

Specific Heat of Lanthanum, Praseodymium, Neodymium, and Samarium Metals between 3 and 25°K†

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Results of specific-heat measurements are reported for lanthanum, praseodymium, neodymium, and samarium metals in the temperature range between 3 and 25°K. The observed anomalies in the specific heat can generally be related to those found in several other physical properties of the metals. Analysis of the total specific heat C_p into its component parts is based on the assumptions that for each metal the electronic term is $C_E = 10.5T$ mJ/mole °K and that the lattice contribution is the same as for nonmagnetic lanthanum. The magnetic specific heat can thus be determined and is investigated in terms of the magnetic behavior of the various metals. Lanthanum displays anomalies at $T_\alpha = 4.88^\circ\text{K}$ and $T_\beta = 5.87^\circ\text{K}$ which are associated with superconducting transitions in the hexagonal and fcc phases of the sample. The Debye Θ below 4°K is 142°K. Praseodymium has a small hump in C_p near 3.2°K, the cause of which is not yet clear. Modifications of existing theoretical models for crystalline-field splitting of the Pr^{3+} ion ground state are suggested. For neodymium the two λ -type peaks at 7.43 and 19.55°K are discussed in relation to Schottky curves for split ground states of ions in hexagonal and cubic sites. The introduction of cooperative effects and exchange interactions would allow the Schottky anomalies to reform into the observed shapes. Samarium shows a small sharp peak in C_p at 9.57°K, the existence of which had not previously been established. This metal also has a large anomaly at 13.3°K associated with antiferromagnetic rearrangement of the ions; the magnetic entropy up to 25°K is very close to the value $\frac{1}{2}R \ln 2$.

I. INTRODUCTION

IN a study of the rare-earth metals it is generally convenient to consider separately two subgroups, the light metals of the cerium family and the heavy metals belonging to the gadolinium family. Following this scheme we present here specific-heat data on lanthanum, praseodymium, neodymium, and samarium between 3 and 25°K; results for europium have already been published elsewhere,¹ and cerium has not been studied by us in the temperature range mentioned above. Data on the gadolinium subgroup have previously been published by us.²

There are four contributions to the observed specific heat C_p of the magnetic rare earths: lattice specific heat C_L , electronic specific heat C_E , magnetic specific heat C_M , and nuclear or hyperfine specific heat C_N . In nonmagnetic lanthanum only the first two contributions are observed. The magnetic contribution is caused by interactions between the localized 4f electronic spins, and C_N arises from splitting of the nuclear hyperfine levels by the magnetic field produced at the nucleus by the 4f electrons.

Previous measurements³ between 0.4 and 4°K and using the same specimens as in this research have

established the values of C_N . Until now detailed experimental work has been lacking in the region between 3 and 25°K where C_M is generally a large percentage of the total C_p . And besides, investigations of magnetic susceptibility and electrical resistivity have shown that in this region many of the rare-earth metals undergo a magnetic transition. This work was therefore undertaken in order to obtain results that could be used in quantitative calculations concerning these transitions and the low-temperature magnetic behavior of the cerium subgroup.

In Sec. II we indicate very briefly the experimental procedure, while Sec. III contains the presentation and analysis of results for the individual metals along with a comparison with earlier specific-heat data. Finally, in Sec. IV a résumé of the important observations arising out of this analysis is presented.

II. EXPERIMENTAL

Since a full description of the cryostat and measuring procedure is given elsewhere,^{1,4,5} only the most important experimental features will be presented here. Using hydrogen exchange gas, which was subsequently effectively removed by cryopumping, the sample was cooled from 300°K to about 13°K. A mechanical heat switch was then employed for reaching the starting temperature of 3°K; thus, absorption of exchange gas onto the surface of the specimen was avoided. Calibration of the germanium resistance thermometer of type

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¹ O. V. Lounasmaa, *Phys. Rev.* **143**, 399 (1966).

² O. V. Lounasmaa and L. J. Sundström, *Phys. Rev.* **150**, 399 (1966).

³ O. V. Lounasmaa, *Phys. Rev.* **134**, A1620 (1964) and other papers listed therein.

⁴ O. V. Lounasmaa and R. A. Guenther, *Phys. Rev.* **126**, 1357 (1962).

⁵ O. V. Lounasmaa, *Phys. Rev.* **133**, A211 (1964).

CG-1, manufactured by Radiation Research Co., was carried out at 43 different points, spaced about evenly in $\log T$, from 2 to 27°K. The accuracy of calibration is about 1 m°K at 3°K, 3 m°K at 10 and 20°K, and 10 m°K at 25°K. At these same temperatures the precision of the C_p values is estimated at 0.6, 0.6, 0.4, and 2%, respectively.¹ The results have been corrected for curvature due to the finite temperature increments used when measuring the specific heat; this correction was never more than 0.2%. The size of the temperature increments may be computed from the separation of successive points in Tables II and IV-VI.

III. RESULTS AND DISCUSSION

1. Lanthanum

The lanthanum sample weighed 219.089 g (=1.5772 mole); this metal was not included in the previous series of measurements by Lounasmaa³ between 0.4 and 4°K. For impurity content we refer to Table I. Two final runs were made, the results of which are given in Table II and shown in Fig. 1.

Lanthanum metal can exist in two crystalline forms: modified hexagonal (α) and face-centered cubic (β). The two anomalies observed in the C_p curve (cf. Fig. 1) near 4.7 and 5.8°K can thus be explained: they are caused by superconducting transitions in the specimen, the first in the hexagonal phase and the second in the fcc phase. The hexagonal phase has a stacking sequence ABACABAC..., with a stacking fault every fourth layer requiring a doubling of the c axis; ions in the A layers have an fcc environment whereas those in B and C layers have an hcp environment.

The present results may be compared with previous specific-heat work by Parkinson, Simon, and Spedding⁶ which showed only one peak at 4.37°K. Their data are 10% lower than the present results near 8°K and approximately 3% lower near 25°K; the specimen was reported as containing both crystal phases. A comparison can also be made with the measurements of Berman,

Zemansky, and Boorse⁷ below 6.5°K. In zero applied field they found transitions at 4.8 and 5.9°K. Their data differ from the present by about 1% below the lower peak, and because the relative concentrations of the two phases present in the samples are probably not the same, we cannot say much about the values of C_p at the peaks except that they are not inconsistent. Finnemore, Johnson, Ostenson, Spedding, and Beaudry⁸ studied a sample which was at least 95% hexagonal phase, and found a single transition in the specific-heat curve at 4.9°K. Their results are generally about 15% higher than ours. It is strange that Parkinson *et al.*⁶ found only one transition at 4.37°K, pointing to a purely hexagonal specimen, and yet have data 22% lower than Finnemore *et al.*⁸ Some doubt is thus placed

TABLE II. The specific heat of lanthanum metal (mJ/mole°K). Experimental results. (At. wt 138.91 g/mole.)

