most other rare earths which have three electrons in the conduction band, europium is divalent. The $4f$ shell is half full in this metal and, consequently, there is no magnetic field produced by the orbital angular momentum of the $4f$ electrons. The observed C_N is mainly caused by core polarization effects and europium thus offers an opportunity for estimating this contribution to the nuclear specific heat.

II. EXPERIMENTAL

Our He³ cryostat and the measuring procedure have been described earlier³; only the most important experimental features thus need to be repeated here. In general, the samples were cooled down to 4.2°K with the help of He⁴ exchange gas; for a description of the special thermal treatment given to the cerium metal we refer to Sec. III. 3. The space surrounding the calorimeter was then evacuated by pumping until a mass-

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† Present address: Wihuri Physical Laboratory, University of Turku, Turku, Finland.

¹ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

² D. H. Parkinson and L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 471 (1957).

³ O. V. Lounasmaa and R. A. Guenther, Phys. Rev. **126**, 1357 (1962).

spectrometer-type leak detector showed a very small helium reading. For further cooling, a mechanical heat switch was employed. In this manner thermal insulation was achieved when the heat switch was opened and desorption of helium gas from the sample was prevented.

For the heat capacity measurements a colloidal graphite (Aquadag) thermometer was used. It was calibrated against the vapor pressure of He⁴ between 4.15 and 2.2°K, against the vapor pressure of He³ between 2.2 and 0.75°K, against a magnetic thermometer (chromium methylamine alum) between 0.75 and 0.4°K, and with the help of an extrapolation formula between 0.4 and 0.35°K. The procedure will be described in detail elsewhere. (Paper on the specific heat of Pr and Nd metals.⁴) He⁴ temperatures were determined according to the T_{58} scale.⁵ For He³ the new 1962 Los Alamos scale⁶ was employed; a correction was made for the 0.5% of He⁴ in our He³ gas by assuming the validity of Raoult's law. For the second cerium experiment calibration points were measured only down to 0.82°K.

III. CERIUM

1. α , β , and γ Cerium

As already briefly mentioned, cerium has, at low temperatures, two crystallographic modifications. We shall now examine the phase transformations in this metal on the basis of detailed researches by Gschneidner,⁷ by Gschneidner, Elliott, and McDonald,⁸ and by Wilkinson, Child, McHargue, Koehler, and Wollan.⁹

A cerium sample which has not previously been cooled has at room temperature a fcc structure (γ cerium) with a lattice constant 5.16 Å. When the metal is cooled below 263°K a new β phase begins to form. This has hexagonal structure with lattice constants $a=3.67$ Å and $c=11.80$ Å; the density change is rather small. The amount of β cerium at a given temperature depends on cooling rate, cold working, and impurities. During cooling β phase continues to grow until at 103°K γ cerium begins to transform into a new collapsed fcc phase (α cerium) with a lattice constant 4.85 Å. The volume change at the $\gamma \rightarrow \alpha$ transformation is very large, -17.1% . At low temperatures, the sample is thus a mixture of α and β phases; sometimes a small amount of γ cerium has also been observed at 4.2°K. If the metal is then warmed up to room temperature all of the α cerium will transform back to γ (for our purposes it is

sufficient to consider the α - γ intermediate phase observed by Gschneidner *et al.*⁸ as identical with the γ phase) but most of the β cerium remains. A sample which has previously been cooled is thus at room temperature a mixture of β and γ phases. The amount of β cerium can be increased by repeated cycling between cryogenic temperatures and 293°K. After about 50 cycles to 4.2°K a stable situation is reached, there being approximately 90% of β cerium present at room temperature. Simultaneously, the paramagnetic susceptibility has increased below 50°K.

These transformations have a profound effect in the heat capacity as has been shown by Parkinson *et al.*¹ and by Parkinson and Roberts.² Since our measurements are confined to the temperature region below 4.2°K we expect to deal mainly with α and β cerium. In the β and γ phases the valence of cerium is the normal $+3$ but in the $\gamma \rightarrow \alpha$ transformation the only $4f$ electron is lifted to the conduction band whereby α cerium has a valence of $+4$. This modification thus has an empty $4f$ shell and its magnetic specific heat is $=0$.

2. The Sample

Our cerium metal was purchased from Research Chemicals, Inc. The following metallic impurities were found in a spectrographic analysis at Argonne (weight %): Ag, 0.018%; Ca, 0.001%; Cr, 0.0015%; Dy, 0.002%; Er, 0.08%; Eu, 0.018%; Fe, 0.015%; Gd, 0.002%; K, 0.0005%; La, 0.0004%; Mo, 0.0015%; Nd, 0.001%; Ni, 0.003%; Ta, 0.01%; Th, 0.018%; and Y, 0.0025%. These data are accurate to a factor of two. A chemical analysis gave the values: H, 0.022%; C, 0.072%; N, 0.0044%; O, 0.074%; and F, 0.034%. The precision is about 10%.

The metal ingot was a cylinder, 4.8 cm long and 2.7 cm in diameter. During the first experiment its weight was 174.05 g (1.24215 moles). Before the second experiment, the sample was again polished and this reduced its weight to 173.45 g (1.2379 moles).

