Calorimetric Investigation of Hyperfine Interactions in Metallic Praseodymium and Thulium†

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The nuclear specific heat due to hyperfine interactions has been measured for the rare-earth metals Pr and Tm in the temperature range 0.02–0.4 K. The results for Pr strongly support the suggestion that the electronic magnetic moments are ordered on only half the sites of the double-hcp lattice, and that this order is sinusoidally modulated in space. The maximum value of the electronic moment is 0.95 μ_B, as compared with the free-ion moment of 3.2 μ_B. The maximum hyperfine splittings are $+0.0624\pm0.0008$ and -0.0032 ± 0.0002 K for the magnetic dipolar and the electric quadrupolar interactions, respectively. The data for Tm are indicative of a magnetic hyperfine splitting of -0.1072 ± 0.0008 K, which is 5% less than expected for the fully saturated electronic moment.

I. INTRODUCTION

IN rare-earth metals, the nuclear specific heat, if present, dominates all other contributions to the heat capacity near 0.1 K. It arises through the interactions of the nuclear magnetic dipole moment and the nuclear electric quadrupole moment with the respective local fields produced by unpaired $4f$ electrons. The local magnetic field is proportional to the $4f$ moment, and thus the nuclear magnetic dipole interaction as deduced from specific-heat measurements is simply related to the magnetic order. For the heavy rare earths, the magnetic structures are considered to be fairly well known, whereas the magnetic structure of some of the light rare earths, and in particular that of Pr, are still open to question.

Pr metal has a double-hexagonal close-packed (dhcp) crystal structure in which alternate layers along the c axis have hcp and fcc nearest-neighbor environments.[1,2] The crystal field splitting of the J multiplet is such as to give singlet ground states with the first excited levels located higher in energy for the fcc sites than for the hcp sites.[2–4] Standard measurements on electrical resistivity,[3,5–7] magnetic susceptibility,[7–9] and heat capacity[10] as a function of temperature gave no indication of a transition to an ordered state. Thus, any exchange interactions were believed to be weak enough for the magnetic levels to be depopulated at temperatures well above those for which ordering would set in.

More recent results, however, are indicative of the presence of magnetic ordering. Neutron diffraction experiments gave evidence of antiferromagnetic order below 25 K.[11] The measurements were carried out on a polycrystalline sample and, therefore, were not considered to be definitive. Nevertheless, and in analogy with similar diffraction patterns obtained for the neighboring rare-earth Nd, the moments were assumed to be aligned antiparallel in alternate hexagonal layers with a sinusoidal modulation within each layer.[12] The maximum moment was found to be either 0.7 or 1.0μ_B, depending on whether the order existed on all or on only half the lattice sites. These values may be compared with the fully saturated moment of 3.2μ_B for the Pr ion. Specific-heat measurements performed above 0.4 K[13–16] indicated a hyperfine interaction with a magnitude which was in qualitative agreement with the relatively small magnetic moments detected in the neutron measurements.

On the other hand, a minimum has been observed near 4 K in the resistivity of dilute alloys of Ce in Pr which is attributed to spin-flip scattering of conduction electrons.[3] This would require an internal field of sufficiently small magnitude not to remove the spin degeneracy of the Ce ions, i.e., it would require that at least a part of the Pr ions not be ordered. A fairly consistent explanation of these diverse experimental results may be obtained from a model in which ordered electronic moments occur on only half the lattice sites.

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Indeed, estimates of crystal field splittings and the exchange interactions based on susceptibility measurements now show that ordering is likely to occur on the hcp sites but not on the fcc sites.[3,4]

For metallic Tm, the magnetic order is known with considerably more certainty. Neutron diffraction measurements on a single crystal have shown that in an antiferromagnetic region, 56–40 K, the moments are aligned along the c axis of the hcp lattice with a sinusoidal modulation repeating every seven lattice layers.[17] Below 40 K, a gradual squaring up of this modulation takes place, leading to a ferromagnetic structure where the moments in three successive layers are directed upwards, say, along the hexagonal axis and in the succeeding four layers downwards. In this fully ordered state, which is complete below about 25 K, all moments have the same value of approximately $7\mu_B$, which is close to the theoretical maximum for the tripositive ion. This model for the magnetic ordering is consistent with measurements on the saturated moment,[18,19] magnetic susceptibility,[20,21] transport properties,[22] and neutron transmission.[23] Mössbauer-effect studies[24] suggest that between roughly 30 and 56 K, the period of the sinusoidal arrangement of moments is slightly incommensurate with the lattice and results in a continuous distribution of hyperfine fields through the lattice, but at lower temperatures the fully ordered moment was also found.[25]