$T^\circ\text{K}$	C_p	$T^\circ\text{K}$	C_p	$T^\circ\text{K}$	C_p
Run 1					
3.1058	53.23	6.0564	228.62	4.4800	160.01
3.3601	67.50	6.1445	239.09	4.6930	181.25
3.5660	80.65	6.2290	249.55	4.7745	185.16
3.7408	93.06	6.3098	259.04	4.8574	175.62
3.8938	105.05	6.4855	282.75	4.9475	154.99
4.0306	116.50	6.9215	348.5	5.2522	167.85
4.1541	127.59	7.4575	445.0	5.6310	201.82
4.2671	138.41	7.9665	551.8	5.8000	216.23
4.3715	148.84	8.5701	696.5	5.9092	220.86
4.4682	158.76	9.1686	864.0	6.1582	241.22
4.5587	168.27	9.8187	1074.1	6.5730	295.81
4.6448	176.82	10.743	1411.6	7.1277	384.4
4.7268	183.54	11.938	1913.3	7.8876	534.1
4.8071	184.01	13.029	2429.6	8.6433	719.5
4.8919	166.85	14.019	2933.7	9.4025	938.9
4.9845	151.51	15.168	3563	10.344	1258.1
5.0991	158.02	16.522	4336	11.316	1642.4
5.2310	165.86	18.095	5275	12.301	2080.9
5.3523	175.88	19.776	6303	13.366	2595.7
5.4667	185.95	21.604	7432	14.483	3180
5.5750	196.44	23.415	8565	15.748	3887
5.6783	205.63	25.001	9615	17.206	4741
5.7764	214.24	Run 2		18.808	5707
5.8714	219.80	3.2151	59.13	20.533	6768
5.9650	222.56	3.4837	75.22	22.329	7882
		3.7855	96.52	24.039	8955
		4.1277	125.20		

TABLE I. The impurity content of specimens (in weight %).^a

Impurity	La ^b	Specimen		
		Pr ^c	Nd ^d	Sm
Ta	...	0.002	0.12	...
H	0.01	0.008	0.001	0.04
C	0.02	0.015	0.025	0.02
N	0.003	0.004	0.070	...
F	0.03	0.029	0.004	...
O	...	0.011	0.13	0.008

^a Chemical and spectrographic analyses performed at the Argonne National Laboratory.

^b Additional metallic impurities are: Al 0.001, Bi 0.001, Ca 0.002, Cu 0.005, Fe 0.002, K 0.005, Na 0.023.

^c Additional metallic impurities are: Fe 0.0015, Na 0.003, Ni 0.04.

^d Additional metallic impurities are: Al 0.015, B 0.0045, Ba 0.0045, Fe 0.065, Gd 0.002, K 0.002, Na 0.050, Ni 0.0015, Y 0.0015.

⁶ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

on the reliability of the results of Parkinson *et al.* It may be that their sample was not sufficiently pure, and furthermore, calorimetric techniques at low temperatures have greatly improved since 1950.

If, in analogy with the results found for the other rare-earth metals⁹ below 4°K, we now assume that the specific heat of the normal conduction electrons in lanthanum is $C_E = 10.5T$ mJ/mole °K, then we can obtain the lattice specific heat of this nonmagnetic metal above the higher transition. Figure 2 shows our results for Θ , which were calculated by using Beattie's¹⁰ tables

⁷ A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

⁸ D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965).

⁹ O. V. Lounasmaa, Phys. Rev. **133**, A219 (1964).

¹⁰ J. A. Beattie, J. Math. Phys. **6**, 1 (1926/27).

of the Debye function. For the normal heat capacity, averaged over the two crystal phases present, Berman *et al.*⁷ found $C_B = 10.09T$ mJ/mole °K and $\Theta = (142 \pm 3)^\circ\text{K}$ below 3°K . By assuming $C_B = 10.0T$ mJ/mole °K Finnemore *et al.*⁸ obtained $\Theta = 123^\circ\text{K}$ at 6°K . If $C_B = 10.5T$ mJ/mole °K is used in the calculations the above values of Θ change to 145°K and 124°K , respectively. Figure 2 shows that our results for Θ can be correlated with those of Berman *et al.*⁷; the dashed line indicates our estimated extrapolation of Θ to 0°K . The maximum uncertainty in C_L below 6°K is about 7%, the effect of which will be most noticeable in subsequent calculations concerning the superconducting electronic specific heat C_{E_s} .

It is likely that the lattice contributions from the α and β phases are different. Indeed, in recent experiments Finnemore and Johnson¹¹ have found the following parameters: $T_\alpha = 4.9^\circ\text{K}$, $B_\alpha = 9.6$ mJ/mole °K², and

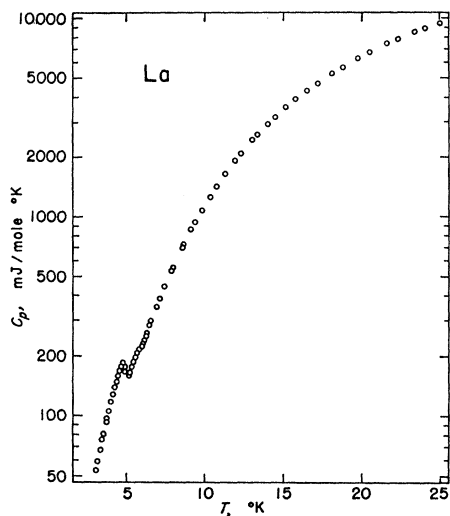


FIG. 1. The specific heat of lanthanum metal.

$\Theta_\alpha = 151^\circ\text{K}$, while $T_\beta = 6.0^\circ\text{K}$, $B_\beta = 11.3$ mJ/mole °K², and $\Theta_\beta = 139^\circ\text{K}$ (B is defined by the relation $C_B = BT$). For a specimen containing equal concentrations of α and β phases the average parameters would be $B = 10.45$ mJ/mole °K² and $\Theta = 144.5^\circ\text{K}$, quite close to our approximations. If, however, anticipating our later analysis, we adopt the concentrations 0.8 and 0.2 for α and β phases, respectively, the corresponding average values would become $B = 9.94$ mJ/mole °K² and $\Theta = 148.3^\circ\text{K}$. These average Θ 's refer to temperatures below 4°K , and we cannot say how our assumed Θ -versus- T curve (cf. Fig. 2) would be affected by introducing the results of Finnemore and Johnson.¹¹ Errors in the choice of C_B are rather unimportant since this contribution of C_p is relatively small.

¹¹ D. K. Finnemore and D. L. Johnson, Ann. Acad. Sci. Fennicae AVI, 210 (1966).

