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Specific Heat of Samarium Metal between 0.4 and 4°K*

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In addition to the usual lattice and electronic terms, proportional to T^3 and T, respectively, the specific heat of most rare earth metals at low temperatures has two other contributions: a magnetic specific heat due to exchange interaction between the electronic spins, and a nuclear specific heat due to splitting of the nuclear energy levels in the strong magnetic field produced by the $4f$ electrons. Samarium metal is antiferromagnetic below 13.6°K and the magnetic specific heat, according to the spin wave theory, should be proportional to T^3. The nuclear specific heat has a T^{-2} temperature dependence in the first approximation; the next term in a series expansion proportional to T^{-4} was also included in the analysis. We may thus write $C_p = AT^3 + BT + DT^{-2} - ET^{-4}$, where the first term represents both the lattice and magnetic specific heats. Values of the constants, as determined by the method of least squares from 71 experimental points between 0.4 and 2.5°K, are (for specific heat in millijoules/mole°K): $A = 0.88 - 1.11$; $B = 12.1$; $D = 8.56$; $E = 0.021$. The magnetic specific heat appears to depend on the time the sample spent in the vicinity of the antiferromagnetic Curie point when it was cooled down, hence the variations in the value of A. Constants B and D are probably accurate to 5% and 2%, respectively. The effective magnetic field at the nucleus, as calculated from the value of constant D, is 3.3×10^6 gauss.

I. INTRODUCTION

Electrons in the unfilled $4f$ shell of the rare earths produce at the nucleus a magnetic field of several million gauss. The interaction of this field with the nuclear magnetic moment can be observed in the specific heat if experiments are carried out at low enough temperatures, below 1°K, so that the Schottky anomaly arising from the hyperfine splitting is the dominant term in the heat capacity.

Such measurements have recently been reported on a number of the higher rare earths.[1-10] In addition to this nuclear specific heat and the usual lattice and the electronic contributions, the rare earth metals also have a magnetic heat capacity due to exchange interaction between the electronic spins. The separation of the specific heat into the various contributions is thus an interesting task but, for reliable results, accurate experimental data are needed over a wide temperature range. The analysis is further complicated by the fact that, presumably due to small amounts of impurities which vary from one sample to another, different investigators have in general not been able to produce the same result. This is particularly true for the temperature region between 1.5 and 4°K; discrepancies of more than 100% are not uncommon. The easiest contribution to determine separately appears to be the nuclear specific heat, provided experiments can be extended to low enough temperatures.

In this paper measurements of the heat capacity of samarium metal between 0.4 and 4.0°K are presented. The experiments were undertaken with the aim of providing accurate data for evaluating the nuclear term and, if possible, for deducing the electronic specific heat as well. The heat capacity of samarium has previously been measured by Roberts[11] between 2 and 20°K; her data do not show the nuclear term. Experiments by Dreyfus, Goodman, Trolliet, and Weil[1] between 0.4 and 2°K clearly revealed the nuclear specific heat; their results show an apparent anomaly near 2°K and display some scatter below 1°K.

II. EXPERIMENTAL

The measurements were carried out in a He^3 cryostat which will be described in another paper[8]; only the most relevant experimental features are mentioned here. He^4 exchange gas was used for cooling the sample down to 4.2°K; the space surrounding the calorimeter was then evacuated, and for further cooling a mechanical heat switch was employed. In this way an exceedingly good insulation could be achieved and desorption of helium gas from the sample during heat capacity measurements was prevented. By pumping on He^3, a temperature of about 0.33°K was reached and maintained for 48 hrs without recondensing. With the heat switch closed the sample was cooled from 4.2 to 0.4°K in about 15 hr.

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TABLE I. Specific heat of samarium metal. Experimental results.

