

Specific Heat of Europium and Ytterbium Metals between 3 and 25°K*

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The specific heats of europium and ytterbium metals have been measured, using a germanium resistance thermometer, between 3 and 25°K. For europium a sharp peak was found at 16.1°K, indicating that a cooperative transformation takes place in the sample at this temperature. The entropy under the peak is so large that the anomaly must be caused by the bulk specimen and not by impurities. The origin of this transition, which has not been observed before, is not clear, but various possibilities are discussed on the basis of available experimental information. According to our earlier measurements, the electronic specific heat of europium is $C_E = 5.8T$ mJ/mole °K (T in °K); the lattice and magnetic contributions, C_L and C_M , respectively, could not be separated. It is clear, however, that C_M is large, particularly at low temperatures. For ytterbium, which is nonmagnetic, there are only two terms in C_p , namely C_L and C_E . Our earlier measurements below 4°K gave $C_E = 2.90T$ mJ/mole °K, and by employing this result C_L was calculated. The Debye temperature Θ decreases from an initial value of 118°K below 3°K to a minimum of 109°K at 14°K and then rises again slowly. The Θ -versus- T curve is rather similar to that observed for many other metals.

I. INTRODUCTION

MOST of the rare-earth metals are ferro- or anti-ferromagnetic at low temperatures and, consequently, their total heat capacity C_p has four different components: the lattice term C_L , the electronic term C_E , the magnetic term C_M , and the nuclear or hyperfine term C_N . A fairly large amount of work has recently been done for establishing the heat capacity of lanthanides in the liquid-helium region and, in particular, below 1°K.¹ As a result, the nuclear specific heat, which is large below 1°K, is well known. Some information has also been obtained about C_L and C_E .

Much less is known about the magnetic specific heat. The reason is, at least partly, that C_M is usually the dominant contribution in the observed C_p and thus most easily separated from the other components, between 3 and 25°K, a temperature range in which experimental data are lacking. As a result we decided to start a program of measuring the heat capacity of all rare-earth metals between 3 and 25°K, and in this paper our data on europium and ytterbium are reported.² Distinct from the majority of the rare earths which are trivalent, these two metals have only two conduction electrons, their 4f shells being half full and full, respectively. Further, most of the lanthanides have a hcp or a hexagonal structure close to hcp, but the lattice of europium is bcc and the lattice of ytterbium is fcc. There are also other differences which have been discussed in earlier papers.^{3,4} It is thus appropriate to

present the experimental data on europium and ytterbium together; they are members of the rare-earth series which differ considerably from the rest of the lanthanides.

II. EXPERIMENTAL

The cryostat used for these experiments was basically the same as that described earlier.^{5,6} A few changes in the inner parts of the apparatus and in the experimental procedure were necessary because of the different temperature range covered compared with the earlier set of measurements from 0.4 to 4°K. Major changes were made in thermometry.

1. The Cryostat

Figure 1 shows those parts of the cryostat which are nearest to the sample. The metal under investigation is surrounded by the inner vacuum case which, in turn, is soldered to the He⁴ pot with Wood's metal. The whole assembly is separated from the main He⁴ bath (in a glass Dewar not shown in the figure) by the outer vacuum case. Copper vanes were soldered to the He⁴ pot to insure rapid equilibrium.

The calorimeter consists of two gold-plated copper caps which are screwed into the sample. In order to increase the heat contact between the specimen and the caps, a small amount of stopcock grease was used between them. A noninductively wound constantan heater was attached to the bottom cap with General Electric No. 7031 adhesive and an indicator wire also soldered to it for determining electrically whether the calorimeter was resting on the platform or not. A small copper capsule, into which a germanium thermometer could be inserted, was soldered to the top cap. For

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¹ O. V. Lounasmaa, Phys. Rev. **134**, A1620 (1964) and other papers listed therein.

² O. V. Lounasmaa, Bull. Am. Phys. Soc. **9**, 657 (1964); also see *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yagub (Plenum Press, Inc., New York, 1965), p. 901.

³ O. V. Lounasmaa, Phys. Rev. **133**, A502 (1964).

⁴ O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

⁵ O. V. Lounasmaa and R. A. Guenther, Phys. Rev. **126**, 1357 (1962).