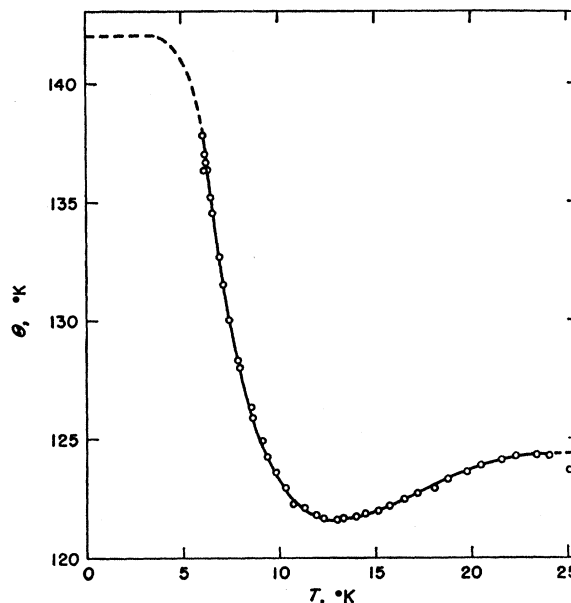


FIG. 2. The Debye characteristic temperature Θ of lanthanum. Measurements by Berman *et al.* (Ref. 7) were used for drawing the curve below 6°K .

In our approach to the superconducting state of lanthanum, we thus assume that the lattice specific heat is unaffected by the state of the metal and that below 6.1°K C_L behaves as indicated by the Debye Θ in Fig. 2. The curve in Fig. 3, which illustrates the electronic specific heat $C_E = C_p - C_L$, shows clearly the two transitions. By extrapolating C_E above and below the transitions and by choosing the transition temperatures in such a way that the entropies under the idealized curves (dashed lines) agree with the experimental values, we obtain $T_\alpha = 4.88^\circ\text{K}$ and $T_\beta = 5.87^\circ\text{K}$. The transition widths of 0.25 and 0.27°K for the α and β phases, respectively, compare favorably with the values of 0.33 and 0.26°K found by Berman *et al.*⁷

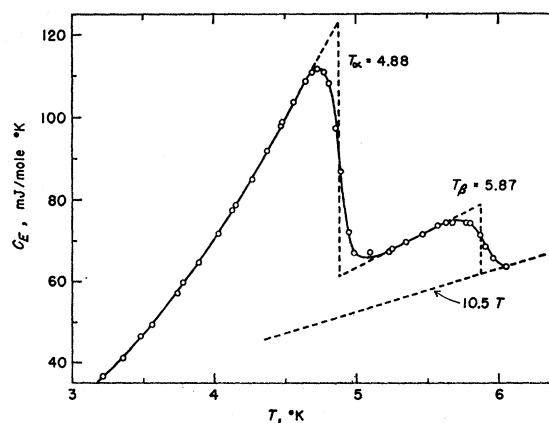


FIG. 3. The electronic specific heat C_E of lanthanum showing clearly the two superconducting transitions.

for their purest sample La III. The peak in C_E associated with the α phase is much the sharper, which is probably due to there being more of this phase in our sample.

If we assume that the electronic specific heat in the superconducting state¹² varies simply as T^3 , the present data would yield $C_{Es}=1.04T^3$ mJ/mole °K for the temperature range below 4.7°K, better agreement being obtained at the low-temperature end. However, we shall use a more general approach. We first take x and $(1-x)$ as the molar concentrations of hexagonal (α) and fcc (β) phases present. For the two crystal phases we then take $C_{Es,\alpha}=xB_\alpha T_\alpha f(t_\alpha)$ and $C_{Es,\beta}=(1-x)B_\beta T_\beta f(t_\beta)$, where $t_\alpha=T/T_\alpha$ and $t_\beta=T/T_\beta$ are the reduced temperatures and $x B_\alpha + (1-x) B_\beta = B = 10.5$ mJ/mole °K². We thus get

$$C_E = x B_\alpha T_\alpha f(t_\alpha) + (1-x) B_\beta T_\beta f(t_\beta) \quad T < T_\alpha, \quad (1)$$

$$C_E = x B_\alpha T + (1-x) B_\beta T_\beta f(t_\beta) \quad T_\alpha < T < T_\beta, \quad (2)$$

$$C_E = x B_\alpha T + (1-x) B_\beta T = BT \quad T_\beta < T. \quad (3)$$

By comparing the theoretical specific-heat discontinuities at T_α and T_β , as calculated from the above relations, with the experimentally observed discontinuities (cf. Fig. 3) $\Delta C_\alpha = 61.5$ and $\Delta C_\beta = 17.1$ mJ/mole °K, we obtain the results $f(1) - 1 = 1.48$, $x B_\alpha = 8.53$ mJ/mole °K², and $(1-x) B_\beta = 1.97$ mJ/mole °K². Finally, if we assume $B_\alpha = B_\beta$, the data indicate the relative concentrations of the two phases in our sample to be approximately 81% hex and 19% fcc.

The theoretical value of $f(1) - 1$ depends on the superconducting model chosen. The BCS theory¹³ predicts $f(1) - 1 = 1.43$; our experimental result is thus in good agreement with this theory. In the BCS model $f(t) = a' \exp(-b'/t)$, where a' and b' are constants of the order of 9 and 1.5, respectively. Using our previously determined value of $x B_\alpha$ we can, in the region between T_α and T_β , find the contribution to C_E from the superconducting fcc (β) phase. A plot of $\log[C_{Es,\beta}/(1-x)B_\beta T_\beta]$ against $1/t_\beta$ gives $a' = 12 \pm 5$ and $b' = 1.8 \pm 0.2$, where the inaccuracies arise mainly from the very short temperature range available for such a plot (cf. Fig. 3). After extrapolating the function thus found for $C_{Es,\beta}$ down to lower temperatures, we find the corresponding parameters for the superconducting hex (α) phase to be $a' \approx 20$ and $b' \approx 2.1$. Although at first sight the agreement between the two sets of results may not appear good, we must remember the approximations introduced in our initial assumptions concerning C_L and the normal C_E .

2. Method for Analyzing the Specific Heat of Praseodymium, Neodymium, and Samarium

Before we can discuss our data on praseodymium, neodymium, and samarium we must explain our method of analyzing C_p into its component parts.

It has often been remarked that the crystal structures of the rare-earth metals form two groups. The heavy metals are ordinary hcp with c/a almost constant, the mean value being 1.577. The magnetic specific heats of these metals were discussed in a previous paper by Lounasmaa and Sundström,² on the basis of the same lattice and electronic specific heats for each of them. We can similarly take account of the fact that the light rare earth metals now under consideration have a lattice similar to lanthanum (cf. Sec. III.1). Lanthanum, praseodymium, and neodymium all have the double hexagonal structure with their mean c/a ratio being 2×1.6117 , whereas samarium has a rhombohedral lattice which repeats itself after 9 layers so that its effective c/a ratio is 4.5×1.6110 . Theoretically, a useful feature of these structures is that their c/a ratios all correspond fairly closely to the value 1.633 of the ideal hcp lattice.