3. Preparation and Thermal Treatment of Sample

As shown by the discussion in Sec. III.1, a knowledge of the thermal history of cerium is very important when the heat capacity results are analyzed.

After distillation, our sample was remelted in a vacuum and cast into a tantalum crucible. The metal was then allowed to cool to room temperature in about $1\frac{1}{2}$ hours whereafter tantalum was machined off. In order to prevent serious surface contamination, the sample was machined to the desired shape under special water-free oil. The metal was then transferred under oil to a glove box where the surface was cleaned in a pure helium atmosphere. After the sample had been weighed it was covered with a thin film of Apiezon T grease (0.26 g) and wrapped in a gold foil (1.28 g). The cerium metal was then removed from the glove box

⁴ O. V. Lounasmaa, *Phys. Rev.* **133**, A211 (1964).

⁵ F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Res. Nat. Bur. Std.* **64A**, 1 (1960).

⁶ R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, Los Alamos Scientific Laboratory Report No. 2701, 1962 (unpublished).

⁷ K. A. Gschneidner, *The Rare Earths*, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons, Inc., New York, 1961), p. 190.

⁸ K. A. Gschneidner, R. O. Elliott, and R. R. McDonald, *J. Phys. Chem. Solids* **23**, 555 (1962).

⁹ M. K. Wilkinson, H. R. Child, C. J. McHargue, W. C. Koehler, and E. O. Wollan, *Phys. Rev.* **122**, 1409 (1961).

and put as rapidly as possible into the cryostat where it was kept under vacuum or in a helium atmosphere. During transfer, surface oxidation was prevented by grease and the gold foil made handling of the metal easier. The latter also prevented grease flakes from falling onto the heat switch during thermal contraction of the sample in the $\gamma \rightarrow \alpha$ transformation.

Next, the metal was cycled four times between 293 and 77°K. Each cooling and warming period was about 1 h. Rapid temperature fluctuations were observed during cooling particularly in the $\gamma \rightarrow \alpha$ transformation region, indicating that the phase change proceeded from one domain to another.

The sample was cooled to 4.2°K by exchange gas and to 0.35°K by the heat switch. Three heat-capacity runs (experiment I, runs I, II, and III) were then made on successive days, without warming the cryostat above 4.2°K in the meantime. These measurements were followed by thermometer calibrations. The cerium metal was then warmed to room temperature, removed from the cryostat, and an x-ray analysis was made, using back reflection techniques. Both β and γ phases were present and from the relative line intensity it was estimated that the sample consisted of 30% of β cerium and 70% of γ cerium. [It should be noted that the strongest fcc line (γ phase) is six times stronger than the strongest hexagonal line (β phase) in a 50-50 mixture of the two modifications.]

For increasing the amount of β cerium, the sample was put into a glass container, which was filled with a small amount of He⁴ exchange gas, and the metal then cycled 16 times between 293 and 77°K. During the last of these cycles the total contraction in length was 0.7 mm (1.45%) as measured by a cathetometer. This corresponds to a total volume change of 4.3% between 293 and 77°K and indicates, on the basis of dilatometric measurements by Gschneidner *et al.*,⁸ 25% of α cerium at 77°K. About 2 hours were allowed for a complete cycle from 293 to 77°K and back. After this heat treatment, an x-ray analysis was again performed and this time there was about 70% of β cerium and 30% of γ cerium in the sample at room temperature.

Some surface oxidation had taken place during the x-ray analyses. Therefore, before the second experiment the sample was again polished in the glove box and then put back into the cryostat. Two more cycles between 293 and 77°K were performed before beginning the second experiment. The final cooling to 4.2°K was made very slowly without any exchange gas and took about 24 hours to complete.

On the basis of our x-ray and dilatometric data and neutron diffraction measurements by Wilkinson *et al.*,⁹ we estimate that during the first experiment our sample consisted of 60% of α cerium and 40% of β cerium; for the second experiment the corresponding figures are 35 and 65%, respectively. The accuracy of these numbers is not better than $\pm 5\%$ owing to the relatively low

precision obtainable by the x-ray analyses and the rather crude nature of our dilatometric measurements.

4. Results

Our experimental results for cerium, experiment I from 0.38 to 4.0°K and experiment II from 1.2 to 4.0°K, are presented in Table I and Fig. 1. All calculations were performed by an IBM 704 digital computer.¹⁰ The results have been corrected for curvature due to finite temperature increments when measuring C_p . The size of these increments may be computed from the separation of successive points in Table I. As can be seen from Fig. 1, the three runs of experiment I agree very well among themselves but, due to the increased percentage of β cerium, experiment II gives a considerably higher specific heat.

Results from experiment I clearly show an anomaly in the specific heat between 0.4 and 1.5°K. This hump was not observed by the earlier investigators^{1,2} since their measurements were not extended to low enough temperatures. Because of the anomaly, it is impossible to represent C_p as a function of temperature with a simple power series.

In the calculations, a correction was made for the heat capacity of the gold foil and grease by adding these to the heat capacity of the empty calorimeter.⁴ For gold we used¹¹ $C_p = 0.0022T^3 + 0.0038T$ mJ/g °K,

TABLE I. Specific heat (in mJ/mole°K) of cerium metal. Experimental results.