II. EXPERIMENTAL

The measurements were done in an adiabatic demagnetization cryostat which has been described in an earlier paper.[26] It was demonstrated empirically that the internal time constant of the calorimeter was short, i.e., that all components were in excellent thermal contact and that effects associated with heat leaks were insignificant. A magnetic thermometer (cerous magnesium nitrate) was used directly, the calibration of this thermometer reproducing to within 1% for all experiments. Temperatures were considered accurate to roughly $\pm 0.2\% \pm 10^{-4}$K and were based on the (1962) He^3 vapor-pressure scale of temperatures. The constant uncertainty of $\pm 10^{-4}$K in the thermometer calibration was due to the shape correction for the magnetic thermometer, and was determined experimentally.[27]

The heat capacity of the empty calorimeter was estimated from the quantities of materials present and, above 0.1 K, was also measured. The two values agreed within 12% at 0.5 K. The heat capacity of the calorimeter requires a correction of $\sim 1\%$ to the measurements of Pr and Tm at 0.4 K and becomes rapidly smaller towards lower temperatures. The total uncertainty in the measurements of the specific heats of Pr and Tm is believed to be within $\pm 1\%$.

The polycrystalline Pr and Tm specimens were cut from larger pieces which previously had been used by Lounasmaa in specific-heat measurements above 0.4 K.[15,28] Their masses were 9 and 11 g, respectively. The original samples, which had been purchased from Research Chemicals, Inc., were prepared from vacuum-distilled material which had been remelted and cast into tantalum crucibles in a vacuum. Their impurity content was analyzed at Argonne National Laboratory; the major impurities are given in Table I. For reasons explained in Sec. III C, the purity of the Tm specimen used in the present measurements was reanalyzed. A semiquantitative mass-spectrographic analysis gave roughly the same amounts of metallic impurities as quoted in Table I, except Ta was of order 2%. Other rare earths were present in quantities less than 10 ppm each, except for Nd (0.1%) and Dy (0.05%). The Ta content was further analyzed by activation analysis and by x-ray fluoresence spectrometry from smaller samples cut from various parts of the specimen. Ta amounts varying locally from 1 to 2% were detected. A chemical analysis on half of the specimen gave $(2.0 \pm 0.1)\%$ Ta. Using an optical microscope and an x-ray fluoresence microanalyzer, it was further confirmed that all Ta present formed separate inclusions in the Tm matrix. The differing results on the Ta content between the Argonne analysis and the present analysis may have been due to a large concentration gradient in the material after casting in the Ta cruci-

TABLE I. Impurity content of samples (% weight).

Impurity	Tm	Pr
Ta	0.12	0.002
Ni	...	0.04
Al	0.03	...
Na	0.02	0.003
Fe	0.01	0.0015
K	0.01	...
Mn	0.01	...
Ti	0.01	...
Mg	0.005	...
Cr	0.003	...
O	0.10	0.011
C	0.014	0.015
H	0.0006	0.008
N	0.20	0.004
F	0.024	0.029

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ble.[29] The Ta problem did not arise in connection with our measurements on the other rare-earth metals, presumably because of their lower melting points.

III. RESULTS

A. General

The total specific heat for rare-earth metals may be written as

$$C=C_L+C_E+C_M+C_N,$$

where the individual terms represent the lattice, electronic, magnetic and nuclear contributions. Estimating $C_L+C_E+C_M$ from measurements made at helium temperatures for Pr[13–16] and for Tm[28,30] reveals that in both cases we measure only C_N below about 0.22 K to within our experimental accuracy of 1%.

The nuclear specific heat obtained after subtracting $C_L+C_E+C_M$[15,28] is fitted by the least-squares method to the hyperfine interaction Hamiltonian of the ordered state,[31]

$$\mathcal{H}=a'I_z+P[I_z^2-\tfrac{1}{3}I(I+1)],$$

where a' is the magnetic dipole interaction parameter $\alpha\langle J_z\rangle$, and P is the electric quadrupole parameter $\alpha\langle J_z^2-\frac{1}{3}J(J+1)\rangle$. Here, I_z and J_z are the nuclear and electronic quantum numbers. The sign of P is determined directly from the data, whereas the sign of a' is calculated from the known sign of the nuclear magnetic moment and the electronic state of the ion.[31] Both Pr and Tm have only one isotope, which simplifies the analysis. In the nuclear ground state, Tm^{169} has spin $I=\frac{1}{2}$ and thus no quadrupole moment, i.e., $P=0$, and the hyperfine energy-level scheme consists of two levels with separation a'. Pr^{141} has nuclear spin $I=\frac{5}{2}$, and the energy level scheme is more complicated, as discussed below.