⁶ O. V. Lounasmaa, Phys. Rev. **133**, A211 (1964).

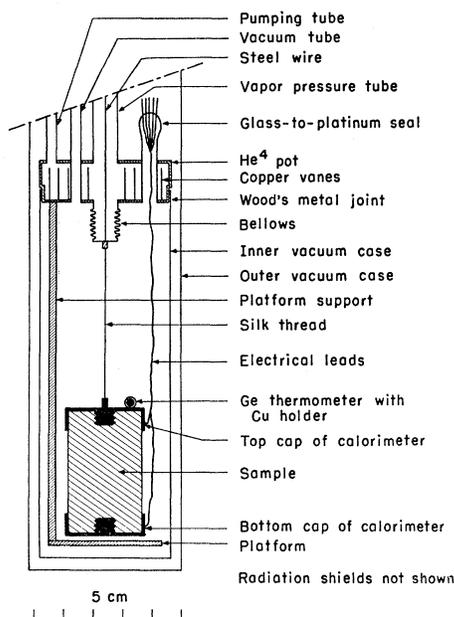


FIG. 1. The inner parts of the cryostat.

increasing the heat contact between the thermometer and calorimeter, stopcock grease was again used. The thermometer and the heater were thus separated from each other by the bulk specimen, and excessive warming of the thermometer during heating periods was thereby eliminated.

When it was desired to break the contact between the sample and the platform, the calorimeter was lifted by means of a motor and screw assembly at the top of the cryostat; this assembly was connected to the calorimeter through a silk thread, bellows, and a stainless steel wire. For improving the heat transfer the surfaces in contact between the platform and the bottom cap were polished flat and gold-plated.

2. Experimental Procedure

The whole cryostat was first cooled to 77°K with liquid N₂, with H₂ exchange gas in the vacuum spaces. After this, liquid He was transferred to the inner Dewar in small quantities at a time. With a little experience the sample could be cooled to about 13°K without solidifying the H₂ exchange gas. Next, the Dewar was filled with liquid He whereby the H₂ exchange gas was removed by cryopumping. Cooling of the sample to 4.2°K was then accomplished by means of the heat switch. By this procedure, the total cooling time from 77 to 4.2°K was about two hours as compared with more than 24 hours had the heat switch only been employed.

After this, He⁴ was condensed to the pot and subsequently pumped down to 2.5°K. The sample was then cooled to the starting temperature of the heat capacity measurements (3°K) with the heat switch.

When the lowest experimental temperature was

reached the sample was lifted from the platform. No heating effects due to the operation of the heat switch were observed. During measurements the He⁴ pot was usually kept at about 3°K, thereby insuring that the vapor pressure of the H₂ exchange gas, absorbed on the walls of the vacuum cases, was truly negligible. In every case and at every temperature where measurements were made, the residual heat-leak to the sample was very small, less than 0.2% of the heating rate through the heater.

The heat-capacity measurements were made in the usual way. After the temperature drift was recorded heat was supplied for 1–2 min. The heating time was determined to 0.01 sec with an electronic timer which automatically switched the heat on and off. For calculating the energy input, the heater resistance was measured during each heating period; the change in the heater resistance with temperature could thus be taken into account. The heating current was determined with a Rubicon No. 2781 potentiometer. The electrical leads from the top of the inner vacuum case to the heater were made of constantan and their resistance was about 20 Ω at low temperatures. The usual assumption that half of the heat generated in the leads was conducted to the calorimeter was made, i.e., the effective lead resistance was about 10 Ω. This was measured once or twice during each experiment. It was also established that the heating currents used (up to 15 mA near 25°K) did not cause large changes in the lead resistance; serious overheating of the leads was thus avoided. Small errors in the value of the lead resistance are totally insignificant since the effective lead resistance was less than 1% of the resistance of the heater (about 1300 Ω).

The voltage across the germanium thermometer and the current (10 μA) through it were measured with a Rubicon No. 2773 double potentiometer. A suitable galvanometer amplifier and a recorder were used to achieve a sensitivity of about 30 mm/μV. For eliminating the effects of thermal emf's, which were sometimes as large as 1 μV and occurred particularly in the copper leads between the He⁴ bath and the top of the cryostat, the voltage readings from the potentiometer were taken both in the normal and reverse directions of the thermometer current.