T, °K	C_p	T, °K	C_p	T, °K	C_p
Experiment I					
Run I					
3.4418	236.2	2.1652	102.9		
3.7021	275.4	2.3625	116.8		
0.3895	15.21	3.9480	319.1	2.5744	134.2
0.4224	16.51			2.8032	156.9
0.4574	18.03	Run II			
0.4947	19.71	0.3751	14.66	3.0471	184.0
0.5349	21.65	0.4056	15.85	3.3119	217.5
0.5771	23.67	0.4395	17.25	3.5912	259.6
0.6216	25.86	0.4757	18.85	3.8626	307.5
0.6707	28.29	0.5143	20.65	Experiment II	
0.7293	31.25	0.5553	22.64	1.1871	64.67
0.7984	34.56	0.5989	24.77	1.2654	69.02
0.8754	38.24	0.6460	27.12	1.3511	74.04
0.9579	42.05			1.4422	79.27
1.0441	45.85	Run III			
1.1357	49.74	0.6999	29.78	1.5423	85.31
1.2359	53.94	0.7635	32.93	1.6590	92.86
1.3438	58.76	0.8366	36.47	1.7949	102.3
1.4574	63.51	0.9162	40.22	1.9477	113.8
1.5804	69.45	1.0005	43.90	2.1112	127.7
1.7224	76.49	1.0902	47.83	2.2897	144.2
1.8860	85.18	1.1866	51.92	2.4858	165.1
2.0676	96.06	1.2911	56.41	2.6978	192.0
2.2595	109.2	1.4024	61.30	2.9240	224.1
2.4659	124.9	1.5201	66.70	3.1542	263.6
2.6907	144.2	1.6523	73.03	3.3879	308.8
2.9315	169.3	1.8051	81.06	3.6083	357.3
3.1851	200.5	1.9772	90.76	3.8000	405.4
				3.9705	452.6

¹⁰ P. R. Roach, Argonne National Laboratory Technical Report No. 6497, 1962 (unpublished).

¹¹ P. H. Keesom and N. Pearlman, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 302.

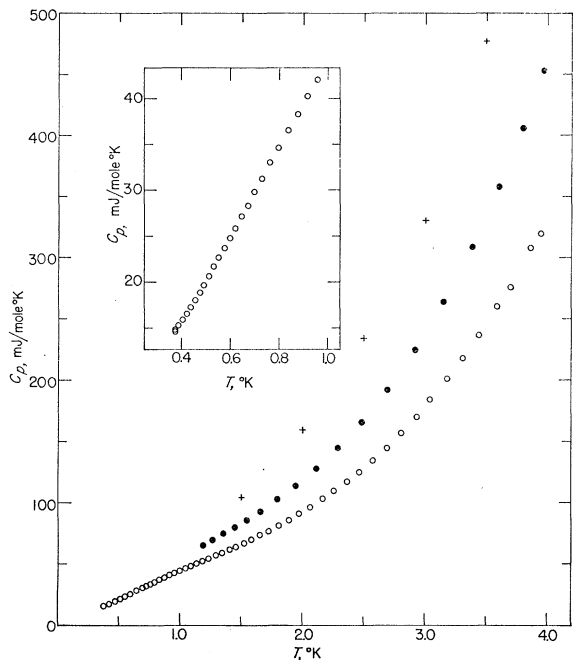


FIG. 1. The specific heat of cerium metal. \circ , experiment I, 62% of α cerium; \bullet , experiment II, 39% of α cerium; $+$, Parkinson and Roberts, (Ref. 2), 3% of α cerium. The inset shows results below 1°K on a larger scale. Only about 50% of the points below 1°K have been plotted to the main graph.

and for Apiezon T grease,¹² $C_p = 0.036T^3$ mJ/g °K. When compared with the heat capacity of the cerium sample the total effect of these corrections is nowhere more than 0.4%.

On the basis of an earlier and rather detailed discussion⁴ we estimate that the accuracy of our C_p measurements is 1.5% at 0.4°K and 0.5% between 1 and 4°K. The random scatter of experimental points is equal to or less than 0.6%.

5. Discussion

Parkinson and Roberts² made five different measurements of the specific heat of cerium between 1.5 and 20°K after the sample had been cooled, at least to 20°K, 1, 3, 50, 51, and 52 times, respectively. As a result of this thermal cycling, the heat capacity increased considerably but appeared to approach a saturation value. Data from the last three experiments are virtually the same; results from a smooth table, based on these runs, have been plotted into Fig. 1. Unfortunately, their data corresponding to experiments after 1 and 3 coolings are published only as a graph from which it is impossible to read values at liquid helium temperatures with any accuracy. It seems, however, that their first run gives a specific heat at 4°K which is rather close to the results from our second experiment. This indicates that other factors, besides thermal treatment, are important in determining the amount of β cerium pre-

sent at low temperatures. Gschneidner *et al.*⁸ found that the amount of β cerium is increased with increased impurity content if the impurity is another rare-earth metal. Parkinson and Roberts² report as the chief impurities of their sample 0.4% of Li and 0.04% of Fe, but it is likely, since analyses of lanthanides have only recently become reliable, that other rare-earth impurities might have been present.