T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)	T (°K)	C_p (millijoules/mole °K)
Run IA		Run IB		Run II		Run III	
0.3899	60.37	0.3951	58.94	1.6332	26.87	0.4460	47.42
0.4208	53.18	0.4259	52.02	1.7542	28.73	0.4769	42.75
0.4550	46.94	0.4608	45.90	1.8852	30.93	0.5151	38.14
0.4938	41.27	0.5004	40.34	2.0240	33.43	0.5626	33.77
0.5380	36.26	0.5454	35.54	2.1834	36.69	0.6161	30.08
0.5879	32.09	0.5964	31.48	2.3603	40.90	0.6756	27.17
0.6443	28.52	0.6536	28.13	2.5580	46.32	0.7408	25.00
0.7071	25.78	0.7171	25.52	2.7717	53.51	0.8110	23.46
0.6577	27.91	0.7864	23.61	2.9935	62.21	0.8848	22.52
0.7217	25.35	0.8604	22.29	3.2166	72.68	0.9608	22.09
0.7913	23.50	0.9377	21.54	3.4519	85.98	1.0376	22.04
0.8657	22.22	1.0169	21.23	3.7081	102.55	1.1140	22.31
0.9437	21.36	1.0966	21.26	3.9703	121.95	1.1891	22.80
1.0234	21.22	1.1755	21.59			1.2764	23.56
1.1033	21.28	1.2530	22.07			1.3743	24.73
1.1899	21.67	1.3283	22.76			1.4776	26.18
1.2824	22.33	1.4074	23.59			1.5934	28.02
1.3717	23.22	1.4975	24.69			1.7172	30.28
1.4669	24.30	1.5998	26.11			1.8558	32.98
1.5743	25.72	1.7244	28.04			2.0142	36.52
1.7009	27.62	1.8575	30.35			2.1911	40.93
1.8416	30.05	1.9977	32.99			2.3872	46.77
1.9892	32.76	2.1583	36.42			2.5992	54.16
2.1518	36.12	2.3357	40.69			2.8188	63.21
2.3316	40.34	2.5321	46.37			3.0486	74.76
2.5314	45.89	2.7456	53.22			3.2988	90.05
2.7484	52.77	2.9693	61.74			3.5642	110.48
2.9741	61.43	3.1947	72.16			3.8294	134.88
3.2004	71.80	3.4318	85.52				
3.4400	84.96	3.6877	103.51				
3.6982	102.25						

It is worth mentioning that due to the large heat capacity of the samarium sample and good thermal insulation, the temperature drift was hardly noticeable when the heat switch was opened.

For the heat capacity measurements a colloidal graphite (Aquadag) thermometer was employed. It was calibrated after every experiment against the vapor pressure of He^4 between 4.0 and 2.2°K, against the vapor pressure of He^3 between 2.2 and 0.75°K, and against a magnetic thermometer (chromium methylamine alum) between 0.75 and 0.4°K. He^4 temperatures were determined according to the T_{58} scale.[12] For He^3 the temperature scale of Sydoriak and Roberts[13] was employed; corrections were made for the 0.6% of He^4 in our He^3 gas and the temperatures were changed to the T_{58} scale. The magnetic thermometer was calibrated against the vapor pressure of He^3. In this way about 30 calibration points were determined for the carbon thermometer. The heat capacity of the empty calorimeter was measured in a separate experiment; it was always less than 1% of the heat capacity of the sample.

III. RESULTS

The vacuum distilled samarium metal was prepared by Research Chemicals (Division of Nuclear Corporation of America) and analyses performed in our Laboratory showed the following impurities: other metals not detected in spectrochemical analysis; hydrogen 0.04%; carbon 0.02%; oxygen 0.008%. The sample, a cylinder 5.0 cm long and 3.2 cm in diameter, weighed 209.28 g (=1.39195 moles).

The experimental results are listed in Table I; points up to 3°K from runs IB and III are plotted in Fig. 1. In calculating the results the calibration points were

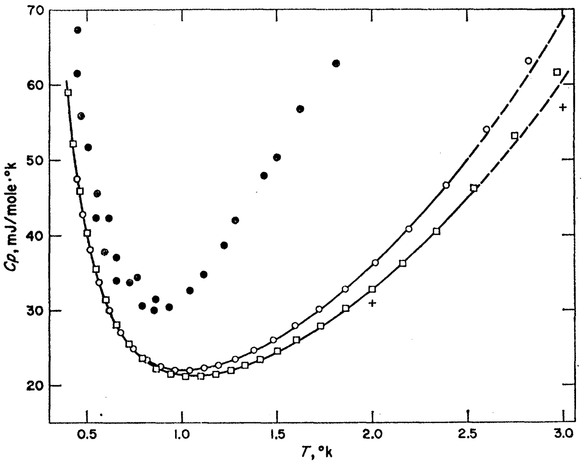

FIG. 1. The specific heat of samarium metal. □, run IB; ○, run III; +, Roberts[11]; ●, Dreyfus *et al.*[1]