3. Thermometer Calibrations

The precision in calorimetry at low temperatures is largely determined by the accuracy which can be achieved in calibrating the thermometer. Further, much of the tedium in specific heat work is due to the long time spent in securing a reliable calibration. During the last few years the situation has improved considerably, first by the use of germanium thermometers, which have a high sensitivity at low temperatures and which keep their calibration between experiments, and second with the help of electronic computers, which enable the

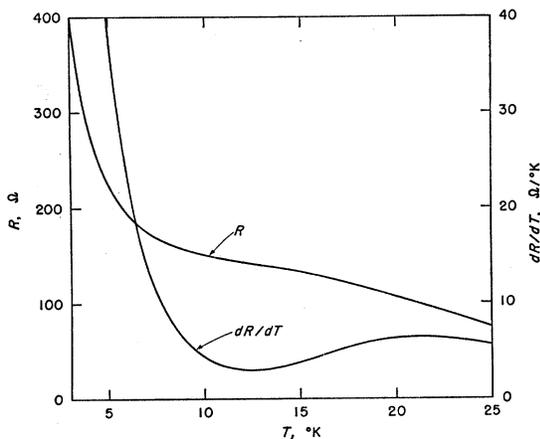


FIG. 2. The resistance R and sensitivity dR/dT of our germanium thermometer.

use of elaborate interpolation formulas to fit the experimental calibration points. Only one master calibration of the thermometer is thus necessary and a calibration formula, however complicated, makes it possible to employ computers for calculating the specific heat, without further need for corrections determined from "deviation plots."

The germanium thermometer used in the present experiments was of type CG-1, manufactured by Radiation Research Co. It had separate terminals for current and potential leads. Our thermometer was calibrated, at 43 different temperatures spaced about evenly in $\log T$ from 2 to 27°K, against another thermometer of the same type and kindly made available to us by Flotow, Osborne, and Schreiner, who had calibrated their thermometer between 0.8 and 27°K against the vapor pressures of He³, He⁴, and H₂ and against a gas thermometer. The calibration points of our thermometer were then fitted by the method of least squares to a formula expressing $\log R$ (R is thermometer resistance) as a 14th degree polynomial of $\log T$. A short summary of the calibration accuracy is given in Sec. II.4 of the present paper. The resistance and sensitivity of our thermometer is shown, as a function of T , in Fig. 2.

To check that the thermometer had not changed between experiments, He⁴ exchange gas was admitted to the inner vacuum space after the heat-capacity measurements were completed and one calibration point then measured at about 3.8°K. The He⁴ pot was used as the vapor-pressure thermometer. Agreement within a few tenths of a millidegree with the master calibration was always found and this was taken as an indication that the thermometer calibration was unchanged. A few times a further check was made at the triple point of H₂; for these measurements liquid H₂ was transferred to the He Dewar and subsequently condensed to the He⁴ pot. Precautions were taken to correct for the slow change in the vapor pressure due to

the orthopara conversion in hydrogen. The agreement was within 0.002°K.

4. Accuracy of Results

Several checks of the vital measuring equipment were made at regular intervals. The Rubicon No. 2781 potentiometer used for determining the heating current was cross checked against the Rubicon No. 2773 double potentiometer, the timer was compared with a crystal controlled oscillator, and standard cells and standard resistors were calibrated against NBS-certified equipment. Possible systematic errors here are thus negligible.

The heat capacity of the empty calorimeter was measured in a separate experiment. The data could be fitted, with 0.5% accuracy, to the formula (C_{cal} in mJ/°K)

$$C_{\text{cal}} = 0.0935T + 0.0326T^2 + 0.01157T^3 + 0.0000014T^5, \quad (1)$$

which was then used for subtracting C_{cal} from the total observed heat capacity of ytterbium. For europium the heat capacities of stopcock grease and gold foil (see Sec. III.1) were added to C_{cal} before this was done. Table I gives C_{cal} at a few representative temperatures

TABLE I. C_{cal} and its comparison (in %) with the total heat capacity of the europium (% Eu) and ytterbium (% Yb) samples.