It would be of considerable interest if the experimental specific heat of cerium could be separated into contributions from the two crystallographic phases. For doing this accurately, a knowledge of the precise amounts of the two modifications in the sample is needed. At the present time, one must be satisfied with a less exact analysis. We found it most satisfactory to proceed as follows:

(1) The specific heat of cerium metal can be written

$$C_p = x[A(\alpha)T^3 + B(\alpha)T] + (1-x)[A(\beta)T^3 + B(\beta)T + C_M], \quad (1)$$

where x is the fraction of α cerium in the sample, $A(\alpha)$ and $A(\beta)$ are the coefficients in the lattice specific heat $C_L = AT^3$ for α and β cerium, respectively, $B(\alpha)$ and $B(\beta)$ are the corresponding coefficients in the electronic specific heat $C_E = BT$, and C_M is the magnetic specific heat of β cerium (for α cerium $C_M = 0$). It was first assumed that $A(\alpha) = A(\beta) = A$, and $B(\alpha) = B(\beta) = B$, and Eq. (1) was then applied for our experiments I and II. Next, the ratio

$$R = [C_p(\text{II}) - AT^3 - BT] / [C_p(\text{I}) - AT^3 - BT] = C_M(\text{II}) / C_M(\text{I}) \quad (2)$$

was calculated and by requiring $R = \text{const}$ the coefficients A and B were determined. On the basis of neutron diffraction measurements by Wilkinson *et al.*,⁹ we then assumed that the sample of Parkinson and Roberts² after 50 thermal cycles contained 92% of β cerium and 8% of α cerium; i.e., $x(\text{PR}) = 0.08$. Wilkinson *et al.* also found 8% of γ cerium in their sample at 4.2°K, but since both β and γ phases are trivalent they have been treated together as pure β cerium. By using the calculated values of A and B and the observed $C_p(\text{I})$, $C_p(\text{II})$, and $C_p(\text{PR})$ at 4°K, the concentrations $x(\text{I}) = 0.63$ and $x(\text{II}) = 0.40$ were then computed from the ratios $C_M(\text{I})/C_M(\text{PR})$ and $C_M(\text{II})/C_M(\text{PR})$. The values of $x(\text{I})$ and $x(\text{II})$ are in reasonably good agreement with our previous estimates based on x-ray and dilatometric analyses (cf., Sec. III.3).

(2) In order to obtain an approximate value of C_M as a function of temperature we then assumed $x(\text{PR}) = 0$, $A(\beta) = 0.612$ mJ/mole (°K)⁴, and $B(\beta) = 10.5$ mJ/mole (°K)², where the values of $A(\beta)$ and $B(\beta)$ have been determined from results on other trivalent lanthanides as described by Lounasmaa.¹³ C_M , together with $x(\text{I})$, $x(\text{II})$, $A(\beta)$, and $B(\beta)$, was then inserted into

¹² E. F. Westrum (private communication).

¹³ O. V. Lounasmaa, Phys. Rev. **133**, A219 (1964).

Eq. (1) and $A(\alpha)T^3+B(\alpha)T$ calculated at various temperatures between 1.5 and 4°K for experiments I and II. Next, by plotting $[A(\alpha)T^3+B(\alpha)T]/T$ versus T^2 the values of $A(\alpha)$ and $B(\alpha)$ were determined.

(3) By using the preliminary results for $x(\text{I})$, $x(\text{II})$, $A(\alpha)$, $B(\alpha)$, and C_M steps (1) and (2) with rather obvious modifications, were then repeated. Somewhat different values were obtained for $B(\alpha)$ from experiments I and II. After repeating the whole calculation a few times good agreement was secured with $x(\text{PR})=0.03$. The final results were: $x(\text{I})=0.62$, $x(\text{II})=0.39$, $A(\alpha)=0.50$ mJ/mole (°K)⁴, and $B(\alpha)=21$ mJ/mole (°K)². We thus get for cerium (C_p in mJ/mole°K)

$$C_p = x(0.50T^3 + 21T) + (1-x)(0.612T^3 + 10.5T + C_M). \quad (3)$$

A considerable increase is observed in C_E due to promotion of a fourth electron into the conduction band. The accuracy of $A(\alpha)$ is poor since this term is small. The value of $B(\alpha)$ should be a little more reliable although it is difficult to give any estimates. The results, of course, are rather sensitive to our assumptions $A(\beta)=0.612$ and $B(\beta)=10.5$. The accuracy is further limited by the low-temperature hump in C_p . It is interesting to note that apparently the sample of Parkinson and Roberts² after 50 cycles contained almost pure β cerium.

The magnetic specific heat C_M is large and is mostly due to the pronounced peak at 12.5°K. Below this temperature, β cerium apparently is antiferromagnetic. Parkinson and Roberts² also observed a small satellite in C_p at 7°K. The low-temperature anomaly, centered around 0.8°K, is rather flat and, as a very rough guess, it may be estimated that the entropy associated with it is about 100 mJ/mole °K. This anomaly is thus caused by a fraction of the sample only. It could possibly be due to the small amount of γ phase still present below 4.2°K.⁹ One would expect that a magnetic transformation in this phase takes place, due to greater symmetry of its lattice, at lower temperatures than in the β phase. Of course, the small peak at 7°K could also be caused by such a transformation.