B. Praseodymium

The results for Pr are presented in Fig. 1 and Table II. The figure also includes the low-temperature data obtained by Trolliet[30] and Lounasmaa.[15] The latter are 15% lower than the present data, but display the same temperature dependence. Large discrepancies between rare-earth specific-heat data of different groups have been common above 0.5 K and are generally associated with magnetic impurities. This cannot, however, explain the present disagreement of 15%, as the sample materials in the two experiments were the same. In our measurements on five other rare-earth metals,[26,32] the agreement with Lounasmaa was good, and thus the reason for the present discrepancy is not obvious. Our thermometer calibrations, as well as the rest of the experimental set up, remained unchanged for all experiments. No effects of thermal or magnetic history were observed.

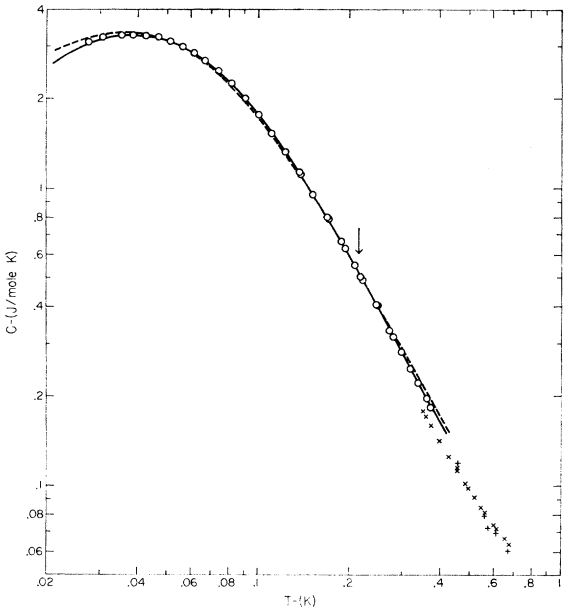

FIG. 1. Nuclear specific heat of Pr versus temperature. ○, present results; ×, Lounasmaa (Ref. 15); +, Trolliet (Ref. 30). The arrow indicates the temperature above which $C-C_N(=24.4T+4.53T^3$ mJ/mole K) is greater than 1% of C. The solid curve represents the best fit to the present data assuming a sinusoidal hf field as explained in the text; the broken curve is the best fit assuming a constant hf field with $a'=+0.0470$ K and $P=+0.0013$ K.

Recently it has been reported[33] that an fcc phase of Pr has been stabilized at room temperature and below. From susceptibility and heat-capacity measurements it was concluded that this phase is paramagnetic above about 8.7 K and exhibits ferromagnetic order below 8.7 K with a moment of $0.7\mu_B$. It was further proposed

TABLE II. Measured specific heat of metallic Pr in J/mole K.

T(K)	C	T(K)	C
0.0353	3.268	0.1881	0.660
0.0386	3.277	0.2085	0.550
0.0425	3.258	0.2220	0.489
0.0468	3.205	0.2460	0.402
0.0513	3.117	0.2724	0.331
0.0562	2.991	0.2985	0.281
0.0614	2.845	0.3184	0.247
0.0669	2.683	0.3380	0.222
0.0738	2.469	0.3606	0.196
0.0817	2.239	0.3716	0.183
0.0906	1.998	0.1380	1.114
0.1005	1.763	0.1708	0.783
0.1114	1.532	0.1938	0.625
0.1232	1.323	0.2186	0.502
0.1368	1.129	0.2466	0.401
0.1523	0.947	0.2800	0.315
0.1693	0.794	0.0275	3.100
		0.0305	3.222

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that various anomalous effects as seen in magnetic and specific-heat measurements on Pr may have been caused by the presence of varying amounts of ferromagnetic clusters of the fcc phase. To explain the present discrepancy, a minimum of an additional 15% of this phase is needed in the specimen of the present measurements relative to that used by Lounasmaa. This possibility cannot be ruled out on the basis of the heat-capacity measurements alone, but in an x-ray crystallographic analysis only lines corresponding to the hexagonal structure were found.