T (°K)	$C_{\text{cal}} + \text{gold}$ $+ \text{grease}$ (mJ/°K)	% Eu	C_{cal} (mJ/°K)	% Yb
3	1.15	0.8	0.886	1.9
6	5.26	1.0	4.24	1.2
10	19.8	1.5	15.9	0.9
20	129	3.9	112	1.2
25	243	5.4	218	1.6

as compared with the corresponding heat capacities of europium and ytterbium. The maximum contribution due to C_{cal} is about 5% for europium and 2% for ytterbium, and thus, by claiming 3% accuracy for C_{cal} , this source of error in the final C_p is never more than about 0.15% and 0.05% for the two metals, respectively.

As was mentioned in Sec. II.2, the temperature drift caused by the stray heat leak to the calorimeter was always less than 0.2% of the heating rate through the heater. Errors due to inaccuracies in determining properly the effect of this slow change of temperature (linear drifts were assumed) are thus very small. This may also be seen from the negligible random scatter of the C_p points (see Secs. III.1 and IV); large drifts invariably result in a large scatter.

The main systematic errors in the final C_p data are probably due to inaccuracies in the calibration of the germanium thermometers. The calculated value of the specific heat not only depends on the calibration curve R versus T but also on the derivative of this curve

TABLE II. The estimated accuracy of T , dR/dT , and C_p .

T (°K)	T (m°K)	Accuracy of dR/dT (%)	C_p (%)
3	1	0.5	0.6
6	2	0.5	0.6
10	3	0.5	0.6
20	3	0.3	0.4
25	10	2.0	2.1

dR/dT versus T (see Fig. 2). Our estimates, based on the measurements by Flotow, Osborne, and Schreiner,⁷ of the precision of T and dR/dT are given in Table II; it also lists the final estimated accuracy of C_p , as judged on the basis of the various sources of errors discussed in this section.

The final values of C_p have been corrected for curvature due to the finite temperature increments used when measuring the specific heat. A graphical method was employed; this correction was never more than 0.2%.

III. EUROPIUM

1. Results

The europium sample used in these experiments was the same as that measured by us between 0.4 and 4°K.³ For a description of how the sample was prepared, how it was prevented by stopcock grease and gold foil from oxidizing in the air, and for the results of spectrographic and chemical analyses of its purity, we refer to our previous paper. Owing to repolishing the weight of the sample, 50.246 g (=0.33065 moles), was a little less than that given before. The amounts of gold foil and stopcock grease used for protecting the metal were 0.356 g and 0.122 g, respectively. The heat capacity of the gold foil was calculated from the measurements by du Chatenier and de Nobel⁸; for stopcock grease a privately circulated data sheet by Westrum⁹ was used. Appropriate corrections were then added to the heat capacity of the empty calorimeter as explained in Sec. II.4.

Three final runs on two successive days were made without warming the specimen above 25°K in the meantime. The results are given in Table III and they are also plotted into Fig. 3. The sharp peak at 16.1°K is the most prominent feature in the heat capacity curve.

Two preliminary runs were also made and the results of these agree well with the final data given in Table III, but they were discarded because the thermometer voltage was not measured in both normal and reverse directions of the current. The sample was warmed to

⁷ H. E. Flotow, D. W. Osborne, and F. Schreiner (private communication).

⁸ F. J. du Chatenier and J. de Nobel, *Physica* **28**, 181 (1962).

⁹ E. F. Westrum (private communication).

TABLE III. The specific heat of europium metal (mJ/mole °K). Experimental results.

T	C_p	T	C_p	T	C_p
Run 1					
3.0185	448.6	16.116	10571	9.2276	3360
3.3602	548.1	16.239	9773	10.141	4016
3.6959	652.4	16.376	8355	11.025	4713
4.0253	760.1	16.529	7961	11.789	5365
4.3527	874.4	16.725	7912	12.544	6056
4.6905	998.2	17.017	8008	13.296	6791
5.0537	1138.7	17.446	8209	13.975	7501
5.4756	1311.1	18.134	8651	14.590	8210
6.0171	1550.3	19.152	9355	15.152	8939
6.7256	1889.1	20.571	10388	15.600	9624
7.4764	2286.3	22.458	11803	15.891	10158
8.1672	2681.6	24.757	13647	16.116	10455
8.8367	3098	Run 2		16.354	8677
9.5328	3571	3.1337	481.4	16.627	7886
10.293	4131	3.4585	578.0	16.983	7973
11.138	4805	3.7854	681.0	17.552	8285
12.042	5601	4.1222	793.4	18.472	8881
12.966	6475	4.4452	907.6	19.796	9817
13.845	7345	4.7913	1035.9	21.596	11142
14.492	8090	5.2535	1218.6	23.909	12932
14.953	8650	5.8776	1486.9	Run 3	
15.384	9271	6.5306	1784.3	4.5273	940.1
15.735	9847	7.1054	2085.4	4.9243	1098.3
15.967	10319	7.7068	2415.3	5.6156	1360.8
		8.4097	2831.3	6.5253	1793.7