Bleaney¹⁴ has used the crystalline field approach for calculating the magnetic specific heat of cerium. The agreement with experimental results is only approximate due to the cooperative nature of the peaks. He predicts the lowest excited level for β cerium at 30°K.

Obviously, an elaborate systematic investigation is needed for determining the reasons of all specific heat anomalies observed in cerium. The temperature range between 0.4 and 20°K should be covered and the experiments should be devised in such a manner that the crystallographic composition of the sample can be changed and is accurately known. A specific heat cryostat in which dilatometric and/or neutron diffrac-

tion measurements can also be made is required for such experiments.

IV. EUROPIUM

1. The Sample

Our europium metal was also purchased from Research Chemicals. The procedure for preventing the metal from oxidizing during machining was similar to that already described for cerium (cf. Sec. III.3). The surface of the sample was polished in the glove box and only slight dulling was observed after the metal had been transferred into the cryostat.

The sample was a cylinder, 1.6 cm long and 2.7 cm in diameter; its weight was 51.09 g (=0.3362 moles). The following metallic impurities were found in analyses at Argonne (weight %): Ag, 0.008%; Al, 0.001%; Ce, 0.006%; La, 0.001%; Mg, 0.06%; Mn, 0.001%; Nd, 0.001%; Sm, 0.003%; Ta, <0.01%, and trace amounts of Fe, Li, Sr, Y, and Yb. These analyses are accurate to a factor of two. For the nonmetallic impurities chemical analyses gave: H, 0.026%; C, 0.079%; N, 0.023%; and F, 0.003%. The accuracy is 10%. Because of the very rapid oxidation of europium in the air an oxygen analysis was not performed.

2. Results

Four experimental runs were made on europium on two successive days, followed by thermometer calibrations. During all this time the sample was never warmed above 4.2°K. The results are presented in Table II and

TABLE II. Specific heat (in mJ/mole°K) of europium metal. Experimental results.

T , °K	C_p	T , °K	C_p	T , °K	C_p
Run I					
0.3835	19.93	2.2636	253.9	0.8654	26.68
0.3947	19.20	2.4192	291.0	0.9228	30.58
0.4178	18.01	2.5867	333.6	0.9864	35.56
0.4467	16.92			1.0551	41.65
0.4788	16.14	Run II			
0.5127	15.73	2.7647	380.6	1.1300	49.19
0.5490	15.65	2.9543	432.3	1.2136	58.66
0.5878	15.93	3.1476	488.0	1.4074	84.71
0.6267	16.59	3.3424	546.0	Run IV	
0.6655	17.53	3.5383	604.7	0.5168	101.8
0.7050	18.78	3.7340	666.9	1.6404	122.9
0.7456	20.36	3.9294	729.1	1.7693	146.7
0.7891	22.38	Run III			
0.8367	24.96	0.3609	21.59	1.9034	173.4
0.8908	28.36	0.3809	20.02	2.0437	203.1
0.9518	32.72	0.4048	18.62	2.1899	235.9
1.0175	38.17	0.4329	17.36	2.3425	272.4
1.0891	44.97	0.4635	16.46	2.5038	312.4
1.1683	53.40	0.4951	15.90	2.6779	357.4
1.2554	63.82	0.5300	15.63	2.8638	407.6
1.3527	76.80	0.5681	15.74	3.0576	463.5
1.4601	92.75	0.6072	16.23	3.2559	520.0
1.5770	111.7	0.6460	17.00	3.4462	576.7
1.7028	134.2	0.6849	18.13	3.6290	630.0
1.8355	159.8	0.7260	19.56	3.8237	695.1
1.9735	188.2	0.7688	21.38	4.0292	760.7
2.1159	219.4	0.8148	23.73		

¹⁴ B. Bleaney (to be published).

Fig. 2. The increase in C_p below 0.6°K is due to the nuclear specific heat C_N .

All the calculations and corrections for the empty calorimeter, gold foil (0.69 g) and grease (0.065 g) were made in a manner already described (cf. Sec. III.4). The total heat capacity of the addenda was never more than 0.5% of the heat capacity of the sample. The precision of our C_p data for europium is estimated as 1.5% at 0.4°K and as 0.5% between 1 and 4°K . The random scatter of the experimental points is about 0.6%.

3. Discussion

Distinct from other rare earths which have hcp or fcc structures or lattices closely resembling these,⁷ europium crystallizes into the more open bcc structure ($a=4.58 \text{ \AA}$). Low-temperature x-ray data by Barrett¹⁵ showed that this form is retained down at least to 5°K . Considering its physical and chemical properties, europium metal is in many respects rather different from the other lanthanides.¹⁶ It is soft and has a relatively low boiling point and its density is low, 5.2 g/cm^3 , as compared with 7.5 and 7.9 g/cm^3 for its neighbors samarium and gadolinium. Europium seems to be divalent with a half-filled $4f$ shell. Thus one cannot expect that the lattice and electronic specific heats of this metal could be determined from the values observed for trivalent lanthanides.¹³

Electrical resistivity measurements by Curry, Legvold, and Spedding¹⁷ and neutron diffraction studies by Olsen, Nereson, and Arnold¹⁸ indicate that europium is antiferromagnetic at low temperatures with a Néel point at about 88°K . The latter investigators found a helical spin structure having a pitch of $3.60a$ and a helix axis in the $[100]$ direction or, alternatively, the observed magnetic reflections could be interpreted in terms of an amplitude modulated structure in the $[100]$ direction with a periodicity of $3.60a$. Similar spin arrangements have been observed for the higher rare earths.¹⁹ According to the simple spin-wave theory,²⁰ which probably is a rather crude approximation, the magnetic specific heat of an antiferromagnetic substance can be written $C_M=CT^3$ where C is a constant.