Because of the similarity of their lattices and outer electronic configurations, and in analogy to our treatment of the heavy metals,² we assume that C_L and C_E of the trivalent rare earths in the cerium subgroup are given by the corresponding values observed for lanthanum. Thus in the remainder of this paper we shall obtain the magnetic specific heat as follows:

$$C_M(X) = C_p(X) - C_L(\text{La}) - 10.5T - C_N(X) \quad T < 6.1^\circ\text{K}, \quad (4)$$

$$C_M(X) = C_p(X) - C_p(\text{La}) - C_N(X) \quad T > 6.1^\circ\text{K}. \quad (5)$$

Here X stands for the metal under consideration, $C_L(\text{La})$ is the lattice specific heat of lanthanum calculated from the Θ -versus- T curve in Fig. 2. $C_p(\text{La})$ was obtained from our experimental data given in Table II, and $C_N(X)$ was found from the results of previous very low temperature measurements.

Table III presents the percentage contributions of C_L , C_E , and C_M to the total specific heat C_p . In obtaining

TABLE III. Percentage contributions of C_L , C_E , and C_M to the total specific heat C_p . At and above 5°K $C_N < 1\%$.

Sample	T (°K)	C_L (%)	C_E (%)	C_M (%)	C_p (mJ/mole°K) ^a
Pr	5	14	9	77	600
	10	26	3	71	4000
	20	47	2	51	8500
Nd	5	2	1	97	4100
	10	19	2	79	5500
	20	56	2	42	11000
Sm	5	36	20	44	260
	10	45	3	52	3300
	20	85	3	12	7300

^a The values of C_p have been rounded off.

¹² See, e.g., H. M. Rosenberg, *Low Temperature Solid State Physics*, (Clarendon Press, Oxford, England 1963), p. 160 *et seq.*

¹³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957); D. Pines, *The Many Body Problem* (W. A. Benjamin, Inc., New York, 1962), Addenda.

these values no attempt was made to remove the effects of the various anomalies. It may be said, however, that for praseodymium over the whole temperature range considered here and for neodymium below 20°K the magnetic contribution is dominant, while for samarium the tendency is for the lattice specific heat to be the greatest term, particularly towards the high-temperature end. These facts will have an obvious effect on the reliability of any analysis of the magnetic specific heats.

We are now in a position to present the results and discussions on praseodymium, neodymium, and samarium metals.

3. Praseodymium

The praseodymium sample weighed 166.798 g (=1.1837 mole), slightly less, on account of repolishing, than when the same specimen was used for measure-

TABLE IV. The specific heat of praseodymium metal (mJ/mole°K). Experimental results. (At. wt 140.91 g/mole.)

$T^{\circ}\text{K}$	C_p	$T^{\circ}\text{K}$	C_p	$T^{\circ}\text{K}$	C_p
Run 1					
3.0486	185.08	11.868	5618	4.8488	546.0
3.3333	219.26	13.077	6702	5.3205	727.9
3.6462	248.19	14.414	7970	5.8395	968.0
3.9548	299.79	15.844	9362	6.4080	1279.5
4.2519	367.3	17.242	10721	7.0367	1666.8
4.5570	451.1	18.614	12069	7.7505	2170.1
4.8737	553.6	19.968	13410	8.5812	2799.1
5.2105	681.2	21.310	14712	9.5184	3553
5.5838	844.9	22.668	16022	10.538	4421
5.9746	1038.7	24.131	17431	11.607	5373
6.3676	1257.5			12.697	6377
6.7802	1509.1	Run 2		13.797	7395
7.2271	1803.1	2.6616	142.02	15.034	8577
7.7231	2149.5	2.8779	164.99	16.460	9965
8.2917	2575.4	3.1190	193.84	17.909	11380
8.9739	3111	3.3801	224.13	19.380	12830
9.8255	3811	3.6770	252.08	20.909	14319
10.789	4643	4.0194	319.3	22.445	15801
		4.4129	409.7	23.921	17208

ments⁵ below 4°K. For impurity content we refer to Table I. The results of the two final runs are given in Table IV and Fig. 4. Apart from the small hump with its maximum at around 3.2°K, the C_p curve is smooth.

The earlier results of Parkinson *et al.*⁶ show considerably more scatter than the present data; there are also systematic deviations, our values being 11% higher at 3°K, 7% lower at 7°K, and 2% higher at 15°K. In addition, Parkinson *et al.* found a broad maximum in C_p at 65°K. The present data are approximately 1% lower than was found before⁵ in the overlapping region between 3 and 4.2°K; this discrepancy is within the experimental errors quoted.

In accordance with Kramers's rule for degeneracy of ions with an even number of 4f electrons, we would anticipate that under the influence of a crystalline electric field the ground state of a praseodymium ion is

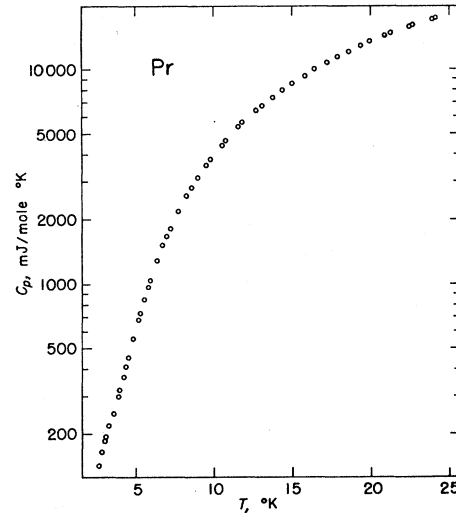


FIG. 4. The specific heat of praseodymium metal.

a singlet.¹⁴ Thus, as was pointed out by Murao,¹⁵ who used slightly different arguments, praseodymium will not exhibit any magnetically ordered phase. This proposal is further borne out by magnetic susceptibility measurements by Graf¹⁶ and Lock,¹⁷ where constancy of the susceptibility at low temperatures agrees with the predictions of the Van Vleck theory of paramagnetism characteristic of an ion with a singlet ground state.¹⁸

There have been, however, indications of antiferromagnetism in praseodymium. Chevalier and Baltensperger,¹⁹ using an *s-f* exchange model, predicted theoretically that an antiferromagnetic state would be more stable than ferromagnetic. And more recently Cable, Moon, Koehler, and Wollan²⁰ have interpreted neutron diffraction results to indicate that praseodymium has antiferromagnetic structure similar to that of neodymium (cf. Sec. III. 4). They found a Néel temperature of 25°K, but it was not established whether only ions in hexagonal (or fcc) sites were antiferromagnetically ordered, or all the ions. Further, they observed no intensity variation in the diffraction pattern between 1.4 and 4.2°K which might have corresponded to a magnetic transition at 3.2°K. Specific-heat results⁵ below 3°K show that approximately $C_M \sim T^{2.7}$, which is close to the T^3 temperature dependence predicted by the spin-wave theory²¹ for an antiferromagnet, while

¹⁴ See, e.g., the review article by K. A. Gschneidner, in *The Rare Earths*, edited by F. H. Spedding and A. H. Daane, (John Wiley & Sons, Inc., New York, 1961), p. 190 *et seq.*

¹⁵ T. Murao, *Progr. Theoret. Phys. (Kyoto)* **20**, 277 (1958).