room temperature between the preliminary and final runs.

2. Discussion

Our measurements³ between 0.4 and 4°K provide the only previously published heat capacity data on europium. Since the thermometry in the present and in the earlier experiment was completely different, it is interesting to compare the results in the overlapping region from 3 to 4°K. When this is done agreement to within 0.2% is observed. Gerstein¹⁰ has recently meas-

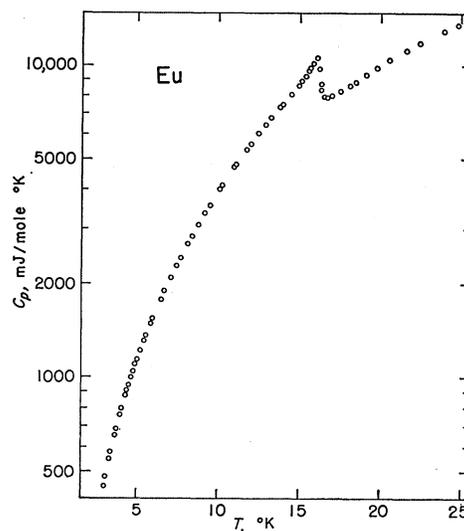


FIG. 3. The specific heat of europium metal.

¹⁰ B. C. Gerstein (private communication).

ured the heat capacity of europium above 15°K and he has very kindly made his data available to us prior to publication. His results do not show any anomaly around 16°K and the points are also several percent higher than ours in the overlapping region between 15 and 25°K. There is no explanation for these discrepancies at the present time except that kinetic effects might be responsible, i.e., the anomaly might only appear if the metal is cooled before heat-capacity measurements well below the transition temperature. Somewhat similar effects have been observed in terbium.¹¹

The most interesting feature of our data is the unexpected peak observed at 16.1°K. The appearance of the anomaly is typical of magnetic transitions, and particularly of the Ising type because C_p decreases very rapidly once the peak has been passed. This would indicate considerable anisotropy in the magnetic structure of europium metal. It is somewhat difficult to estimate the entropy under the peak but the value is about 1.2 J/mole °K, 7% of $R \log 8$. The anomaly is thus so large that it must be due to a property of the bulk specimen and not caused by impurities. We must now try to find a plausible explanation for the peak and it thus becomes necessary to discuss other types of measurements on europium.

Neutron-diffraction experiments on metallic europium have been conducted by Nereson, Olsen, and Arnold¹² from room temperature to 4°K. Their data show that the metal undergoes a transition to an antiferromagnetic state at a Néel temperature of 91°K and that this ordering process continues until saturation develops at about 20°K. There is no sign of anything unusual happening at 16°K. A model which conforms to the neutron-diffraction data consists of a helical-spin structure with the magnetic moments lying parallel to a cube face and with the rotation axis directed perpendicular to the moments along the [100] direction. The measured magnetic moment $5.9 \mu_B$ lies between the maximum theoretical values of $7 \mu_B$ and $3 \mu_B$ expected from di- and trivalent europium ions with ground states of $^8S_{7/2}$ and 7F_0 , respectively. These data thus do not exclude the possibility that at low temperatures europium metal is a mixture of di- and trivalent phases. A different explanation of the discrepancy between the theoretical and experimental values of μ_B is given by Nereson, Olsen, and Arnold¹²; they argue that only Eu^{2+} ions are present.

Klemm and Bommer¹³ estimated from their magnetization measurements a paramagnetic Curie temperature of 15°K for europium. These measurements are, however, almost 30 years old and thus are less reliable

because of the impossibility of obtaining reasonably pure rare-earth samples prior to 1950. It is interesting to note that recent unpublished data by Olsen¹⁴ show an anomaly in the electrical resistivity of europium around 12–15°K.