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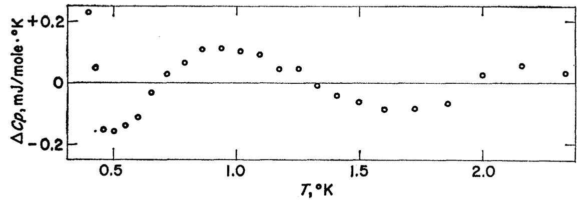

FIG. 2. Deviation plot for run IB. ΔC_p (millijoules/mole °K) $=0.897T^3+11.86T+8.63T^{-2}-0.021T^{-4}-C_p$ (experimental). (cf. Table II).

first fitted into a six-constant equation by the method of least squares. The program[14] for the IBM 704 computer also makes the usual curvature correction due to the finite temperature increments (about 10% of T) in the measurements of C_p. Runs IA and IB were made on successive days and, since the cryostat was kept continuously at helium temperatures, the same calibration was used for both.

All the experiments agree below 0.8°K; above this temperature run III gives systematically higher values of C_p. There is also a slight difference between runs IA and IB; the latter results are a little higher above 2°K. The difference is only about 1% but the discrepancy is probably real and not due to experimental errors. The possible reasons for these differences are discussed in Section V.

After a heating period the sample came to equilibrium in less than 10 sec. The rapid equilibrium time as well as the good thermal insulation of the calorimeter are the reasons for a very small random scatter (~0.1%) of experimental points (cf. Fig. 2). Systematic errors in timing, heating current, heater resistance, and the heat capacity of the empty calorimeter total not more than 0.2% in the final results. The scatter of the calibration points was, with a few exceptions, less than 2 mdeg and the He^4 and He^3 calibrations joined smoothly together. The calculated temperature is thus probably within 1 mdeg of the temperature defined by the He^4 and He^3 scales. Uncertainties of about 2 mdeg can arise from the extrapolation of the magnetic thermometer calibration below 0.75°K. Aside from possible errors in the He^3 temperature scale, which may be several mdeg off, the accuracy of the present results is estimated as ~0.5% between 1.5 and 4°K and 1.5% at 0.4°K; the reason for a wider margin of errors at the lowest temperatures is the very rapid variation of C_p as a function of T.

IV. ANALYSIS OF RESULTS

As mentioned earlier, the measured heat capacity of samarium is the sum of four different contributions: the lattice specific heat C_L, the electronic specific heat C_E, the magnetic specific heat C_M, and the nuclear specific heat C_N. The first two of these are observed for all metals and, at sufficiently low temperatures, they are proportional to T^3 and T, respectively.

Below 13.6°K, samarium is antiferromagnetic.[11] At low temperatures, where the magnetization differs only slightly from that at absolute zero, the magnetic specific heat can, at least approximately, be calculated by the method of spin waves. In this theory it is assumed that the magnetism is entirely due to electronic spins regularly spaced in the crystal. In the antiferromagnetic case a T^3 temperature dependence is predicted for C_M. However, due to anisotropy effects, the spin wave theory should be applied with considerable caution to antiferromagnetic conductors.[15] In samarium the closeness of the antiferromagnetic Curie point might make the T^3 temperature dependence a rather crude approximation.

Marshall[16] has shown that at low enough temperatures, where the electron spins are completely aligned due to the strong interatomic exchange forces, the nucleus is in a temperature-independent effective magnetic field H_{eff}. This field is the sum of the local magnetic field at the nucleus, the effective magnetic field arising from the contact interaction with the polarized-conduction electrons, and the effective field due to the $4f$ electrons of the same atom. In this field the nucleus with a magnetic moment μ and spin I will have, relative to H_{eff}, $2I+1$ possible spin orientations, their population being determined by the Boltzmann factor $\mu H_{\mathrm{eff}}/2IkT$. In the temperature range where $kT\approx\mu H_{\mathrm{eff}}/2I$ a redistribution among the spin orientations takes place and this gives rise to an additional specific heat. In practice, the nuclear specific heat is observed below 1°K. Bleaney and Hill[17] and Bleaney[18] have shown that often effects due to nuclear-electric-quadrupole interaction are also important; for samarium the quadrupole contribution is negligible.[18] In this case the nuclear specific heat becomes[16,18]

$$C_N=\frac{I+1}{3I}R(\mu H_{\mathrm{eff}}/kT)^2-\frac{(I+1)(2I^2+2I+1)}{30I^3}R(\mu H_{\mathrm{eff}}/kT)^4. \quad (1)$$

The series expansion is valid sufficiently far above the maximum in C_N, which occurs at a temperature $T\approx\mu H_{\mathrm{eff}}/2Ik$.