¹⁶ P. Graf, *Z. Angew. Phys.* **13**, 534 (1961).

¹⁷ J. M. Lock, *Proc. Phys. Soc. (London)* **B70**, 566 (1957).

¹⁸ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 232 *et seq.* and p. 273; see also Ref. 12, p. 301 *et seq.*

¹⁹ J. Chevalier and W. Baltensperger, *Helv. Phys. Acta* **34**, 859 (1961).

²⁰ J. W. Cable, R. M. Moon, W. C. Koehler, and E. O. Wollan, *Phys. Rev. Letters* **12**, 553 (1964).

²¹ J. Van Kranendonk and J. H. Van Vleck, *Rev. Mod. Phys.* **30**, 1 (1958).

above the hump at 3.2°K there is definitely no simple power law describing C_M . In these calculations $C_N = 20.9T^{-2}$ mJ/mole °K was assumed.⁵

In an analysis based on the specific-heat data of Parkinson *et al.*,⁶ Bleaney²² determined the energy-level splittings due to the crystalline field at both the hexagonal and the fcc sites in the double hexagonal lattice. The energy levels are expressed as functions of the ratio $z = b_6'/b_4'$ and b_4' , where $b_4' = 60B_4'$ and $b_6' = 1260B_6'$ with B_4' and B_6' being the coefficients of the fourth and sixth degree terms in the expansion of the crystalline-field potential. Using Bleaney's expressions for the energy levels, we recalculated the associated Schottky specific heat in an attempt to find the best fit with experiment up to 170°K. It turns out that, in spite of being able to make comparison with our new results below 25°K, our best fit corresponds to $z = 0.22$ and $b_4' = 2.8$, in agreement with Bleaney's estimation from previous specific-heat data.⁶ In the temperature region from 4 to 18°K, however, the disagreement between theory and experiment is well outside the errors introduced by our approximations for C_E and C_L . (For a qualitative picture of this disagreement we refer the reader to Fig. 2 of Ref. 22.) Even if we were to assume the parameters for the hexagonal phase of lanthanum as found by Finnemore and Johnson,¹¹ the discrepancy would remain. We have decided therefore, that the model used either is wrong or requires modification. As the model now stands it appears that for the z values required to reproduce the correct order of magnitude of the total Schottky peak, the first two levels for the hexagonal ions are separated too much from the higher levels. These lower levels dominate the low-temperature side of the peak and give it a shape which is incompatible with our experimental observations.

The exact form of the hump at 3.2°K is unfortunately indeterminable with the present estimations of the magnetic specific heat. But we can say that the associated entropy is of order 100 mJ/mole °K. It is tentatively proposed that the anomaly may be of Schottky type arising from antiferromagnetic ordering of a small fraction of praseodymium alloyed with traces of other rare earths.²³ A preliminary discussion of the possible causes of this anomaly has been given by Lounasmaa.⁵ There is further experimental evidence for a magnetically ordered state of praseodymium in the presence of magnetic impurities; we are referring to measurements by Dreyfus, Lacaze, and Michel^{23a} on a $\text{Pr}_{0.27}\text{Gd}_{0.73}$ alloy. The observed C_N corresponds to almost complete electronic magnetization of praseodymium ions.

²² B. Bleaney, Proc. Roy. Soc. (London) **A276**, 39 (1963).

²³ We are grateful to Professor B. Bleaney for suggesting to us the possible significance of recent work on alloys of the rare earths by Professor W. E. Wallace of Pittsburgh.

^{23a} B. Dreyfus, A. Lacaze, and J. C. Michel, Compt. Rend. **257**, 3355 (1963).

4. Neodymium

The neodymium specimen weighed 192.827 g (= 1.3368 mole), again slightly less than before when the same sample was used for measurements⁵ below 4°K. The results for the three final runs are given in Table V and are plotted into Fig. 5. The most prominent features of the specific-heat curve are the two maxima centered at 7.43 and 19.55°K. There is also a definite shoulder near 5.4°K, which indicates the existence of an anomaly superimposed on the lower peak.

The present results for C_p are almost indistinguishable from those found previously by Lounasmaa⁵ in the region of overlap, i.e., between 3 and 4°K. Our data may also be compared with the measurements of Parkinson *et al.*,⁶ whose corresponding anomalies occurred at 7.5 and 19°K. Our results are generally higher by an amount ranging from 3 to 12%, the difference tending to 5% at higher temperatures.

The magnetic specific heat was calculated as described in Sec. III.2 by using⁵ $C_N = 7T^{-2}$ mJ/mole °K. From 1.6 to 5.4°K $C_M \sim T^2$, approximately. Janovec and Morrison²⁴ have recently analyzed Lounasmaa's⁵ heat-capacity data on neodymium below 4°K. On the basis of theoretical studies by Cooper and by Mackintosh,^{25,26} Janovec and Morrison propose the relation $C_M = AT^n \exp(-E_0/kT)$ for the magnetic specific heat and show that agreement with experimental results is obtained between 0.4 and 3°K, with the parameters $A = 1030$ mJ/mole °K, $n = 1$, and $E_0/k = 2.44$ °K. Here E_0 is the energy gap at the bottom of the spin-wave spectrum. The agreement is better than with the simple

TABLE V. The specific heat of neodymium metal (mJ/mole °K). Experimental results. (At. wt 144.24 g/mole.)

T°K	C_p	T°K	C_p	T°K	C_p
Run 1		5.6210	5116	Run 3	
3.0945	1689.0	6.2316	5576	7.4383	6612
3.3903	2003.6	6.8547	6209	7.6815	6795
3.7328	2395.9	7.4103	6987	7.9234	6632
4.0998	2892.0	7.9487	6613	8.1768	6206
4.4888	3425	8.4743	5827	8.4907	5776
4.9043	4098	9.0564	5505	8.9382	5540
5.3073	4735	9.7119	5473	9.5533	5453
5.6661	5147	10.350	5580	10.325	5556
5.9996	5405	10.978	5765	11.463	5948
6.3176	5627	11.676	6063	12.492	6460
6.6209	5865	12.535	6488	13.572	7123
6.9112	6261	13.566	7105	14.729	7912
7.1787	6764	14.812	7974	15.788	8674
7.4287	7148	16.161	9038	16.886	9653
		17.428	10125	18.006	10594
		18.391	10887	18.926	11266
Run 2		19.103	11383	19.554	11826
3.2703	1873.8	19.782	11762	20.307	11097
3.5828	2224.1	20.600	10851	21.395	10848
3.9228	2641.3	21.817	10974	22.651	11289
4.2460	3062	23.234	11570	23.961	11958
4.6208	3626	24.565	12322		
5.0931	4406				

²⁴ V. Janovec and J. A. Morrison, Phys. Letters **17**, 226 (1965).

²⁵ B. R. Cooper, Proc. Phys. Soc. (London) **80**, 1225 (1962).