The magnetic susceptibility of metallic europium has been measured by Bozorth and van Vleck¹⁵ between 1.3 and 300°K. They found that at low temperatures the metal is not ferromagnetic but that it nevertheless does not exhibit typical antiferromagnetic behavior. 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. Bozorth and van Vleck mention in their paper the possibility that some kind of valence adjustment takes place in europium; a serious difficulty here is that a valence change should be accompanied by a change in the lattice parameters which are constant, according to Barrett¹⁶ and Nereson, Olsen, and Arnold,¹² within less than 1% between 5 and 300°K.

As discussed in our earlier paper³ the heat-capacity measurements of europium between 0.4 and 4°K could be interpreted by assuming that 43% of the specimen showed divalent and 57% trivalent characteristics at low temperatures. This analysis was based on the magnitudes of the electronic and nuclear contributions of C_p as compared with experimental data on other rare-earth metals and with theoretical calculations.

The previous discussion describes briefly what is known about some of the properties of europium at low temperatures. Obviously, on this basis, it is difficult to determine the cause of the anomaly; the fact that the transition is only observed in heat-capacity measurements (some anomalous behavior was found by Olsen¹⁴ in his electrical-resistivity data) again demonstrates the usefulness of specific heat for "detective" work. It appears to us that there are two possible explanations for the peak. The first of these is that europium metal changes from purely divalent character to a mixture of di- and trivalent phases when the temperature is lowered over the anomaly. The other possibility is that a magnetic transformation, for instance, from sinusoidal to spiral structure, takes place. Such a transformation could remain undetected in neutron-diffraction experiments. A similar transition occurs in erbium.¹⁷

Besides discussing the anomaly, we have the further task of separating the different contributions of C_p from each other. The nuclear term is totally negligible above 3°K and the electronic specific heat can be

¹¹ O. V. Lounasmaa and L. J. Sundström, Phys. Rev. (to be published).

¹² N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **135**, A176 (1964).

¹³ W. Klemm and H. Bommer, Z. Anorg. Allgem. Chem. **231**, 138 (1937).

¹⁴ C. E. Olsen (private communication).

¹⁵ R. M. Bozorth and J. H. van Vleck, Phys. Rev. **118**, 1493 (1960).

¹⁶ C. S. Barrett, J. Chem. Phys. **25**, 1123 (1956).

¹⁷ J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **140**, A1896 (1965).

written, on the basis of our earlier measurements,³ $C_E = 5.8T$ mJ/mole °K, when T is in °K. The main difficulty lies in separating the lattice and magnetic contributions.

There is very little information available about the lattice specific heat of europium. Our data³ below 4°K did not yield a Debye Θ in the T^3 region because, on theoretical grounds (see below), the temperature dependence of C_L and C_M was assumed to be the same. Nereson, Olsen, and Arnold¹² have calculated from their nuclear-diffraction-intensity data the following values of Θ (accuracy about 15%): $T = 100^\circ\text{K}$, $\Theta = 68^\circ\text{K}$; $T = 120^\circ\text{K}$, $\Theta = 88^\circ\text{K}$; $T = 150^\circ\text{K}$, $\Theta = 102^\circ\text{K}$; $T = 293^\circ\text{K}$, $\Theta = 123^\circ\text{K}$. It is not possible to extrapolate these data towards lower temperatures with any confidence in the numerical values thus obtained, but qualitatively we may assume that Θ will reach a minimum and then rise again towards lower temperatures, perhaps being close to the value $\Theta_0 = 100^\circ\text{K}$ at the absolute zero. This type of behavior would be in agreement with observations on substances with open crystal structures, e.g., silicon, germanium, and grey tin.¹⁸ No help can be obtained from other rare earths, for instance ytterbium, since they all have nearly close packed structures as compared with the quite open bcc lattice of europium.

