

## Specific Heat of Praseodymium and Neodymium Metals Between 0.4 and 4°K†

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The specific heat  $C_p$  of praseodymium and neodymium metals has been measured between 0.4 and 4°K in a He<sup>3</sup> cryostat. After assuming, on the basis of earlier research,  $C_L=0.554T^3$  (specific heat always given in mJ/mole°K) and  $C_E=10.5T$  for the lattice and electronic specific heats of praseodymium, the remaining  $C_p$  was analyzed into a nuclear contribution  $C_N=20.9T^{-2}$  and into a magnetic contribution  $C_M$ . If compared with Bleaney's calculations based on fully magnetized electronic states in the metal, our experimental  $C_N$  shows that 2.0% of the sample was in a cooperative state, probably ferromagnetic, the rest of the metal being paramagnetic.  $C_M$  was further separated into a Schottky contribution with an excited electronic level at 28°K (ions in hcp surroundings corresponding to 50% of the sample) and into a smeared-out cooperative peak with a maximum at 3.2°K. The entropy under the latter curve is 95 mJ/mole °K as compared with the value  $0.020 \times R \ln 2 = 115$  mJ/mole°K which would be expected as a result of magnetic ordering in 2.0% of the sample. Both  $C_N$  and  $C_M$  thus suggest that 2% of the sample enters a cooperative phase below 3.2°K. This mechanism to explain  $C_N$  and  $C_M$  must be considered as preliminary. Our value of  $C_N$  is rather different from earlier results. A sample-dependent  $C_N$  is consistent with the picture of ferromagnetic domains. Below 2°K the specific heat of praseodymium can be written, with 1% accuracy,  $C_p=4.53T^3+24.4T+20.9T^{-2}$ . At higher temperatures  $C_p$  cannot be represented by a simple power series. The magnetic contribution to the specific heat of neodymium is huge due to cooperative peaks at 7 and 19°K; even at 1°K  $C_M$  represents 88% of the total  $C_p$ . Below 7°K neodymium is antiferromagnetic. After adopting  $C_L=0.502T^3$  and  $C_E=10.5T$  an analysis gave  $C_N=(7 \pm 0.7)T^{-2}$ . This value is about 50% smaller than that calculated by Bleaney if full electronic magnetization is assumed. However, the splitting of the electronic levels is rather large in neodymium and one cannot assume that  $\langle J_z \rangle$  in a cooperative state tends to  $J = \frac{3}{2}$ , but rather reaches a lower limiting value at  $T=0$ °K. This explains the smaller experimental  $C_N$ . Between 0.4 and 1°K the specific heat of neodymium may be written with 1% accuracy  $C_p=125.7T^3+22.5T+6.4T^{-2}$ . The accuracy of these measurements is estimated as 1.5% at 0.4°K and as 0.5% between 1 and 4°K. While checking the performance of our cryostat the specific heat of copper was found to be  $C_p=0.0510T^3+0.698T$ .

### I. INTRODUCTION

AFTER completing our studies of the specific heat  $C_p$  of higher rare earths between 0.4 and 4°K,<sup>1-7</sup> we have now turned our attention to metals at the lower end of the lanthanide series. In this paper, measurements of  $C_p$  between 0.35 and 4.06°K for praseodymium and between 0.40 and 3.77°K for neodymium are presented. These two metals are in many respects rather similar and it is, thus, convenient to discuss them together.

The heat capacity of praseodymium and neodymium was first measured by Parkinson, Simon, and Spedding<sup>8</sup> between 2 and 180°K in 1950. They found for praseodymium a very large anomaly with a flat maximum at 65°K, whereas neodymium showed two sharper peaks at 7 and 19°K, respectively. These anomalies were attributed to crystalline field splitting of the electronic states of the 4f electrons. Since 1950, and particularly during the last few years the rare-earth metals have

become commercially available in states of relatively high purity (99.9%) and a large amount of research has been done on them. In the heat-capacity field, the most striking phenomenon found is the huge nuclear specific heat  $C_N$ , first discovered by Kurti and Safrata<sup>9</sup> in terbium, and later observed for most of these metals. The largest contribution to  $C_N$  comes usually from the interaction between the nuclear magnetic moment and the intense magnetic field (several MG) produced by the 4f electrons at the site of the nucleus. In some cases, the interaction of the nuclear electric quadrupole moment with the electric field gradient is also of importance. At the present time, the nuclear specific heat is well understood for the higher lanthanides in most cases, and good agreement exists between values obtained for the magnetic hyperfine and quadrupole coupling constants when these are calculated either from heat capacity or other type of measurements (EPR, ENDOR, NMR, atomic beam, and Mössbauer). These calculations are based on fully magnetized electronic states in the metal. Extensive comparisons have been made by Bleaney.<sup>10</sup>

For praseodymium, on the other hand, recent measurements of the heat capacity between 0.5 and 4°K by Dreyfus, Goodman, Lacaze, and Trolliet<sup>11</sup> and between 0.3 and 4.2°K by Dempsey, Gordon, and Soller<sup>12</sup> show

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<sup>1</sup> O. V. Lounasmaa, Phys. Rev. **126**, 1352 (1962).

<sup>2</sup> O. V. Lounasmaa and R. A. Guenther, Phys. Rev. **126**, 1357 (1962).

<sup>3</sup> O. V. Lounasmaa and P. R. Roach, Phys. Rev. **128**, 622 (1962).

<sup>4</sup> O. V. Lounasmaa, Phys. Rev. **128**, 1136 (1962).

<sup>5</sup> O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

<sup>6</sup> O. V. Lounasmaa, Phys. Rev. **133**, A219 (1964).

<sup>7</sup> O. V. Lounasmaa, Phys. Rev. (to be published).

