Specific Heat of Gadolinium and Ytterbium Metals between 0.4 and 4°K*

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The heat capacities of gadolinium and ytterbium metals have been measured between 0.4 and 4°K in a He⁸ cryostat. For gadolinium, in qualitative agreement with earlier results, anomalous humps were observed in C_p at 1.1, 1.6, and 3.7°K. The ground state of the Gd³⁺ ion is ${}^8S_{7/2}$ and consequently, due to zero orbital angular momentum of the $4f$ electrons, the nuclear specific heat is small. The observed C_p is much larger than one would expect for the metal alone; the excess entropy could be attributed to magnetic ordering of Gd^{3+} ions in the Gd_2O_3 impurity (0.54% of oxygen in our sample). The specific heat of ytterbium, between 0.4 and 4°K, can be expressed accurately by $C_p(mJ/mole^{\circ}K) = 1.180T^3 + 2.90T + 0.012T^{-2}$. The lattice specific heat corresponds to a Debye $\theta = 118.1^{\circ}\text{K}$, which is considerably lower than the value $\theta \sim 160^{\circ}\text{K}$ observed for other higher rare earths. The electronic specific heat of ytterbium $C_E = 2.90T$ is also much smaller than the usual value $C_{\mathcal{B}}\sim 10T$. In the nonmagnetic ytterbium metal the 5d electron, normally in the conduction band, is added to the $4f$ shell which thereby becomes full. This explains the differences between the specific heat of ytterbium and of the other rare earths. The small term in C_p proportional to T^{-2} , is probably caused by long-range exchange-type coupling between the electronic moments of rare-earth impurities in our ytterbium sample.

I. INTRODUCTION

IN addition to the usual lattice and electronic contributions, $C_L = AT^3$ and $C_E = BT$, respectively, the N addition to the usual lattice and electronic conspecific heat of most rare-earth metals at low temperatures has two other terms. These are the magnetic specific heat C_M , caused by interatomic exchange interaction between the 4/ electronic spins, and the nuclear specific heat C_N . In many cases C_N can be easily observed if experiments are carried out below 1° K where the other contributions to C_p are small. Such measurements have recently been reported for a number of rare earths.¹⁻¹¹ The results, together with theoretical calculations¹² and with electron paramagnetic resonance measurements on dilute rare-earth salts, show that C_N is mainly caused by interaction between the nuclear magnetic moment and the intense effective magnetic field *Heu* (several MG) produced by the orbital angular momentum of the $4f$ electrons. Smaller contributions to H_{eff} are due to the spin angular momentum of the $4f$ electrons and to polarization of the conduction electrons. For some metals, the effect of nuclear electric quadrupole coupling has also been observed.9-11

In this paper measurements of the specific heat of gadolinium and ytterbium between 0.4 and 4°K are reported. The orbital angular momentum of the $4f$ electrons is zero for both of these metals and a small *CN* would thus be expected.

The heat capacity of gadolinium has previously been measured between 0.2 and 6°K by Kurti and Safrata¹ and between 1.3 and 5°K by Crane.¹³ Both these experiments revealed anomalous humps in *Cp* which are probably caused by impurities. The present measurements on gadolinium were undertaken for studying these anomalies further with a specimen of accurately known impurity content.

The specific heat of ytterbium has not been measured previously in the liquid-helium range. Such experiments are of interest for comparing the heat capacity of divalent ytterbium with that of other trivalent rare earths.

II. EXPERIMENTAL

The measurements were carried out in a He³ cryostat which has been described earlier¹⁰; only the most relevant experimental features are mentioned here. He⁴ exchange gas was used for cooling the sample down to $4.2\textdegree K$; the space surrounding the calorimeter was then evacuated and for further cooling a mechanical heat switch was employed. In this way exceedingly good insulation could be achieved and desorption of helium gas from the sample during heat capacity measurements was prevented. By pumping on He^{3} a temperature of about 0.33 °K was reached and maintained for

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48 h without recondensing. With the heat switch closed the samples were cooled from 4.2 to 0.4°K in 2-4 h. It is worth mentioning that due to the large specimens and good thermal insulation, the temperature drifts, with the heat switch open, were hardly noticeable except for ytterbium near 0.4°K where somewhat larger drifts were encountered.