²⁶ A. R. Mackintosh, Phys. Letters **4**, 140 (1963).

power law $C_M \sim T^2$, which is hardly surprising in view of the two additional adjustable parameters (n and E_g). Also, a very high electronic specific heat, $C_E = 58T$ mJ/mole $^\circ\text{K}$, had to be used in fitting the data. This would yield, at 300°K , $C_E = 17.4$ J/mole $^\circ\text{K}$ and leave, because for neodymium $C_p = 27.5$ J/mole $^\circ\text{K}$ at room temperature,²⁷ only 10.1 J/mole $^\circ\text{K}$ for the lattice specific heat, a value which is much too low. On the basis of this and because the power of T is theoretically wrong ($n = \frac{3}{2}$ for a ferro- and $n = 3$ for an antiferromagnetic metal according to the spin-wave theory²¹), it appears to us that the values of A , n , and E_g found by Janovec and Morrison²⁴ have no real significance and that the exponential factor in the expression of C_M has not been proven. Nor, however, has a simple power law been proven.

Neodymium has the double hexagonal lattice described in Sec. III.1 for lanthanum. The magnetic structure of neodymium has been investigated by Moon, Cable, and Koehler²⁸ using neutron diffraction techniques. They proposed as a good first approximation a model in which the onset of magnetic ordering occurs at 19°K with the hexagonal sites ordering in an antiferromagnetic arrangement between alternate hexagonal layers, and with a sinusoidal modulation within each layer; the cubic sites are considered as ordering antiferromagnetically at 7.5°K with a sinusoidal structure.

In an attempt to explain the observed magnetic susceptibility of neodymium,¹⁷ Arrott²⁹ has proposed that between 8 and 20°K neodymium may have a magnetic structure describable by a spin wave whose spectrum is linear in the wave vector \mathbf{q} , which results²¹ in $C_M \sim T^3$. Below 8°K there may be a combination of helical and linear spin density waves such that ferromagnetism could exist in very high fields. Thus the 7.5°K transformation is termed order-order,³⁰ while that at 19°K is order-disorder. This would also have a bearing on the somewhat different shapes of the two peaks in the specific heat.

We next consider the influence of the crystalline electric field on the ground-state multiplet, $J = \frac{9}{2}$, of the neodymium ions on hexagonal and cubic lattice sites. In this case exchange effects are apparently of more consequence³¹ than in praseodymium. Thus only an approximate level scheme has been proposed by Bleaney,³² with the following features: Ions on cubic

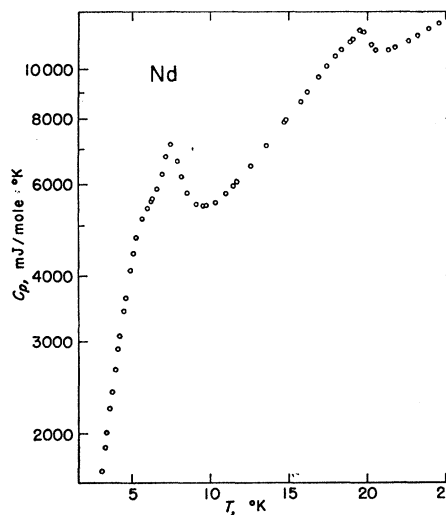


FIG. 5. The specific heat of neodymium metal.

sites have a quartet ground state, an excited doublet at 50°K , and a second quartet at 220°K , while ions on hexagonal sites have five doublets about evenly spaced up to 80°K . In order to make a qualitative comparison with our experimental results, the Schottky curve arising from such a scheme was calculated; no indication of a peak at 7.4°K was found. We are thus led to consider the suggestion³² that quadrupole-quadrupole interaction³³ splits the cubic ground-state quartet into two doublets. This splitting may be as much as 10°K .³⁴ Using this splitting and Bleaney's approximate levels given above as an initial estimate, it is found that certain features of our experimental curve are reproduced by a scheme in which the hexagonal ion levels are evenly spaced at 25°K intervals, while the cubic-ion levels have quadrupole-quadrupole splitting of 10°K , an excited doublet at 45°K , and the final quartet at 220°K (cf. Fig. 6).

We do not, of course, expect from a Schottky calculation to be able to reproduce the observed, obviously cooperative anomalies. However, it is worth noting that the individual contributions from hexagonal and cubic ions have between them the same number of humps (namely 4) as the experimental curve (cf. Fig. 6). And moreover, the theoretical and experimental humps, or peaks, occur at roughly corresponding temperatures. Variations of the level schemes were investigated in an attempt to make the humps coincide better with the observed temperatures, but with no positive success. We realized that there would be no sense in making drastic and theoretically unjustifiable alterations to the energy-level schemes. It was thus concluded that the estimation shown in Fig. 6 gives the most meaningful

²⁷ F. H. Spedding, *Progress in Nuclear Energy, Series V. Metallurgy and Fuels*, edited by Finneston (Pergamon Press, Ltd., London, 1956).

²⁸ R. M. Moon, J. W. Cable, and W. C. Koehler, *J. Appl. Phys.* **35**, 1041 (1964).

²⁹ A. Arrott, *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IIB.

³⁰ S. Araj, R. V. Colvin, and H. Chessin, *J. Less-Common Metals* **8**, 186 (1965).

³¹ See, e.g., R. J. Elliott, *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 406.

³² B. Bleaney, in *Proceedings of the Third Conference on Rare*

Earth Research (Gordon and Breach Science Publishers, Inc., New York, 1964), p. 417.

³³ B. Bleaney, *Proc. Phys. Soc. (London)* **77**, 113 (1961).

³⁴ R. J. Elliott, *Phys. Rev.* **124**, 346 (1961).

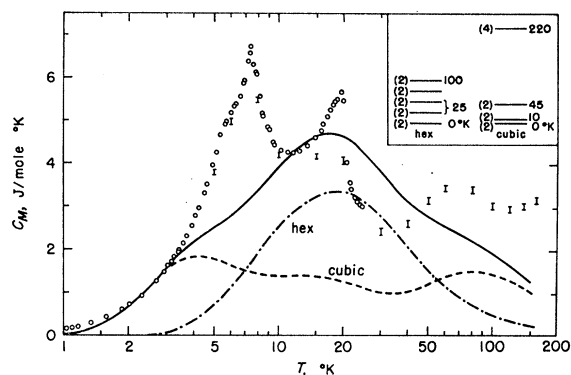


Fig. 6. The magnetic specific heat of neodymium. The circles are the present results for C_M and the bars are points obtained by subtraction of the specific heat of lanthanum from that of praseodymium, both measured by Parkinson *et al.* (Ref. 6); these latter points have been given an arbitrary error of 2% of the total specific heat. The full line shows the calculated Schottky curve for the level scheme indicated. The dashed and chained lines are the calculated curves for ions on cubic and hexagonal sites, respectively.

results. Introduction of cooperative effects, presumably stronger in the case of the cubic levels because of the hexagonal ions having ordered at 19.55°K , would cause the levels to shift with temperature. Thus we could conceivably obtain the observed peaks from the proposed level scheme. One slightly disturbing feature is that the total entropy of the experimental C_M curve up to 170°K is greater than $R \ln 5$. However, it is most likely that such a discrepancy can be accounted for by the technique of subtracting the specific heat of lanthanum as an approximation for $(C_L + C_B)$ of neodymium.