<sup>8</sup> D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

<sup>9</sup> N. Kurti and R. S. Safrata, Phil Mag. **3**, 780 (1958).

<sup>10</sup> B. Bleaney, J. Appl. Phys. **34**, 1024 (1963).

<sup>11</sup> B. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, Compt. Rend. **253**, 1764 (1961).

<sup>12</sup> C. W. Dempsey, J. E. Gordon, and T. Soller, Bull. Am. Phys. Soc. **7**, 309 (1962).

that there is no agreement at all. These experiments agree with each other in the size of the nuclear term. However, anticipating Sec. III 1 of our paper, the present measurements give a quite different  $C_N$ , but which still is not in agreement with calculations.<sup>10</sup> A discrepancy also exists in the case of neodymium (Sec. IV 1).

In addition to the magnetic specific heat  $C_M$ , due to Stark splitting of the  $4f$  electronic levels and the nuclear specific heat  $C_N$ , there are the usual lattice and electronic contributions:  $C_L=AT^3$  and  $C_E=BT$ , respectively. The total specific heat of praseodymium and neodymium below  $4.2^\circ\text{K}$  thus becomes

$$C_p = AT^3 + BT + DT^{-2} - FT^{-4} + C_M, \quad (1)$$

where we have written  $C_N = DT^{-2} - ET^{-4}$ .<sup>2</sup> The  $T^{-3}$  term is absent because we assume no quadrupole interactions. When attempts have been made to analyze the observed  $C_p$  of rare-earth metals into its contributions,<sup>1-4</sup> the main stumbling block in the past has been that there are too many terms involved. The problem has now become easier, however, since new measurements on lutetium<sup>6</sup> allow us to make a fair estimate of  $C_L$  and  $C_E$  of all trivalent lanthanides.  $C_N$  can be calculated with relatively good precision from measurements below  $1^\circ\text{K}$ . We are thus in the position to determine  $C_M$  quite accurately.

## II. EXPERIMENTAL

### 1. Procedure

The measurements were carried out in a  $\text{He}^3$  cryostat which has been described earlier<sup>2</sup>; only the most relevant experimental features thus need to be mentioned here. However, due to a small change in the method of securing the  $T$  versus  $R$  relation for the carbon thermometer, the calibration procedure will be explained in more detail.

$\text{He}^4$  exchange gas was used for cooling the samples down to  $4.2^\circ\text{K}$  and, in the case of neodymium, due to its huge heat capacity, down to  $2.5^\circ\text{K}$ . The space surrounding the calorimeter was then evacuated by pumping until a mass-spectrometer-type leak detector showed a very small helium reading. For further cooling a mechanical heat switch was employed. In this way good thermal insulation was achieved when the heat switch was opened and desorption of helium gas from the sample during heat-capacity measurements was prevented. By pumping on  $\text{He}^3$ , a temperature of about  $0.33^\circ\text{K}$  was reached and maintained in the  $\text{He}^3$  pot for 48 h without recondensing.

### 2. Thermometer Calibrations and the Specific Heat of Copper

For the heat-capacity measurements a colloidal graphite (Aquadag) thermometer was employed; it was calibrated against the vapor pressure of  $\text{He}^4$  be-

tween  $4.15$  and  $2.2^\circ\text{K}$ , against the vapor pressure of  $\text{He}^3$  between  $2.2$  and  $0.75^\circ\text{K}$ , and against a magnetic thermometer (chromium-methylamine-alum) between  $0.75$  and  $0.4^\circ\text{K}$ .  $\text{He}^4$  temperatures were determined according to the  $T_{58}$  scale.<sup>13</sup> For  $\text{He}^3$  the new Los Alamos 1962 scale<sup>14</sup> was employed; a correction was made for the  $0.5\%$  of  $\text{He}^4$  in our  $\text{He}^3$  gas by assuming the validity of Raoult's law.

In order to test our cryostat in general and the accuracy of thermometer calibrations at the lowest temperatures in particular, the heat capacity of copper (99.99% pure, 3.9426 moles) was measured in three different experiments with a new carbon thermometer each time. Results from one of the measurements are shown in Fig. 1. The three experiments agree within  $0.5\%$ . By writing

$$C_p = \alpha T^3 + \beta T \quad (2)$$

for copper, we get as average values  $\alpha = 0.0510$  mJ/mole $^\circ\text{K}^4$  and  $\beta = 0.698$  mJ/mole $^\circ\text{K}^2$ . Our results are in excellent agreement with earlier data; for a summary see O'Neal.<sup>15</sup>

By assuming that the specific heat of copper follows Eq. (2) down to our lowest experimental temperatures, calibration of the carbon thermometer against the chromium salt can be checked. After examining all the data from our three copper experiments we find that between  $1$  and  $0.35^\circ\text{K}$  the calibration curve may be written

$$R = \rho/T + \sigma/T^2, \quad (3)$$

where  $R$  is the resistance of the carbon thermometer and  $\rho$  and  $\sigma$  are constants. This formula represents the true calibration curve between  $0.35$  and  $1^\circ\text{K}$  within  $0.2\%$  of the absolute temperature. Relation (3) was used for smoothing the calibration points below  $0.45^\circ\text{K}$

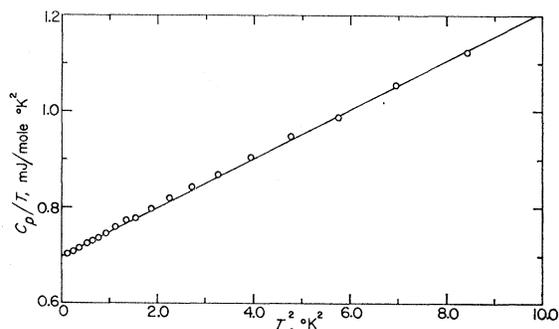


Fig. 1. The specific heat of copper plotted as  $C_p/T$  versus  $T^2$ . The straight line corresponds to relation  $C_p = 0.0510T^3 + 0.698T$  mJ/mole $^\circ\text{K}$ .