The magnetic susceptibility of metallic europium has been measured between 1.3 and 300°K by Bozorth and van Vleck.²¹ They found that at low temperatures the

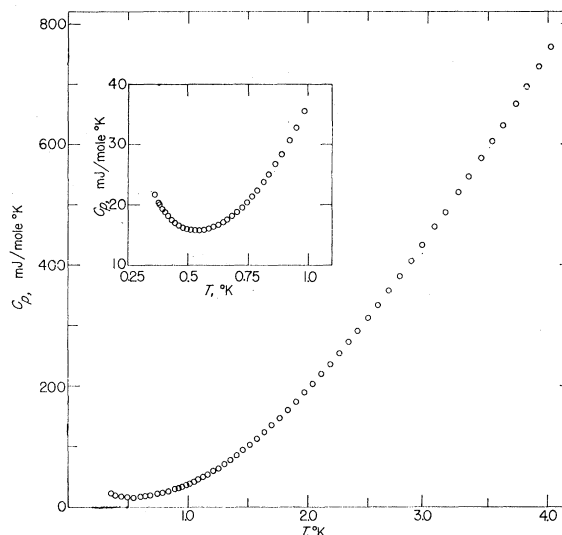


Fig. 2. The specific heat of europium metal. The inset shows results below 1°K on a larger scale. Only about 50% of the points below 1°K have been plotted to the main graph.

metal is not ferromagnetic but that it does not exhibit typical antiferromagnetic behavior either. A high paramagnetic susceptibility, about forty times larger than for the free ion, was observed. The high-temperature results could be explained by assuming that europium is divalent. However the magnetic behavior at low temperatures was hard to interpret on the basis of Eu^{2+} ions and could more readily be explained by assuming that the metal is trivalent.

The nuclear specific heat of rare-earths metals has been discussed in detail by Bleaney,²² and by Kondo.²³ Ignoring interactions between neighboring nuclei, the splitting of the nuclear energy levels is given by the Hamiltonian

$$\mathcal{H} = a'i + P[i^2 - \frac{1}{3}I(I+1)], \quad (4)$$

where I is the nuclear spin and the terms represent magnetic hyperfine and electric quadrupole interactions. For the various levels i has the values $-I, -I+1, \dots, I$. The magnetic hyperfine constant a' should vary as $\langle J_z \rangle$, which measures the electronic magnetization, and the quadrupole coupling constant P as $\langle J_z^2 - \frac{1}{3}J(J+1) \rangle$, which is a measure of the average value of the electronic quadrupole moment. J corresponds to the ground state of the lanthanide ion. Once the nuclear energy levels are known, C_N can be calculated from the partition function in the usual way and, by expanding the nuclear specific heat in inverse powers of T , we obtain

$$C_N = DT^{-2} - \dots \quad (5)$$

If quadrupole interactions are ignored one finds

$$D = (R/3)a'^2I(I+1). \quad (6)$$

²² B. Bleaney, *J. Phys. Soc. Japan* **17**, Suppl. B-I, 435 (1962); *J. Appl. Phys.* **34**, 1024 (1963).

²³ J. Kondo, *J. Phys. Soc. Japan* **16**, 1690 (1961).

¹⁵ C. S. Barrett, *J. Chem. Phys.* **25**, 1123 (1956).

¹⁶ F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 368.

¹⁷ M. A. Curry, S. Legvold, and F. H. Spedding, *Phys. Rev.* **117**, 953 (1960).

¹⁸ C. E. Olsen, N. G. Nereson, and G. P. Arnold, *J. Appl. Phys. Suppl.* **33**, 1135 (1962).

¹⁹ J. W. Cable, H. R. Child, W. C. Koehler, M. K. Wilkinson, and E. O. Wollan, *Pile Neutron Research in Physics* (International Atomic Energy Agency, Vienna, 1962), p. 379.

²⁰ J. van Kranendonk and J. H. van Vleck, *Rev. Mod. Phys.* **30**, 1 (1958).

²¹ R. M. Bozorth and J. H. van Vleck, *Phys. Rev.* **118**, 1493 (1960).

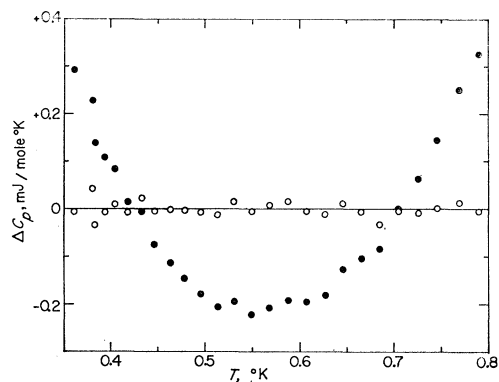


FIG. 3. Deviations of experimental C_p points from smooth curves calculated by the method of least squares for europium between 0.36 and 0.8°K. ○, deviations from the curve $C_p = 29.24T^3 + 5.30T + 2.385T^{-2}$; ●, deviations from the curve $C_p = 33.34T^3 + 2.90T + 2.511T^{-2}$. In the latter case the coefficient of the linear term was fixed to 2.90.