On the basis of entropy considerations it is qualitatively seen that only half of the Pr ions are in a hyperfine field. The argument is based on the fact that, for the ratios of a'/P appropriate for rare earths, roughly half of the total nuclear-spin entropy $R\ln(2I+1)$ is removed in cooling to temperatures corresponding to the maximum of the Schottky anomaly. Thus it is possible to extract the approximate spin entropy even though the entire specific-heat curve has not been obtained. For Pr, this part of the spin entropy is close to $\frac{1}{4}R\ln(2I+1)$.

We are therefore led to assume that only half of the lattice sites are in an ordered state and to fit the data to a nuclear energy-level scheme with a sinusoidal distribution of hyperfine fields as suggested by neutron diffraction, namely,

$$\mathcal{H}=I_z\hat{a}'\sin\theta+\hat{P}\left\{\left[\left(\frac{\hat{a}'}{a_s'}\right)J\sin\theta\right]^2-\tfrac{1}{3}J(J+1)\right\}\times[I_z^2-\tfrac{1}{3}I(I+1)].$$

Here, a_s' is the magnetic hyperfine interaction parameter expected for a fully saturated electronic moment, and has been calculated by Bleaney[31] for the ion in the metal by using EPR data on Pr^{3+} in an ionic salt ($a_s'=+0.210\pm0.002$ K). An excellent fit to our data is obtained with

$$\hat{a}'=+0.0624\pm0.0008\text{ K},$$
$$\hat{P}=+0.00061\pm0.00004\text{ K}.$$

The uncertainties quoted are the standard deviations for the parameters. The value for the maximum amplitude of the magnetic hyperfine interaction corresponds to $0.95\mu_B$, in agreement with the neutron diffraction experiments.

The shape of the nuclear-specific-heat curve measured for the neighboring rare-earth metal Nd is not compatible with a sinusoidal distribution in the hyperfine fields, but points rather to a structure with all electronic moments on equivalent sites having attained the same magnitude.[32] This magnitude is approximately equal to the maximum amplitude of the sinusoidal arrangement deduced from the neutron diffraction measurements at higher temperatures,[17] and is explained as a gradual squaring up of the modulation of the moments with reduction in temperature. A similar change in the modulation is known to occur for the heavy rare earths Er [34] and Tm.[35] Such a change in the order does not seem to occur in Pr. At 1.6 K, which was the lowest temperature measured in the neutron diffraction experiments, the magnetic specific heat of Nd is an order of magnitude larger than that of Pr,[28] which indicates a more stabilized structure in the latter case.

No agreement between the present measurements and a model which includes magnetic ordering on *all* lattices sites, whether modulated or unmodulated, can be obtained. This has already been noted above simply on the basis of entropy calculations. In the present temperature range of 0.025–0.4 K, the resolution between a sinusoidal and a constant distribution of hyperfine fields on half the lattice sites is not good (Fig. 1); nevertheless, the former case is clearly favored. The residual deviation per point, on the average, is three times larger for a fit assuming a uniform hyperfine field than for a modulated field.

C. Thulium

The results for Tm are presented in Fig. 2 and Table III. For comparison, the low-temperature data

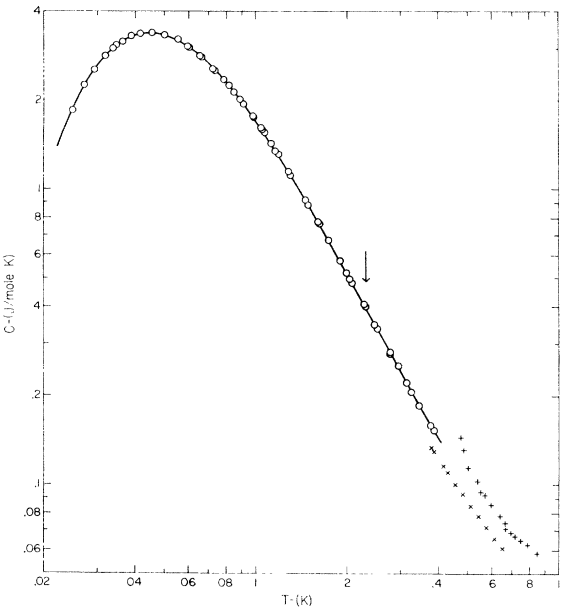

FIG. 2. Specific heat of Tm versus temperature. ○, present results; ×, Lounasmaa (Ref. 28); +, Trolliet (Ref. 30). The arrow indicates the temperature above which $C-C_N(=17.9T+2.84T^3$ mJ/mole K) is greater than C by 1%. The solid curve represents the optimum fit $a'=-0.1072$ K, the Schottky curve being scaled by the factor 0.950, as explained in the text. In these figures, clusters of data have been represented as a single point, for clarity.