<sup>13</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **A64**, 1 (1950).

<sup>14</sup> R. H. Sherman, S. G. Sydorik, and T. R. Roberts, Los Alamos Scientific Laboratory Report No. 2701, 1962 (unpublished).

<sup>15</sup> H. R. O'Neal, University of California Lawrence Radiation Laboratory Report, UCRL 10426, 1963 (unpublished).

and for calculating some extrapolated points below 0.4°K to secure the right slope for the calibration curve at the low temperature end. Constants  $\rho$  and  $\sigma$  were determined in each case from measurements between 0.45 and 1°K.

Figure 2 shows, as a typical example, the precision with which the magnetic thermometer calibration points can be fitted to the formula<sup>16</sup>

$$M = \gamma + \delta(T + 0.0028/T + \Delta)^{-1}. \quad (4)$$

Here  $\gamma$ ,  $\delta$ , and  $\Delta$  are constants to be determined by a least-squares analysis and  $M$  is the mutual inductance reading of the bridge.

For final calculation of  $C_p$ , all the calibration points (about 35), as determined from He<sup>4</sup> or He<sup>3</sup> vapor pressure measurements and by applying Eqs. (3) and (4), were fitted by the method of least squares to a single formula of the type

$$1/T = a/R^{5/2} + b/R + c + dR^{1/2} + eR + fR^2 + g/(\ln R)^{1/2} + h \ln R, \quad (5)$$

where  $a, \dots, h$  are constants. Figure 3 shows the deviations of measured points from the calculated equation for the first neodymium experiment. The deviations are small and no further corrections are necessary when calculating  $C_p$ .

### 3. Accuracy of Results

Methods commonly employed in adiabatic calorimetry were used in our heat-capacity measurements. The heating current was determined with a Rubicon No. 2781 potentiometer and timed with an electronic timer controlled by a tuning fork frequency standard. The potentiometer was cross checked against a Rubicon No. 2773 double potentiometer, the timer compared with radio signals over a 24 h period, and standard cells and standard resistors calibrated against NBS-certified equipment. Possible systematic errors here are thus negligible. The electrical leads between the He<sup>4</sup> bath and the calorimeter were made of lead-covered constantan and were superconducting below 7°K. As described in another paper,<sup>6</sup> it is likely that the coating had tiny cracks at which a small amount of heat was

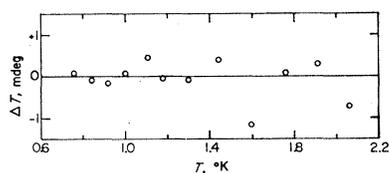


FIG. 2. Deviations  $\Delta T$  of the magnetic-thermometer-calibration points from equation  $M = -140.66 + 112.34(T + 0.0028/T + 0.007)^{-1}$ , where  $M$  is the reading of the mutual inductance bridge [cf., Eq. (4)]. 1st neodymium experiment.

<sup>16</sup> M. Durieux, H. van Dijk, H. ter Harmsel, and C. van Rijn, *Temperature: Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1962), Vol. 3, p. 383.

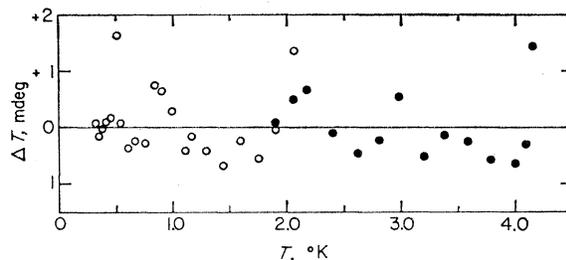


FIG. 3. Deviations  $\Delta T$  of the carbon thermometer calibration points from a smooth relation [cf., Eq. (5)] for the first neodymium experiment. O, points based on the vapor pressure of He<sup>3</sup> or the magnetic thermometer; ●, points based on the vapor pressure of He<sup>4</sup>.

generated. Due to this, there might be an error of 0.1% in the effective heater resistance ( $R_H = 362.13 + 0.03T \Omega$ ).

The heating periods were 1 min at the low-temperature end. Towards higher temperatures, however, they were gradually increased and for neodymium, because of its very large heat capacity at 4°K, they were finally 20 min long. This was done for not exceeding a heating current of 2 mA and, thereby, destroying the superconductivity of the lead-coated leads.<sup>6</sup> No accuracy was lost by the longer heating periods since the heat leak to the calorimeter was mostly so small that it could not be detected during a 10 min period. When measurable, a correction was applied for it by assuming linear drifts. The very small scatter of the experimental  $C_p$  points is attributable to the small or negligible heat leak.

The heat capacity of the empty calorimeter ( $C = 0.0090T^3 + 0.116T$  mJ/°K) was known from an earlier experiment. It is 0.3% of the heat capacity of our praseodymium sample at 4°K and smaller elsewhere; for neodymium it never is more than 0.1%. Possible uncertainties here may cause only negligible errors in the final results.

The largest systematic errors are probably due to inaccuracies in the calibration of the carbon thermometer. On the basis of previous discussion (Sec. II 2) it is believed that the absolute temperature, as defined by the He<sup>3</sup> and He<sup>4</sup> scales,<sup>14,18</sup> is everywhere within 1 mdeg. of the temperature determined by Eq. (5). Taking this uncertainty in the absolute temperature and probable errors in the slope of the calibration curve into account, allowing for inaccuracies in the temperature scales themselves, and adding 0.1% for possible errors in the heater resistance, we estimate the accuracy of our  $C_p$  measurements as 1.5% at 0.4°K and 0.5% between 1 and 4°K.