Here R is the gas constant. For higher rare earths, the calculated and experimental specific heats are in good agreement,²² if complete electronic magnetization is assumed, i.e., if J_z is replaced by J in $\langle J_z \rangle$ and in $\langle J_z^2 - \frac{1}{3}J(J+1) \rangle$. D is thus a constant in the temperature range where C_N is appreciable, i.e., below about 2°K.

The ground states of Eu^{2+} and Eu^{3+} ions are $^8S_{7/2}$ and 7F_0 , respectively. For an S state the orbital angular momentum of the $4f$ electrons is zero. The magnetic field produced at the nucleus of the Eu^{2+} ion is mainly due to polarization of electrons in closed shells by the spin moments of the $4f$ electrons.^{22,23} Europium thus offers an opportunity for determining this interaction, which is completely masked in other rare earths by a much larger field due to the orbital angular momentum of the $4f$ electrons. On the basis of ENDOR measurements for Eu^{2+} in CaF_2 by Baker and Williams,²⁴ Bleaney²² has calculated $D = 4.2 \text{ mJ}^\circ\text{K}/\text{mole}$ for divalent europium. His data show that quadrupole interactions in Eq. (4) and higher terms in Eq. (5) may be ignored above 0.36°K. For Eu^{3+} the nuclear specific heat is $=0$ (because $J=0$).

According to the preceding discussion the total specific heat of europium metal can be written

$$C_p = AT^3 + BT + CT^3 + DT^{-2}, \quad (7)$$

where the terms represent C_L , C_E , C_M , and C_N , respectively. In order to separate the various contributions several least-squares analyses were performed on our experimental data. It was first found that Eq. (7) fits the results very well between 0.36 and 1.2°K, but that at higher temperatures the experimental data fall below the calculated curve. Since the temperature dependence of C_L , C_E , and C_N are well known, the discrepancy must be caused by the magnetic specific heat. By writing $C_M = CT^n$ the results indicate that

²⁴ J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London) **A267**, 283 (1962).

$n=3$ below 1.2°K, but that n becomes gradually smaller as the temperature is increased towards 4°K. Together with the high observed C_p of europium between 3 and 4°K, as compared with other rare earths,^{3,4,13,25-28} this points to a specific heat anomaly, centered probably somewhere between 4 and 10°K.

From 0.36 to 1.2°K the specific heat of europium metal can be represented, with 0.8% maximum deviation from experimental points, by the relation (C_p in $\text{mJ}/\text{mole}^\circ\text{K}$)

$$C_p = 27.96T^3 + 6.18T + 2.333T^{-2}. \quad (8)$$

The lattice and magnetic specific heats [cf., Eq. (7)] cannot be separated since their temperature dependences are assumed to be the same. However, the coefficient of the T^3 term is so large that probably more than 95% of it is due to C_M . If experimental points between 0.36 and 0.8°K are only included in the least-squares analysis, the coefficients in Eq. (8) become 29.24, 5.30, and 2.385, respectively, and the maximum deviation is reduced to 0.2% (cf., Fig. 3). This shows that C_E is not determined very precisely; its coefficient was reduced by 14%. On the other hand, C_N changed only by 2%. In Eq. (8) the T^3 term is the dominant contribution down to 0.61°K; below this temperature the T^{-2} term is the largest. From these calculations and earlier error estimates we conclude (C_E and C_N in $\text{mJ}/\text{mole}^\circ\text{K}$):

$$C_E = (5.8 \pm 1.0)T, \quad C_N = (2.36 \pm 0.07)T^{-2}. \quad (9)$$

Our experimental nuclear specific heat is considerably smaller than the value $C_N = 4.2T^{-2} \text{ mJ}/\text{mole}^\circ\text{K}$ calculated by Bleaney.²² However, the magnetic hyperfine constant in europium is known to vary somewhat with the environment and thus the interaction is different in the metal from that in CaF_2 . By using the relation

$$D = R(\mu H_{\text{eff}}/k)^2(I+1)/3I, \quad (10)$$

and our experimental value $D = 2.36 \text{ mJ}^\circ\text{K}/\text{mole}$ the effective field H_{eff} at europium nuclei can be computed. The calculation was made by assuming normal isotopic composition for the metal, i.e., 47.77% of Eu^{151} and 52.23% of Eu^{153} , a nuclear spin $I = \frac{5}{2}$ for both isotopes, and a magnetic moment μ (in nuclear Bohr magnetons) 3.42 and 1.51 for the two isotopes.^{29,30} The magnetic field thus becomes $H_{\text{eff}} = 260 \pm 4 \text{ kG}$. This value is in excellent agreement with $H_{\text{eff}} = 264 \pm 8 \text{ kG}$ deduced from Mössbauer experiments on europium metal by Barrett and Shirley.³¹ The magnetic hyperfine constant can now be calculated from

$$a' = \mu H_{\text{eff}}/kI. \quad (11)$$

²⁵ O. V. Lounasmaa, Phys. Rev. **126**, 1352 (1962).