5. Samarium

The weight of the samarium sample, whose impurity contents are given in Table I, was 207.445 g (= 1.3797 mole), again somewhat less than during previous experiments³⁵ because of repolishing. The results of the four final runs are given in Table VI and are also plotted into Fig. 7. The most noticeable features are the large anomaly at 13.3°K and the sharp peak at 9.57°K .

In measurements³⁵ below 4°K it was found that one run (III) gave systematically higher results than the others (IA, IB, and II), which agreed within less than 1%. It was argued that this was perhaps due to the sample having spent less time in the anomalous region during runs IA, IB, and II than during run III, thus allowing in the later case the magnetic transformation to proceed further towards completeness. To check this idea, the cooling speed from 20 to 4°K was varied considerably in the new experiments. The result was, however, that all the new runs agreed with each other and were 1–1.5% lower than the previous runs IA, IB, and II. The discrepancy is perhaps just outside experimental errors and could still be due to thermal

³⁵ O. V. Lounasmaa, *Phys. Rev.* **126**, 1352 (1962).

hysteresis not detected during the present experiments.

Other investigations of the heat capacity of samarium are by Roberts³⁶ and by Jennings, Hill, and Spedding.³⁷ Roberts found a peak at 13.6°K and an irregularity at 9.5°K , which was just outside the experimental error. Below the large peak our data are 8 to 20% higher than hers, while above the peak the two sets of results cross and at 20°K ours are lower by 10%. Jennings *et al.*,³⁷ who made measurements above 13°K , found a λ -type anomaly, similar to that expected from magnetic ordering, at 105.8°K , and a second λ -anomaly near 13°K . Their data agree with ours to within about 2% and show conclusively that the major contribution to the entropy of samarium comes from the transition at 105.8°K .

In the absence of neutron diffraction measurements it is not clear what the detailed magnetic structure of samarium is, although the metal is apparently antiferromagnetic below 14°K . The magnetic susceptibility¹⁷ shows a maximum at 14.8°K and a kink between 110 and 150°K . In samarium,³⁸ as different from praseodymium and neodymium, the first excited J multiplet, $J = \frac{7}{2}$, is near the ground level, $J = \frac{5}{2}$, and the L - S coupling of the $4f$ electrons is weak, so that an admixing of the first two J multiplets may occur, at least at high temperatures. Moreover, samarium does not have

TABLE VI. The specific heat of samarium metal (mJ/mole $^\circ\text{K}$). Experimental results. (At. wt 150.35 g/mole.)

$T^\circ\text{K}$	C_p	$T^\circ\text{K}$	C_p	$T^\circ\text{K}$	C_p
Run 1					
3.1231	66.94	12.652	10328	8.9076	2022.6
3.4222	82.40	12.917	11719	9.6022	3392
3.7050	100.93	13.155	12401	10.194	3029
3.9999	124.78	13.386	12512	11.077	4227
		13.636	11243	11.864	6389
		13.922	9091	12.507	9601
		14.288	6922	13.015	12254
		14.807	5600	13.464	12096
Run 2					
2.9921	61.26	15.440	5341	14.003	8666
3.2832	74.74	16.082	5507	14.789	5772
3.5575	90.74	16.776	5773	15.763	5441
3.8302	110.38	17.625	6151	16.734	5754
4.1315	137.40	18.700	6654	17.825	6262
4.4551	173.98	20.018	7338	19.187	6948
4.8000	222.63	21.568	8046	20.772	7689
5.1511	284.16	23.193	8927	22.438	8523
5.4955	356.5	24.775	9882	24.084	9471
5.8616	449.1				
6.2820	574.8				
6.7480	743.4	Run 3		Run 4	
7.2914	993.0	4.3851	165.63	8.2757	1604.6
7.9081	1384.1	4.7000	207.76	8.6876	1859.3
8.5900	1781.2	5.0165	259.33	9.0455	2131.2
9.2868	2610.9	5.3325	321.17	9.3538	2509.4
9.9860	3265	5.6702	398.8	9.5732	4648
10.746	3654	6.0669	507.3	9.7505	3534
11.438	4991	6.5123	654.2	9.9760	2815.1
11.952	6657	6.9746	838.8	10.220	3062
12.340	8524	7.5325	1137.0	10.471	3330
		8.1903	1560.6	10.789	3732

³⁶ L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 434 (1957).

³⁷ L. D. Jennings, E. D. Hill, and F. H. Spedding, *J. Chem. Phys.* **31**, 1240 (1959).

³⁸ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 245 *et seq.*

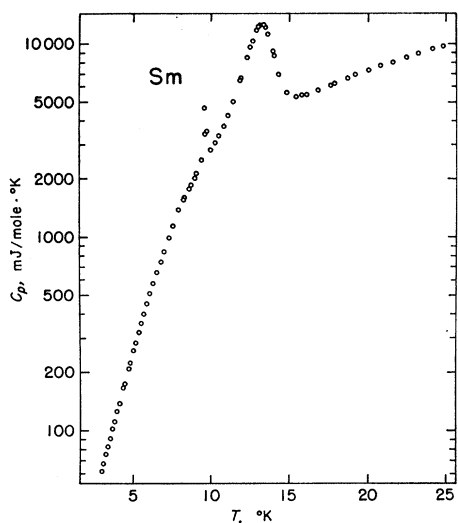


FIG. 7. The specific heat of samarium metal.

precisely the double hcp structure of the metals considered above (cf. Sec. III.2). Thus the approach used in praseodymium and neodymium for calculating C_M cannot be relied upon in the case of samarium. However, at the low temperatures considered here, it is still likely that the crystalline electric field gives rise to a Stark splitting of the ground state, ${}^6H_{5/2}$, of the samarium ion. Jennings *et al.*³⁷ found the total magnetic entropy up to 200°K to be $R \ln(2J+1)$, with $J = \frac{5}{2}$.

We have calculated the magnetic specific heat of samarium from the present and earlier³⁵ C_p data in the way described in Sec. III.2, with $C_N = 8.56 T^{-2}$ mJ/mole °K. Between 2.5 and 10°K $C_M \sim T^4$, which is contrary to the T^3 behavior of an antiferromagnet according to simple spin-wave theory.²¹ If we question the validity of the T^4 behavior, then the main source of error is probably the lattice specific heat.

The total magnetic entropy of samarium between 0 and 25°K is about 2.9 J/mole °K, which is remarkably close to the value $\frac{1}{2}R \ln 2 = 2.89$ J/mole °K. This last figure would be obtained if only half of the total number of ions and two energy levels of the same degeneracy were involved within this temperature range. It also appears that in samarium short-range order does not persist above the transformation at 13.3°K.