All the calculations were performed by an IBM-704 digital computer.<sup>17</sup> The results have been corrected for curvature due to finite temperature increments (5–10% of  $T$ ) used when measuring  $C_p$ .

<sup>17</sup> P. R. Roach, Argonne National Laboratory Technical Report No. 6497, 1962 (unpublished).

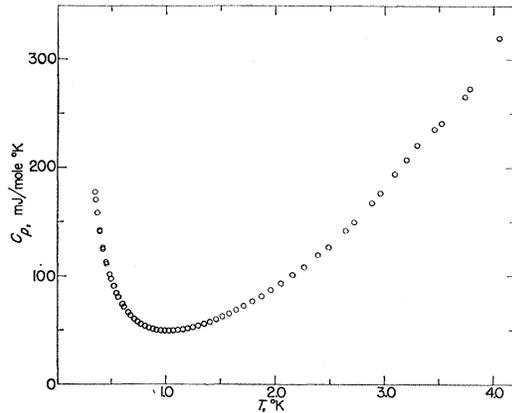


FIG. 4. The specific heat of praseodymium metal. Experimental points.

### III. PRASEODYMIUM

#### 1. Results

Our praseodymium metal was purchased from Research Chemicals, Inc. (Division of Nuclear Corporation of America). It was vacuum distilled, then remelted in a vacuum and cast into a tantalum crucible. Next, the sample was machined in an argon atmosphere into cylindrical form, 4.1 cm long and 2.8 cm in diameter. Its weight was 167.40 g (= 1.1880 moles). For protecting the metal from oxidizing when handling it in the air, the sample was covered with a thin layer of Krylon lacquer. The weight of the coating was 0.04 g and its heat capacity could thus be ignored. The spectrographic laboratory at Argonne found the following metallic impurities in our praseodymium sample (weight %): Fe, 0.0015%; Na, 0.003%; Ni, 0.04%; Ta, 0.002%; and trace amounts (total 0.0036%) of Ag, Al, B, Ca, Cu, Er, Gd, K, La, Li, Lu, Mn, Mo, Sr, V, and Y. These analyses are accurate by a factor of two. The Argonne chemical laboratory detected: H, 0.008%; C, 0.015%; N, 0.004%; O, 0.011%; F, 0.029%. The chemical analyses are accurate to about 10%. As these numbers show, the total impurity content of our sample was remarkably low. In an x-ray crystallographic analysis at room temperature only lines corresponding to hexagonal structure were found.

Our experimental results on praseodymium are presented in Table I and Fig. 4. The three runs, which agree very well, were made on successive days and were then followed by the thermometer calibration. During all this time the sample was never warmed above 4.2°K. The increase in  $C_p$  at the lowest temperatures is due to  $C_N$ . A small anomaly is observed between 3.0 and 3.5°K; this will be discussed later (Sec. III 2).

In Fig. 5 the present results are compared with earlier heat-capacity data on praseodymium. Parkinson, Simon, and Spedding<sup>8</sup> published their measurements in the form of a smoothed table which has only three entries in the liquid helium range (at 2.5, 3, and 4°K);

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

$T$ (°K)	$C_p$	$T$ (°K)	$C_p$	$T$ (°K)	$C_p$
Run I					
0.3585	170.9	1.7183	72.18	0.7442	57.64
0.3972	142.0	1.8748	81.24	0.8113	53.70
0.4276	125.1	2.0543	93.05	0.8824	51.17
0.4578	111.7	2.2607	108.4	0.9562	49.94
0.4973	97.85	2.4879	126.7	1.0310	49.70
0.5483	84.35	2.7241	149.6	1.1125	50.39
0.6007	74.07	2.9615	176.2	1.2024	51.93
0.6537	66.38	3.2024	207.0	1.2994	54.44
0.7123	60.23	3.4596	235.3	1.4057	57.86
0.7765	55.56	3.7416	265.3	1.5209	62.58
0.8452	52.36			1.6482	68.58
0.9173	50.47	Run III			
0.9912	49.64	0.3507	177.9	1.7940	76.50
1.0708	49.85	0.3731	158.7	1.9613	87.01
1.1577	51.01	0.3981	141.4	2.1593	101.0
		0.4249	126.4	2.3922	119.0
		0.4534	113.5	2.6447	141.9
		0.4853	101.7	2.8832	167.3
Run II					
1.2499	53.06	0.5209	91.02	3.0967	194.0
1.3519	55.97	0.5627	81.15	3.3012	220.5
1.4623	60.11	0.6153	71.65	3.5252	240.4
1.5822	65.30	0.6784	63.55	3.7848	272.8
				4.0565	319.3

the curve in Fig. 5 has been drawn through these points. The paper by Dreyfus, Goodman, Lacaze, and Trolliet<sup>11</sup> merely gives the specific heat as an equation. No details have been reported about the experiments or results. Measurements by Dempsey, Gordon, and Soller<sup>12</sup> have only been published in abstract form but a detailed graph, kindly supplied to us by Dr. Dempsey, has been at our disposal. This graph was used in drawing the appropriate curve into Fig. 5.

Below 22°K the measurements of Parkinson, Simon, and Spedding<sup>8</sup> were made by using constantan and leaded-brass thermometers, which have a relatively low sensitivity in the liquid helium range. Due to this and other reasons (the techniques of calorimetry below 4.2°K have improved a great deal since 1950), we feel

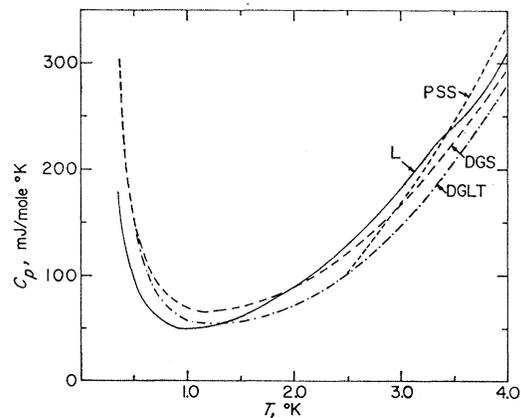


Fig. 5. Comparison of various specific-heat measurements on praseodymium. L, present results; PSS, Parkinson, Simon, and Spedding (Ref. 8); DGLT, Dreyfus, Goodman, Lacaze, and Trolliet (Ref. 11); DGS, Dempsey, Gordon, and Soller (Ref. 12).

that the agreement with our results is within the experimental error.