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TABLE III. Measured specific heat of metallic Tm in J/mole K.

T(K)	C	T(K)	C
0.0339	3.065	0.0249	1.888
0.0363	3.210	0.0271	2.302
0.0389	3.373	0.0293	2.604
0.0417	3.437	0.0318	2.890
0.0454	3.463	0.0347	3.157
0.0500	3.407	0.1489	0.899
0.0552	3.286	0.1737	0.684
0.0604	3.080	0.1990	0.530
0.0662	2.867	0.2306	0.408
0.0733	2.580	0.2530	0.344
0.0814	2.303	0.2785	0.284
0.0885	2.063	0.3146	0.226
0.0974	1.809	0.1300	1.135
0.1068	1.577	0.1461	0.936
0.1165	1.371	0.1606	0.788
0.0597	3.111	0.1744	0.681
0.0657	2.880	0.1897	0.585
0.0721	2.627	0.2081	0.491
0.0784	2.399	0.2283	0.416
0.0846	2.170	0.2474	0.355
0.0909	1.983	0.2779	0.287
0.0975	1.798	0.2951	0.257
0.1041	1.643	0.3266	0.212
0.1050	1.624	0.3781	0.162
0.1133	1.458	0.3821	0.156
0.1193	1.341	0.3460	0.189
0.1283	1.166	0.2054	0.506
0.1627	0.778		

of Trolliet[30] and Lounasmaa[28] are included in the figure. The disagreement between the three measurements is appreciable in both the magnitude and the temperature dependence of the specific heat.

The present data can only be made to fit the Schottky anomaly expected for a two-level energy scheme if $(95.0\pm0.8)\%$ of the specimen (by weight) is assumed to contribute to C_N, i.e., if all points in the figure are shifted vertically to a 5% higher value. (The Schottky anomaly is only a function of a'/T for Tm, and thus all curves have the same maximum height when plotted in Fig. 2, independent of the value of a'.) With such a shift, an excellent fit is obtained with $a'=-0.1072 \pm 0.0008$ K, as is reflected by the small standard deviation. The data were obtained from two separate runs with separate thermometer calibrations and with the specimen remounted between runs. The sample was also run after exposure to magnetic fields <10 G and $>10^4$ G. All data are included, and no difference can be detected between the various runs. The 2% of Ta impurity has been subtracted from the weight of the specimen, the Ta itself having only a negligible specific heat in this temperature range.[36]

The value of $a'=-0.107$ K agrees well with Mössbauer[25] and neutron transmission[23] measurements which gave $a'=-0.105$ and -0.103 K, respectively. From atomic beam measurements, Bleaney has calculated the value $a'=-0.113$ K[31] for the fully saturated ion in the metal.

IV. SUMMARY

The measured nuclear specific heat of Pr has been found to agree with a sinusoidally modulated, antiferromagnetic arrangement of electronic moments present at only half the lattice sites of the dhcp structure, as suggested by neutron diffraction experiments. The maximum moment $0.95\mu_B$ is reduced far below the free-ion value and is found to be in good agreement with the neutron diffraction result. The data on Tm, ignoring a constant shift of 5% in the data, yield a hyperfine splitting in close agreement with Mössbauer and neutron transmission measurements and corresponds nearly to the fully saturated electronic moment on each ion. The required 5% shift remains unexplained.

Specific-heat measurements on rare-earth metals at He temperatures have proved to be remarkably irreproducible due to impurity effects. Our data on Pr and Tm are also in poor agreement with earlier calorimetric measurements at the high-temperature end of the data where comparison is possible. This is contrary to our measurements on Ho, Tb, Nd, Sm, and Dy, where agreement with earlier data is generally good. Nevertheless, whenever other types of measurements are possible on the rare-earth metals, the hyperfine parameters are found to agree closely with the results of our low-temperature calorimetric determinations.

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