In view of the preceding discussion the specific heat of samarium can be written

$$C_p=AT^3+BT+DT^{-2}-ET^{-4}. \quad (2)$$

The lattice and magnetic specific heat cannot be separated without additional information since their tem-

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TABLE II. Specific heat of samarium metal. Constants in equation C_p (millijoules/mole °K)$=AT^3+BT+DT^{-2}-ET^{-4}$. The limits of error are statistical only.

Run	A	B	D	E
IA	0.877 ± 0.014	11.89 ± 0.05	8.64 ± 0.01	0.021
IB	0.897 ± 0.012	11.86 ± 0.04	8.63 ± 0.01	0.021
III	1.113 ± 0.010	12.61 ± 0.04	8.41 ± 0.01	0.021
Average	···	12.12	8.56	0.021

perature dependence is assumed to be the same. BT is the electronic and $(DT^{-2}-ET^{-4})$ the nuclear specific heat. The constants in (2) [of which D and E are interdependent through (1)] were determined by the method of least squares, but in order to minimize the uncertainty concerning the functional form of the magnetic specific heat, points below 2.5°K only were included in the analysis. In this way the fit to experimental data was improved by more than an order of magnitude. The results are given in Table II; the limits of error are statistical only.

The calculated specific heat curves for runs IB and III have been drawn into Fig. 1. A deviation plot for run IB is shown in Fig. 2; deviation plots for other runs are similar.

V. DISCUSSION

It is satisfying to note from Table II that the mathematical analysis gives for all three runs quite similar electronic and nuclear specific heats, the maximum differences being 6% and 2.5%, respectively. The term AT^3 in (2) thus appears to be mainly responsible for the observed discrepancies between runs. The value obtained for D is insensitive to the functional form of (2). Therefore, it is believed that the average result $D=8.56$ millijoules °K/mole is correct within about 2%. As one would expect, the coefficient B in the electronic specific heat depends to some extent on the mathematical form of (2); for instance, a T^5 term could be included for a better representation of the experimental data. However, since the functional form of C_M is known to some certainty only at the lowest temperatures where its effect on the coefficient B is relatively small, it was felt that most reliable values for B are secured by excluding experimental points above 2.5°K, and not by trying to add terms to (2). The average result $B=12.1$ millijoules/mole °K^2 is probably correct to 5%.

The discrepancies in the term AT^3 are almost certainly caused by the antiferromagnetic Curie point at 13.6°K. The measurements of Roberts[11] revealed at this temperature a very pronounced maximum in the specific heat of samarium. Similar magnetic anomalies were found in the heat capacities of lower rare earths by Parkinson, Simon, and Spedding.[19] Fufthermore, they observed that the height of the heat capacity peak depends on the time the sample spends in the anomalous region when it is being cooled down. Specific heat measurements by Jennings, Hill, and Spedding[20] on samarium disagree somewhat around 14°K with those of Roberts[11]; the difference was attributed to the fact that in the former case the sample was never cooled below 13°K. Since the cooling rate was not controlled in the present experiments, individual differences might have occurred between runs and thus the magnetic transformation would have gone through to a different degree of completeness. This readily explains the discrepancies in the magnetic heat capacity. The lattice specific heat probably was the same for all of the runs.

One observation was made which further supports the above conclusion: During run III, after the sample was cooled to 4.2°K, the exchange gas was immediately pumped out. After twelve hours the sample had warmed up considerably; new exchange gas was then admitted and the metal again cooled to 4.2°K. During runs IA, IB, and II the sample never warmed up above 6°K once it was cooled down and it thus spent less time in the anomalous region than during run III. This is consistent with the observed higher magnetic specific heat for run III. It is also in agreement with the slightly higher specific heat for run IB as compared with IA, since in the former case the sample had spent more time in the 4–6°K region. In order to study the effects of cooling speed more thoroughly it would be necessary to measure the specific heat up to 20°K, at least, and since our apparatus cannot be used above 4°K, the matter was not investigated further.