Above 2°K the results by Dempsey, Gordon, and Soller<sup>12</sup> are nowhere more than 8% below our data, but at the lowest temperatures a much more serious discrepancy exists, indicating large differences in the observed  $C_N$ . This will be discussed in detail below (Sec. III 2). The measurements of Dreyfus, Goodman, Lacaze, and Trolliet<sup>11</sup> fall below the other data above 2°K but join those of Dempsey, Gordon, and Soller at their low-temperature end.

None of the earlier authors report an anomaly in  $C_p$  between 3.0 and 3.5°K. This is not surprising in view of the smallness of the "hump." It can only be detected by detailed measurements with negligible scatter. For instance, Dempsey, Gordon, and Soller<sup>12</sup> investigated the temperature region above 2°K rather cursorily by measuring only five heat-capacity points between 2 and 4.2°K. For this reason, the discrepancies between these and our measurements above 2°K can barely be considered significant.

## 2. Discussion

Our specific-heat points between 0.36 and 2.0°K can be fitted within 0.9% maximum deviation to the relation ( $C_p$  in mJ/mole°K)

$$C_p = 4.53T^3 + 24.4T + 20.9T^{-2}. \quad (6)$$

This equation was calculated by the method of least squares.<sup>17</sup> If experimental points up to 3.0°K are included in the analysis the first three constants in Eq. (6) change to 3.82, 26.1, and 20.7, respectively, and the maximum deviations increase to 2.2%. Too much significance must thus not be attached to the numerical values of the first two coefficients, whereas the nuclear specific heat,  $C_N = 20.9T^{-2}$ , seems to be rather unambiguously determined. The result for  $C_N$  should be accurate to about 2%.

Dreyfus, Goodman, Lacaze, and Trolliet<sup>11</sup> deduced from their measurements  $C_N = 35T^{-2}$  mJ/mole°K and Dempsey, Gordon, and Soller<sup>12</sup> found  $C_N = 37.5T^{-2}$  in the same units. These two expressions, while they agree within the experimental error among themselves, are in serious disagreement with our results.

Bleaney<sup>10,18</sup> has discussed in detail the nuclear specific heat of praseodymium. The splitting of the nuclear levels is given in general by the Hamiltonian

$$\mathcal{H} = a'i + P \left[ i^2 - \frac{1}{3}I(I+1) \right] - \frac{1}{2} \sum_{j \neq k} 2(\mathbf{I}_j \cdot \mathbf{K}_{jk} \cdot \mathbf{I}_k), \quad (7)$$

where the first two terms represent magnetic hyperfine and electric quadrupole interactions and the third is the interaction between neighboring nuclei. 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 trivalent lanthanide ion. For higher rare earths, the calculated and experimental specific heats are in good agreement if complete electronic magnetization is assumed, i.e.,  $\langle J_z \rangle$  is replaced by  $J$  and  $\langle J_z^2 - \frac{1}{3}J(J+1) \rangle$  by  $J^2 - \frac{1}{3}J(J+1)$ . This type of calculation yields for praseodymium  $C_N = 1070T^{-2} - 88T^{-4}$  mJ/mole°K (if quadrupole interactions and higher terms are ignored).<sup>10</sup> The much smaller experimental values show that praseodymium does not have a cooperative phase and remains paramagnetic. They also indicate that the only electronic level populated at liquid helium temperatures is a singlet state since otherwise a very large interaction specific heat would be observed (but see later). This picture is consistent with heat-capacity measurements by Parkinson, Simon, and Spedding<sup>8</sup> who found that the entropy associated with  $C_M$  is close to the value  $R \ln 9$  (the ground state of  $\text{Pr}^{3+}$  ion is  $^3H_4$ ), indicating that the degeneracy of the  $J=4$  state is completely lifted by the crystal field. A singlet ground level is also in agreement with the constant magnetic susceptibility of praseodymium below 4°K as observed by Lock.<sup>19</sup>

According to Bleaney's<sup>10,18</sup> calculations, the main difficulty in explaining the nuclear specific heat of praseodymium is not why the experimental  $C_N$  is so small but why it is so large. The problem is that with an electronic singlet state the magnetic interaction in Eq. (7) is zero and the quadrupole interaction is relatively small. It also seems impossible to find large enough internuclear exchange interactions. For a detailed discussion of the various possibilities we refer to Bleaney.<sup>10,18</sup>

Now that different experimental values have been observed for the nuclear specific heat, it is likely that  $C_N$  is largely sample dependent. There are several mechanisms which could produce the observed interactions and which would vary from one sample to another.  $C_N$  might be due to impurities or to a fraction of the praseodymium ions being in other than  $\text{Pr}^{3+}$  valence states. The former possibility can probably be ruled out because of the low impurity content of our sample; in any case, there is no basis for much speculation here since analyses of the other investigators<sup>11,12</sup> samples are lacking. No evidence has been presented for valence states other than 3 in praseodymium metal. Bleaney<sup>18</sup> has shown that in order to explain the electronic susceptibility of praseodymium interactions are needed which are almost sufficiently strong to produce ferromagnetism in the metal. Small ferromagnetic clusters might thus be formed and in those the nuclear specific heat would have its full strength,  $C_N = 1070T^{-2}$

<sup>18</sup> B. Bleaney (to be published).