According to the simple spin wave theory,¹⁹ the magnetic specific heat of an antiferromagnetic substance, well below the Néel point, has a T^3 temperature dependence. In a metal where conduction electrons complicate the situation, this prediction might, however, be a rather crude approximation. If the substance is magnetically anisotropic C_M is also proportional to $\exp(-E_g/kT)$, where E_g is the energy gap at the bottom of the spin-wave spectrum.^{20,21} We should thus have

$$C_M = AT^n \exp(-E_g/kT), \quad (2)$$

where A is a constant and $n=3$. More complicated formulas have also been proposed.²¹ Janovec and Morrison²² have recently reanalyzed our heat capacity data³ below 4°K and they find for the parameters in Eq. (2): $A = 275$ mJ/mole °K², $n=1$, $E_g/k = 2.5^\circ\text{K}$. Agreement with experimental data is obtained between 0.4 and 1.5°K as compared with the simple T^3 temperature dependence of C_M which gives a good fit only below 1.2°K. We feel, however, that with two additional parameters (E_g and n) this improvement is not surprising. With the power of T ($n=1$) theoretically wrong and with no knowledge of the lattice contribution (admittedly small), it appears to us that the values of A , E_g , and n have no real significance and that the

mathematical form of Eq. (2) has not been experimentally proven for europium.

We must conclude that there is no reliable basis, at the present time, for separating C_L and C_M . It is, however, clear that the magnetic specific-heat of europium is large. By first subtracting C_E and by then calculating the "apparent" Θ from the remaining C_p one obtains, at 4°K, $\Theta = 55^\circ\text{K}$; this value of Θ is too low indicating a considerable contribution from C_M .

IV. YTTERBIUM

The ytterbium sample was also the same as used previously by us⁴ for measurements between 0.4 and 4°K; its weight was 204.216 g (=1.1802 moles), again slightly less than before, owing to repolishing. Ytterbium oxidizes only slowly in air; protection with grease and gold foil was thus unnecessary. Results of chemical and spectrographic analyses of the specimen are given in our earlier paper.⁴

Two final heat-capacity runs were made without warming the sample above 25°K in the meantime. The results are given in Table IV and they are also plotted into Fig. 4. Agreement with our earlier data in the overlapping region from 3 to 4°K is excellent except above 3.8°K where the old points are about 1% lower, probably due to the proximity of the end of the calibration range.

Lock²³ has measured the magnetic susceptibility of ytterbium metal between 1.3 and 80°K and at 300°K; he found the inverse of the susceptibility to be a linear function of temperature. According to Lock's interpretation the results show that although most of the atoms are in the nonmagnetic 1S_0 state, one atom in 260 is in the paramagnetic $^2F_{7/2}$ state. A more likely explanation

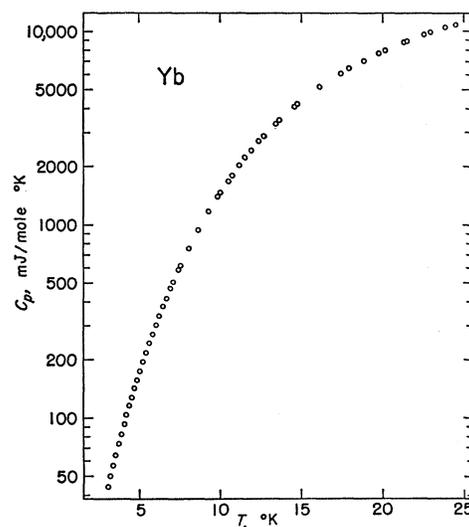


FIG. 4. The specific heat of ytterbium metal.

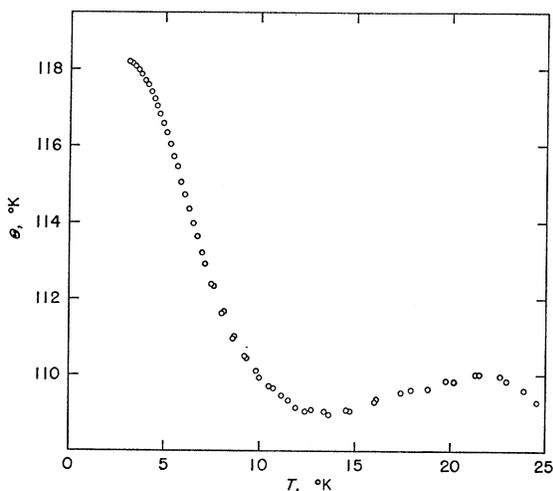
¹⁸ R. W. Hill and D. H. Parkinson, *Phil. Mag.* **43**, 309 (1952).
¹⁹ J. van Kranendonk and J. H. van Vleck, *Rev. Mod. Phys.* **30**, 1 (1958).
²⁰ A. R. Mackintosh, *Phys. Letters* **4**, 140 (1963).
²¹ B. R. Cooper, *Proc. Phys. Soc. (London)* **80**, 1225 (1962).
²² V. Janovec and J. A. Morrison, *Phys. Letters* **17**, 226 (1965).