Equation (1) and the numerical value of constant D in Eq. (2) allow us to compute H_{eff} at samarium nuclei. The calculation was made by assuming normal isotopic composition for the metal, i.e., 14.94% of Sm^{147} and 13.85% of Sm^{149} (the other stable isotopes are even-even nuclei and do not contribute to C_N), a nuclear spin $I=\frac{7}{2}$ for both isotopes, and magnetic moments of -0.83 and -0.68 nuclear Bohr magnetons for the two isotopes. The effective field thus becomes $H_{\mathrm{eff}}=3.3\times10^6$ gauss.

The $4f$ electrons, responsible for the magnetic properties of rare earths, are well shielded and thus the magnetic field produced at the nucleus should largely be independent of the environment of the rare earth atom. Bleaney[18] has calculated the constant D for several rare earth metals from electron-spin resonance data on dilute salts. By using the values 600 Mc/sec and 500 Mc/sec for the magnetic hyperfine constant of Sm^{147} and Sm^{149}, respectively, he obtains $D=8.9$ millijoules °K/mole. Because the effect of crystal field admixtures from the excited $J=\frac{7}{2}$ state (the ground state of Sm^{3+} is $^6H_{\frac{5}{2}}$) is quite large in the salts of samarium, this value of D is uncertain up to 10%. However, the agreement with the calorimetric D is good and thus the contribution to H_{eff} from polarized conduction electrons must be relatively unimportant. It would be of interest to

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measure the hyperfine coupling in samarium by Mössbauer techniques; a more accurate comparison with the calorimetric D could thus be made.

Even at the lowest experimental temperature of 0.4°K the first term in (1) accounts for 98.5% in the nuclear specific heat. If the experiments were extended to still lower temperatures the higher terms in C_N would become important and a maximum in the specific heat would be observed at about 0.01°K.

Roberts'[11] smooth values for the specific heat of samarium are shown as crosses in Fig. 1; the agreement with our results is as good as can be expected. The filled circles represent results from recent experiments by Dreyfus *et al.*[1] The agreement here is rather poor, especially at higher temperatures. For the coefficient D in the nuclear specific heat they deduced the value 11 ± 2 millijoules °K/mole. The discrepancies are perhaps entirely due to impurities since similar effects have been found in other rare earths.[2–8,10] Measurements by Crane[21] show that at 2°K the specific heat of gadolinium increases by 70% when the oxygen impurity is increased from 0.11 to 0.22%. At 4°K this effect is still 30%. The amount of oxygen in the sample of Dreyfus *et al.*[1] was not determined, but it was probably larger than the exceptionally low oxygen content of our sample. Oxide impurity usually forms a separate phase in rare earth metals and thus it would be of interest to measure the heat capacity of Sm_2O_3 between 1 and 4°K. If the degeneracy of the lowest energy level is removed in this temperature range an anomaly would result in the specific heat. Even a relatively small oxide impurity could then account for the observed differences in the heat capacity.

From measurements above 15°K Jennings *et al.*[20] estimated $\theta_L=150$°K for the Debye characteristic temperature of samarium. This result would yield $C_L=0.58T^3$ millijoules/mole °K and thus for run IB, $C_M=0.32T^3$ millijoules/mole °K and $\theta_M=183$°K.

The value 12.1 millijoules/mole °K^2 for the coefficient B in the electronic specific heat of samarium can be compared with the experimental result $B=10.1$ for lanthanum,[22] 9.0 and 9.5 for dysprosium,[6,8] and 9.5 for lutetium.[23] For the first two of these metals the coefficients were deduced from measurements below 4°K; for lutetium experimental data are not available below 13°K. It thus seems that C_E is similar for these rare earths, a result which one would perhaps expect and which can be used in the analysis of the heat capacity measurements of other metals in this group. For samarium Jennings *et al.*[20] deduced $B=13$ millijoules/mole °K from the measurements of Roberts.[11] This value is bound to be somewhat high since the nuclear specific heat was ignored in the analysis.

However, recent measurements by Dreyfus, Goodman, Lacaze, and Trolliet[10] gave for the coefficient B (in millijoules/mole °K^2): Pr, 19.0; Ho, 26; Er, 13; Tm, 21.5. The experiments have been reported only very briefly but since the magnetic specific heat was ignored in the analysis of the data, it is quite possible that the above values are too high. More experiments are required to settle these questions.

This work has been briefly reported at the New York Meeting (January, 1962) of the American Physical Society.[24]

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