<sup>19</sup> J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).

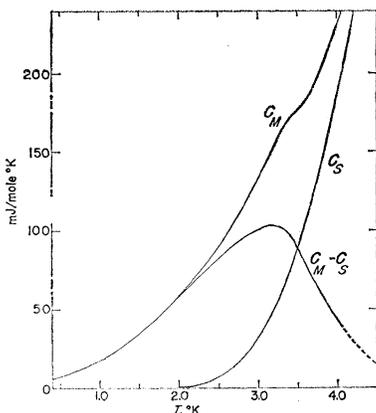


FIG. 6. An analysis of the magnetic specific heat of praseodymium  $C_M = C_p - 0.554T^3 - 10.5T - 20.9T^{-2}$  mJ/mole°K.  $C_S = 4159(28/T)^2 \exp(-28/T)$  mJ/mole°K. For further explanations, see text.

$-88T^{-4}$  mJ/mole°K. By comparing the  $T^{-2}$  term with our experimental result  $C_N = 20.9T^{-2}$  mJ/mole°K we find that the observed  $C_N$  would be explained if 2.0% of the sample were in these clusters. This percentage would be reduced provided that some of the observed  $C_N$  is due to the paramagnetic parts of the metal. However, the  $T^{-4}$  term, quite large below 1°K according to Bleaney's<sup>10</sup> calculation, is absent from our experimental  $C_N$  which can be expressed with a  $T^{-2}$  term only. This is rather puzzling and probably speaks against the cluster hypothesis.

On the basis of considerations described in an earlier paper<sup>6</sup> we estimate that the lattice heat capacity of praseodymium at liquid helium temperatures should correspond to a Debye characteristic temperature  $\theta = 152^\circ\text{K}$  giving  $C_L = 0.554T^3$ , and that  $C_E = 10.5T$  ( $C_L$  and  $C_E$  in mJ/mole°K). The major contribution to the first and second terms in Eq. (6) thus comes from  $C_M$ .

Bleaney<sup>18</sup> has used the crystal-field approach for calculating the magnetic specific heat of praseodymium. The crystal structure of this metal is hexagonal with a double  $c$  axis, with ions in alternate layers having their nearest and next nearest neighbors in fcc and hcp arrangement. Only two parameters are needed in the theory. Their values were found by matching the calculated and experimental magnetic specific heats. The latter was determined from measurements of Parkinson, Simon, and Spedding<sup>8</sup> on praseodymium and on non-magnetic lanthanum by using the relation  $C_M(\text{Pr}) = C_p(\text{Pr}) - C_p(\text{La})$ . A reasonably good fit was obtained for the whole temperature range between 2.5 and 180°K. According to this calculation,<sup>18</sup> the lowest excited level, corresponding to ions with hcp surroundings, is at 23°K above the ground level; the second excited level is at 63°K. For ions in cubic environment the lowest excited level is at 87°K.

In Fig. 6 we show the magnetic specific heat of

praseodymium as calculated from the relation  $C_M = C_p - 0.554T^3 - 10.5T - 20.9T^{-2}$  (in mJ/mole°K). By comparing Fig. 6 with Fig. 4, one can easily see that  $C_M$  is the major contribution in  $C_p$  above 1.5°K. After calculating the Schottky specific heat  $S_S$  corresponding to Bleaney's<sup>18</sup> first excited level at 23°K for ions in hexagonal environment, we find that  $C_S$  exceeds  $C_M$  above 3.2°K (at 4°K  $C_S \cong 2C_M$ ). Further calculations show that no good fit can be obtained by changing the level spacing. This, of course, is also evident from the hump between 3.0 and 3.5°K, which points to an anomaly in  $C_M$  with a maximum somewhere in this temperature region. Entropy considerations, however, immediately prove that the anomaly cannot be associated with the whole sample.

In order to study this hump, we have assumed that its effect is negligible above 5°K, have adopted the value 485 mJ/mole°K (after we have subtracted  $C_L$ ,  $C_E$ , and  $C_N$ ) for  $C_M$  at 5°K,<sup>8</sup> and then matched  $C_M$  with  $C_S$  at this same temperature. We thus get 28°K for the position of the first excited level for ions in hcp surroundings. The higher levels have been ignored in the calculation since their contribution is small below 5°K. The Schottky curve  $C_S = 4159(28/T)^2 \exp(-28/T)$  mJ/mole°K (only 50% of the ions are involved) has been plotted into Fig. 6. It seems to approach  $C_M$  at 4°K in a reasonable manner. We then have calculated  $C_M - C_S$  and obtain what looks like a smeared-out cooperative anomaly with a maximum at 3.2°K (cf., Fig. 6). The appearance of the anomaly is rather similar to those observed for cerium and neodymium<sup>8</sup> and which have been attributed to antiferromagnetic transitions.

The entropy under the  $C_M - C_S$  curve is 95 mJ/mole°K. This is relatively close to the value  $0.020R \ln 2 = 115$  mJ/mole°K to be expected if the anomaly corresponds to magnetic ordering in 2.0% of the sample. We thus have here some independent evidence for ferromagnetic clusters in praseodymium as proposed by Bleaney.<sup>18</sup> Of course, our analysis is very approximate, but until new measurements become available, especially above 4°K, it is impossible to obtain more definite proof from heat-capacity data. At this point it should also be admitted that susceptibility measurements<sup>19</sup> give no indication of ferromagnetic domains. At the moment, the cluster hypothesis must be regarded only as a possibility for explaining  $C_N$  and  $C_M$  of praseodymium.