The entropy associated with the sharp peak at 9.57°K is only 0.064 J/mole °K. This anomaly may be caused by some impurity, which would necessarily be common to our specimen and that of Roberts.³⁶ Her temperature increments when measuring C_p were too large for providing a detailed picture of the anomaly.

IV. CONCLUSIONS

Our primary concern, apart from providing specific-heat data in the previously not intensively studied region between 3 and 25°K, has been a study of the nature and cause of each of the anomalies observed in

the specific heats of lanthanum, praseodymium, neodymium, and samarium metals. In this we have been particularly interested in the behavior of the magnetic specific heat C_M , which has been separated off from the total specific heat C_p . The assumptions on which this separation rests are that in accord with previous observations the electronic term C_E is taken as 10.5T mJ/mole °K, and that in view of the similar crystal structures of these metals we can take C_L of nonmagnetic lanthanum as representing the lattice term of all of them. It is not possible to estimate quantitatively the errors introduced by our assumptions, but since C_E is itself small it introduces little error. As is indicated in Table III, the greatest error will arise in samarium, where C_L is the dominant term.

The specific heat of lanthanum shows clearly the two superconducting transitions (cf. Fig. 3) associated with the two crystal phases present: $T_\alpha = 4.88^\circ\text{K}$ and $T_\beta = 5.87^\circ\text{K}$, which agree well with other observations on lanthanum metal.^{7,8,17} The effective Debye Θ (cf. Fig. 2), which was found after subtracting C_E from the total C_p , is consistent with the value $\Theta = 142^\circ\text{K}$ below 4°K. Analysis of the superconducting state, in which each crystal phase obeys a law of the type $C_{Es} = BT_c^2 f(t)$ [cf. Eqs. (1) and (2)], where T_c is the transition temperature, gives $f(1) - 1 = 1.48$ in good agreement with the BCS theory.¹³ It appears that our sample contained about 81% hexagonal phase.

In praseodymium the only anomaly in C_p is a small hump centered around 3.2°K with an associated entropy of order 100 mJ/mole °K. This hump may perhaps be attributed to a small percentage of the praseodymium ions being in such an environment, caused by impurities, that it undergoes an antiferromagnetic transition. Investigation of the paramagnetic Schottky curve including high-temperature results⁶ suggests modification of the theoretical model of the crystalline-field splitting proposed by Bleaney.²² In particular the theoretical behavior in the temperature range 4 to 18°K disagrees with the experimentally determined magnetic specific heat.

For neodymium we found two distinct cooperative peaks in C_p at 7.43 and 19.55°K. The best level scheme (cf. Fig. 6) for crystalline-field splitting of the ground-state multiplet, $J = \frac{9}{2}$, of the neodymium ions indicates that the ground-state quartet of the ions on cubic sites is split by quadrupole-quadrupole interaction. This is not surprising since, once the ions on hexagonal sites have ordered at 19.55°K, the field acting at the cubic sites will be considerable, thus introducing asymmetric effects.

The behavior of samarium is not yet well understood. The metal probably becomes antiferromagnetic at around 106°K,³⁹ and undergoes rearrangement of mag-

³⁹ R. M. Bozorth and C. D. Graham, Jr., *Handbook of Magnetic Materials and Their Properties*, edited by P. A. Albert and F. E. Luborsky (to be published by Reinhold Publishing Corporation, New York).

netic ordering near 14°K. The entropy associated with our observed peak in C_p at 13.3°K is strikingly close to the value $\frac{1}{2}R \ln 2$, which is difficult to dismiss as purely coincidental. Between 2.5 and 10°K $C_M \sim T^4$ is fairly well obeyed. It is suggested that the rhombohedral lattice of samarium is the key to the problem and that the lattice specific heat of this metal cannot very well be approximated by $C_L(\text{La})$. The sharp peak at 9.6°K is probably due to traces of some impurity which undergoes a magnetic transition at that temperature.

Most of the observations in this work can be correlated with results from other properties of the metals, such as magnetic susceptibility and electrical resistivity.

In comparison with previous specific-heat measurements covering the range from 3–25°K, the present work gives more accurate results, owing to improved techniques and higher-purity specimens.

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Kinetics of Oxide Film Growth on Metal Crystals : Electron Tunneling and Ionic Diffusion

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Numerical computations have been made for the growth rate of oxide and other dielectric contact films for the case of ion transport by diffusion and electron transport by tunneling. In the early phase of growth, electronic equilibrium prevails and the oxide growth rate can be limited by the diffusion of ions aided by a relatively large negative electrical contact potential V_M between metal and adsorbed oxygen. In the later phase of growth, ionic equilibrium prevails and the rate can be limited by the tunneling of electrons through the oxide aided by a positive electrical ionic diffusion potential V_D . The growth law in the early phase is of the Mott-Cabrera form, while in the later phase it is very nearly direct-logarithmic. The rather sharp transition between the two growth laws occurs at film thicknesses of the order of 20 to 30 Å, and is accompanied by a change in sign of the electrical potential across the oxide. The oxide growth rate in the early stages depends primarily on the value of the Mott potential V_M (defined as the difference in metal Fermi level and the O^- level in adsorbed oxygen) and the parameters associated with ionic diffusion. For the later stages of growth, the metal-oxide electronic work function χ_0 is the most important parameter, with the ratio of ionic boundary concentrations playing a lesser role through V_D . An increase in temperature increases the growth rate exponentially in the early growth stages, but increases the rate only moderately through V_D in the later stages.

I. INTRODUCTION

IN 1939 Mott proposed a model^{1,2} to explain the limiting-thickness behavior of the growth kinetics of thin oxide films on metals. The model was for low-temperature oxidation; the thermal excitation of electrons from the metal into the conduction band of the oxide was thus considered to be unimportant, so that electrons could penetrate the film only by the quantum-mechanical tunnel effect.^{3,4} The electron current J_e could thus be large only for oxide films less than a few tens of angstroms in thickness. The metal ions were

considered to diffuse⁵ through the oxide film, however, so that the temperature had to be high enough to allow some thermal motion of the ions. Therefore, the limits of applicability of this model are that the thermal energy kT must be sufficiently low relative to the metal-oxide work function to eliminate thermionic emission but large enough relative to the activation energy for ionic diffusion to allow thermal motion of ions. This requires in general that the electron metal-oxide work function χ_0 for the system be larger than the activation energy W for ionic motion, assuming no drastic differences in the pre-exponential factors.

Neglecting the effect of electric fields, the ionic current for this model according to Mott is given by

$$J_i = -D_i dC_i/dx, \quad (1.1)$$

⁵ W. Jost, *Diffusion* (Academic Press Inc., New York, 1952).

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¹ N. F. Mott, *Trans. Faraday Soc.* **35**, 1175 (1939).

² N. F. Mott, *Trans. Faraday Soc.* **36**, 472 (1940).

³ J. Frenkel, *Phys. Rev.* **36**, 1604 (1930).

⁴ A. Sommerfeld and H. Bethe, *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Springer, Berlin, 1933), Vol. XXIV/2, p. 450.