²⁶ O. V. Lounasmaa and P. R. Roach, Phys. Rev. **128**, 622 (1962).

²⁷ O. V. Lounasmaa, Phys. Rev. **128**, 1136 (1962).

²⁸ O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

²⁹ I. Lindgren, Nucl. Phys. **32**, 151 (1962).

³⁰ B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

³¹ P. H. Barrett and D. A. Shirley, Phys. Rev. **131**, 123 (1963).

The results are: Eu^{151} , $\alpha' = 0.013^\circ\text{K}$ ($= 270$ Mc/sec); Eu^{153} , $\alpha' = 0.0057^\circ\text{K}$ ($= 120$ Mc/sec).

Finally, it should be mentioned that our C_E and C_N results [cf. Eq. (9)] can be interpreted in a different way. The experimental C_E is in between the values $C_E = 10.5T$ and $C_E = 2.9T$ as observed for trivalent lanthanides¹³ and for divalent ytterbium.²⁸ Similarly, our experimental C_N is near the mean of $C_N = 0$ and $C_N = 4.2T^{-2}$ as calculated by Bleaney²² for Eu^{3+} and Eu^{2+} . In fact, if we assume that at low temperatures 43% of our sample showed trivalent and 57% divalent character and use the above values for C_E and C_N , we get (C_E and C_N in mJ/mole $^\circ\text{K}$):

$$C_E = 0.43 \cdot 10.5T + 0.57 \cdot 2.9T = 6.2T, \quad (12)$$

$$C_N = 0.57 \cdot 4.2T^{-2} = 2.4T^{-2}. \quad (13)$$

These results agree well with our experimental C_E and C_N . The possibility that europium is at low temperatures a mixture of di- and trivalent phases is an interesting one, particularly in view of the magnetization measurements by Bozorth and van Vleck,²¹ which were discussed earlier in this section. However, this

interpretation is made less attractive by the excellent agreement of H_{eff} , calculated from our experimental C_N assuming 100% of Eu^{2+} , with the Mössbauer result of Barrett and Shirley,³¹ and by the fact that electrical resistivity¹⁷ and neutron diffraction¹⁸ studies did not in Fig. 3 demonstrates quite conclusively that the average electronic specific heat of our europium sample is not as low as $C_E = 2.9T$ mJ/mole $^\circ\text{K}$.

The present results reveal interesting possibilities for the behavior of europium metal at low temperatures. It would be particularly desirable to extend the measurements of C_p to higher temperatures in the hope of finding a heat capacity anomaly. If such an anomaly is found, magnetization measurements are also in order.

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Magnetization of Cubic Laves Phase Compounds of Rare Earths with Cobalt

J. W. ROSS AND J. CRANGLE

Department of Physics, The University, Sheffield, England

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These compounds are strongly magnetic. For the heavier rare earths, the gross magnetic moment appears to arise from opposed alignment of the rare earth and the cobalt atoms. If we assume the rare earths to have characteristic localized magnetic moments Jg , the moments on the cobalt atoms are about $1.7 \mu_B$ in the Tb, Dy, Ho, and Er compounds, a little less in the Gd compound, and zero in the Pr, Nd, and Sm compounds. The basic coupling mechanism is that of indirect exchange through the conduction electrons between rare-earth spins.

BINARY intermetallic compounds existing between rare-earth metals and cobalt, having the MgCu_2 (cubic Laves) type of structure have been found by Wernick and Geller.¹ We have measured the magnetization of most of the members of this series.

The compounds of cobalt with Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er were prepared by arc melting the pure constituents together in an argon atmosphere. Chemical analysis was not carried out, but the weight loss on melting the stoichiometric amounts was only 1.5% in the case of CeCo_2 and less than half this in all the others. Also, the measured lattice parameters which are shown in Table I agree well with those of Wernick and Geller.

Magnetizations (σ) were measured in the temperature range 10 to 430 $^\circ\text{K}$ in ten different magnetic field strengths (H) between 6.2 and 17.6 kOe. They were

measured using a Sucksmith ring balance,² relative to pure iron, to which the absolute data of Weiss and Forrer³ were assumed to apply. Spontaneous magnetiza-

TABLE I. Lattice parameters in \AA .

	Present work (± 0.002)	Wernick and Geller ^a (± 0.005)
CeCo_2	7.162	7.161
PrCo_2	7.305	7.312
NdCo_2	7.300	7.300
SmCo_2	7.260	7.260
GdCo_2	7.257	7.255
TbCo_2	7.209	7.206
DyCo_2	7.188	7.187
HoCo_2	7.168	7.168
ErCo_2	7.151	7.144

^a See Ref. 1.

² W. Sucksmith, Proc. Roy. Soc. (London) **A170**, 551 (1939).

³ P. Weiss and R. Forrer, Ann. Phys. (Paris) **12**, 297 (1929).

¹ J. H. Wernick and S. Geller, Trans. AIME **218**, 806 (1960).