#### IV. NEODYMIUM

##### 1. Results

Our neodymium sample was also purchased from Research Chemicals and machined and handled in a manner already described for praseodymium. The metal ingot was 4.4 cm long, 2.8 cm in diameter, and its weight was 193.54 g (= 1.3418 moles). It was covered with 0.02 g of Krylon. The following metallic impurities were found in a spectrographic analysis at Argonne

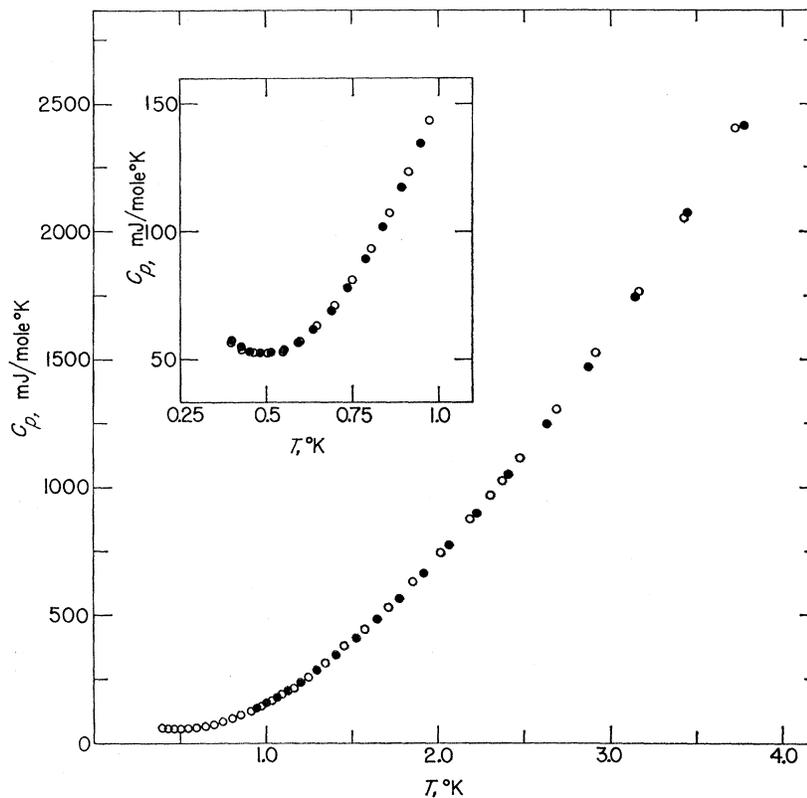


FIG. 7. The specific heat of neodymium metal. O, first experiment; ●, second experiment. The inset shows results below 1°K on a larger scale. Points from the first experiment only have been plotted to the main graph below 1°K.

(weight %): Al, 0.015%; B, 0.0045%; Ba, 0.0045%; Fe, 0.065%; Gd, 0.002%; K, 0.002%; Na, 0.050%; Ni, 0.0015%; Ta, 0.12%; Y, 0.0015%; and trace amounts (total 0.0028%) of Ca, Cr, Er, La, Li, Lu,

Mg, Sc, Sr, and Zn. In a chemical analysis, it was detected: H, 0.0012%; C, 0.025%; N, 0.070%; O, 0.13%; and F, 0.004%. The spectrographic analyses are accurate by a factor of two and the chemical analyses by about 10%. X-ray diffraction patterns indicated only lines corresponding to hexagonal structure at room temperature.

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

$T$ (°K)	$C_p$	$T$ (°K)	$C_p$	$T$ (°K)	$C_p$
Experiment I		2.0182	743.1	0.8378	102.3
		2.1848	873.7		117.7
Run I		2.3713	1026		135.0
0.3966	56.76			1.0048	155.4
0.4273	54.32	Run II		1.0649	177.6
0.4632	53.02	2.3036	968.6	1.1284	204.1
0.5039	52.89	2.4771	1115	1.2033	237.7
0.5476	53.89	2.6874	1301	1.2965	282.5
0.5964	57.67	2.9193	1522	1.4060	340.6
0.6470	63.66	3.1631	1765	1.5227	407.2
0.6979	71.55	3.4295	2050	1.6451	481.0
0.7499	81.46	3.7236	2404	1.7731	563.5
0.8030	93.46			1.9104	661.5
0.8573	107.7	Experiment II		2.0629	772.8
0.9129	123.8	0.3982	57.98	2.2231	897.7
0.9731	143.7	0.4240	55.40	2.4088	1051
1.0331	165.9	0.4509	53.89	2.6301	1249
1.0924	188.5	0.4801	53.21	2.8712	1470
1.1611	218.7	0.5133	53.28	3.1421	1743
1.2459	258.0	0.5503	54.16	3.4476	2069
1.3462	308.8	0.5913	57.09	3.7729	2414
1.4574	370.6	0.6370	62.26		
1.5780	443.5	0.6857	69.49		
1.7101	526.8	0.7353	78.62		
1.8578	628.4	0.7857	89.48		

Our specific heat results for neodymium are presented in Table II and Fig. 7. The two experiments are completely independent except that they were done in the same cryostat. The sample was warmed to room temperature between them and a different carbon thermometer was used in each case. The agreement is at 0.4°K, 2.1% and between 0.6 and 4°K, 0.7% or better.

When compared with the present data, the results of Parkinson, Simon, and Spedding<sup>8</sup> are 20% lower at 2°K, 12% lower at 3°K, and 3% lower at 4°K. On the same grounds as was already discussed for praseodymium, we feel that the agreement is satisfactory. Unpublished measurements on the specific heat of neodymium by Dempsey, Gordon, and Soller<sup>20</sup> have also been at our disposal in the form of a graph showing the experimental points. (We are indebted to these authors for making the data available to use.) Their results are everywhere above ours, the differences being about 20% at 0.4°K, 30% at 1°K, 6% at 2°K.