²³ J. M. Lock, *Proc. Phys. Soc. (London)* **B70**, 476 (1957).

TABLE IV. The specific heat of ytterbium metal (mJ/mole °K). Experimental results.

T	C_p	T	C_p	T	C_p
Run 1					
3.0991	44.03	11.900	2439.0	5.6415	243.13
3.4044	56.47	12.700	2904.3	6.0590	304.2
3.7519	73.57	13.631	3494	6.4919	378.2
4.0818	93.11	14.760	4238	6.9452	469.1
4.4013	115.61	16.060	5124	7.4449	586.5
4.7255	142.33	17.453	6095	8.0164	742.4
5.0668	175.30	18.840	7087	8.6470	940.8
5.4362	217.39	20.168	8011	9.3027	1180.1
5.8416	271.47	21.522	8930	9.9860	1467.2
6.2622	337.5	22.971	9926	10.720	1805.9
6.6791	414.4	24.529	10995	11.510	2217.9
Run 2					
7.1036	504.9	3.2484	49.83	12.401	2730.4
7.5616	614.9	3.5769	64.53	13.403	3341
8.0601	753.7	3.9137	82.79	14.573	4109
8.6029	927.6	4.2401	103.86	16.127	5167
9.2106	1145.5	4.5600	128.22	17.947	6443
9.8435	1401.1	4.8895	157.58	19.766	7722
10.489	1695.2	5.2489	195.18	21.340	8812
11.174	2037.5			22.606	9667
				23.871	10538

is, however, that the observed paramagnetism was due to a small trace of neighboring lighter rare-earth elements. A small term proportional to T^{-2} in the heat capacity of ytterbium⁴ below 1°K could similarly be explained as being due to long-range exchange-type coupling between the electronic moments of rare-earth impurities. We may thus conclude that the magnetic contribution to the observed C_p of ytterbium should be

FIG. 5. The Debye characteristic temperature Θ of ytterbium metal.

negligible and we thus have only the lattice and electronic terms.

Our earlier measurements⁴ below 4°K gave: $\Theta_0=118.1^\circ\text{K}$, $C_E=2.90T$ mJ/mole °K. The lattice term may now be easily calculated and the resulting Debye temperature is plotted into Fig. 5. After being initially constant Θ drops rapidly and reaches a minimum of 109°K at about 14°K; it then increases slowly towards higher temperatures. The slight drop in Θ near 25°K is probably due to experimental errors caused by inaccuracies in the value of dR/dT towards the end of the calibration range (see Table II). The general appearance of the Θ -versus- T curve is quite familiar and is caused by the fact that the vibrational spectrum rises at low frequencies more rapidly than the ν^2 prediction of the Debye theory. This effect has been experimentally observed for many metals; zinc, silver, and lead are examples. The total variation in Θ for ytterbium is about 8% and the minimum occurs approximately at a temperature of $\frac{1}{3}\Theta$. Both of these numbers are quite reasonable and similar figures have been observed for other metals.

The heat capacity of ytterbium is quite different from the heat capacity of the trivalent lanthanides. Their Debye temperatures are about 150–210°K and their electronic heat capacities are more than three times larger than for ytterbium; this is because the trivalent metals have an extra $5d$ electron in the conduction band. Only limited conclusions may thus be drawn from our results on ytterbium concerning trivalent lanthanides.

The specific heat of ytterbium has been measured between 15 and 300°K by Gerstein, Mullaly, Phillips, Miller, and Spedding.²⁴ Their points are 2–3% higher than ours in the overlapping region from 15 to 25°K. There is no explanation for this discrepancy which is slightly outside experimental error.

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²⁴B. C. Gerstein, J. Mullaly, E. Phillips, R. E. Miller, and F. H. Spedding, J. Chem. Phys. 41, 883 (1964).