<sup>20</sup> C. W. Dempsey, J. E. Gordon, and T. Soller (private communication).

9% at 3°K, and 13% at 4°K. In view of the fact that these investigators measured a large number of points in this temperature range and that no hysteresis effects associated with the peaks at 7 and 19°K have been observed,<sup>8</sup> the discrepancies are rather surprising since they are well outside the experimental error.

## 2. Discussion

The magnetic specific heat of neodymium is very large even at 1°K. No simple power series can be found to fit the data over any extended temperature range. It is thus impossible to determine  $C_L$  and  $C_E$  from our results and we are again forced to use estimated values<sup>6</sup>:  $\theta=157^\circ\text{K}$ ,  $C_L=0.502T^3$ ,  $C_E=10.5T$  ( $C_L$  and  $C_E$  in mJ/mole°K).  $C_N$ , however, can be calculated from our measurements with fair precision. If the experimental points (Table II) between 0.4 and 2°K are used in a least-squares analysis, in which the linear term in the expression for  $C_p$  is fixed to  $10.5T$  and the coefficients of the  $T^3$  and  $T^{-2}$  terms are allowed to float, we obtain  $C_N=10.2T^{-2}$  mJ/mole°K. By using only points below 1.5°K or below 1.0°K we find  $C_N=8.3T^{-2}$  and  $C_N=7.4T^{-2}$ , respectively. When the temperature range is shortened, the experimental points naturally fit much better to the calculated curve. By allowing also the linear term in  $T$  to float we obtain between 0.4 and 1.0°K

$$C_p=125.7T^3+22.5T+6.4T^{-2} \quad (8)$$

(in mJ/mole°K). This relation fits the experimental points below 1°K within 1%. On the basis of these calculations we adopt for the nuclear specific heat of neodymium  $C_N=7T^{-2}$  mJ/mole°K. The estimated accuracy is 10%.

Dempsey, Gordon, and Soller<sup>20</sup> found that if successive measurements of  $C_p$  are made without warming the sample above 4.2°K,  $C_N$  increases each time even though the results are unchanged above 0.7°K. Their first run gives a nuclear specific heat which is in fair agreement with our  $C_N$  but subsequent results are up to 40% higher. Unfortunately, we learned about these peculiarities only after our measurements were completed and thus could not check whether  $C_N$  in our sample is affected by cycling between 0.4 and 4°K. This seems unlikely, however, since our two experiments agree within estimated error even though the cooling history is somewhat different. In both cases the sample was brought from room temperature to 4.2°K in about one hour with the help of exchange gas. During the first experiment, it was then cooled to 1.1°K, warmed to 2.5°K, and finally cooled to 0.33°K after which the heat-capacity measurements were begun. During the second experiment, the sample was cooled first to 2.5°K and then straight to 0.33°K. In each case it was held at 2.5°K for about 12 h for pumping out the exchange gas.

Below 7°K neodymium metal is antiferromagnetic. By assuming full electronic magnetization Bleaney<sup>10</sup>

has calculated, on the basis of ENDOR (electron nuclear double resonance) measurements by Halford,<sup>21</sup>  $C_N=14.3T^{-2}$  mJ/mole°K. This value is about twice as large as our experimental result. However, as has been pointed out by Bleaney, the crystal-field splittings in neodymium are large and one cannot expect  $\langle J_z \rangle$  in the cooperative state to tend to  $J=\frac{9}{2}$  (the ground state of Nd<sup>3+</sup> ion is  $^4I_{9/2}$ ). Our experimental  $C_N$  would give  $\langle J_z \rangle=2.2$  which is relatively close to the value  $\langle J_z \rangle=11/6$  to be expected from a cubic crystalline field of the fourth degree. However, as in the case of praseodymium, only half of the ions have their neighbors in a cubic array, the other half of them having hcp surroundings. An accurate calculation is difficult but it is qualitatively easily understood why  $\langle J_z \rangle$  should be considerably smaller than  $J=\frac{9}{2}$ . For improving the experimental accuracy in evaluating  $C_N$  and for studying possible quadrupole interactions, it is clearly necessary to extend the heat-capacity measurements to 0.1°K or lower where the other contributions to  $C_p$  finally become small.

If the observed  $C_N$  and the estimated  $C_L$  and  $C_E$  are subtracted from the total specific heat, a large magnetic contribution remains. This is caused by pronounced peaks at 7 and 19°K.<sup>8</sup>  $C_M$  accounts for 88% of  $C_p$  at 1°K and for 96% between 2 and 4°K. The thermal expansion coefficient of neodymium is also large and anomalous in this region.<sup>22</sup> Bleaney<sup>23</sup> has attempted to explain the observed  $C_M$  by a crystalline field calculation similar to that described for praseodymium (Sec. III 2). A moderate success was achieved despite the cooperative nature of the peaks at 7 and 19°K. To provide more accurate data for theoretical calculations new measurements of  $C_p$  above 4°K are in order.

A least-squares calculation for both praseodymium and neodymium gave for coefficient  $B$  [cf., Eqs. (1), (6), and (8)] a value which is rather similar in each case and which is considerably larger than  $B=10.5$  mJ/mole°K<sup>2</sup> as assumed<sup>6</sup> for the electronic specific heat. On the basis of present results it is impossible to decide whether  $C_E$  for these metals is substantially larger than our assumed value or whether the excess is entirely due to  $C_M$ . A reliable check could be made by measuring the specific heat of a neodymium sample with even-even isotopes only down to 0.1°K. For such isotopes  $C_N=0$ .

## ACKNOWLEDGMENTS

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<sup>21</sup> D. Halford, Phys. Rev. **127**, 1940 (1962).

<sup>22</sup> K. Andres, Phys. Rev. Letters **10**, 223 (1963).

<sup>23</sup> B. Bleaney (to be published).