For the heat capacity measurements a colloidal graphite (Aquadag) thermometer was employed. It was calibrated after every experiment against the vapor pressure of He⁴ between 4.0 and 1.9°K, against the vapor pressure of He³ between 2.0 and 0.75° K, and against a magnetic thermometer (chromium methylamine alum) between 0.75 and 0.4°K. He⁴ temperatures were determined according to the T_{58} scale.¹⁴ For He³ the temperature scale of Sydoriak and Roberts¹⁵ was employed; corrections were made for the 0.5% of He⁴ in our He³ gas and the temperatures were changed to T_{58} scale. The magnetic thermometer was calibrated against the vapor pressure of He³. In this way about 30 calibration points were determined for the carbon thermometer.

After a heating period the samples came to equilibrium in less than 5 sec. The rapid equilibrium time as well as the good thermal insulation of the calorimeter are the reasons for a very small random scatter $(\sim 0.2\%)$ of the experimental points. Systematic errors in timing (by an electronic timer using a tuning fork frequency standard), heating current, heater resistance, and the heat capacity of the empty calorimeter (measured in a separate experiment) total not more than 0.2% in the final results. The scatter of the calibration points was, with a few exceptions, less than 1 mdeg and the He⁴ and He³ calibrations joined smoothly together. The calculated temperature is thus probably within 1 mdeg of the temperature defined by the He⁴ and He³ scales. Uncertainties of about 2 mdeg can arise from the extrapolation of the magnetic thermometer calibration below 0.75°K. Aside from possible errors in the He³ temperature scale the accuracy of the present results is estimated as 0.5% between 1.5 and 4° K and 1.5% at 0.4°K. All calculations were done on an IBM-704 digital computer.¹⁶ The results have been corrected for curvature.

III. RESULTS AND DISCUSSION

1. Gadolinium

Our vacuum distilled gadolinium metal was prepared by Research Chemicals and analyses performed in our Laboratory showed the following impurities: tantalum 0.1%, other metals not detected in spectrochemical analysis; hydrogen 0.006% , carbon 0.023% ,

FIG. 1. The specific heat of our gadolinium specimen. O, run **I**; ●, run **II**.

nitrogen 0.043% , oxygen 0.54% . The sample, a cylinder 4.9 cm long and 2.8 cm in diam, weighed 242.325 g $(=1.5409 \text{ moles}).$

The experimental results are shown in Fig. 1; anomalous humps were observed in *Cp* at 1.1, 1.6, and 3.7°K. The general appearance of our specific heat curve is similar with earlier results. Kurti and Safrata¹ found a clear maximum at 1.6°K and some evidence for humps at about 1.1 and 3.3°K. Their points show large scatter above 2.5°K which was attributed to thermal hysteresis. Crane¹³ observed peaks at 1.66 and 3.4°K. His and our points scatter very little and it thus seems that the scatter found by Kurti and Safrata is due to experimental difficulties rather than thermal hysteresis. Crane demonstrated, by varying the oxygen content in his specimen, that the anomalies are most probably caused by the oxide impurity. The total excess entropy below 5°K was very close to the value *2R* ln8 to be expected from magnetic ordering of the Gd^{3+} ions in the Gd_2O_3 molecules.

We have made a similar calculation. In order to determine the excess entropy, the specific heat of pure gadolinium metal was first estimated as follows: (1) The lattice and electronic specific heats should be roughly equal to those observed for other neighboring rare earths. We have adopted $C_L(m_J/mole^{\circ}K) = 0.58 T^3$ and $C_E=10 T$, where the former is the lattice specific heat as determined by Lounasmaa and Roach¹¹ for terbium and the latter is an "average" C_E for all trivalent rare earths on which measurements have been made. (2) The magnetic specific heat can be computed, according to the simple spin wave theory, from the formula $C_M = cR(kT/2KS)^{3/2}$. Here *c* is a numerical constant which depends on the crystal structure $(c=0.028$ for hcp lattice), $K=1.8$ *k* is the exchange integral, its value being determined from magnetization measurements by Elliott, Legvold, and Spedding,¹⁷

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 12 ю ¥ Cp.J/mole $\overline{0.2}$ 0.406 $\overline{20}$ $\overline{\mathbf{6}}$ $8₁₀$ \mathbf{r},\mathbf{K}

FIG. 2. The specific heat of Gd_2O_8 (see text). \bigcirc , run I; \bigcirc , run II; \Box , Westrum and Justice (reference 19).

and $S = \frac{7}{2}$ is the ionic spin quantum number. This yields $C_M(mJ/mole^oK) = 5.2 T^{3/2}$. Theoretical calculations by Goodings¹⁸ indicate that the simple spin wave theory should be reasonably accurate for gadolinium. (3) The ground state of the Gd³⁺ ion is ${}^8S_{7/2}$ and, since the orbital angular momentum is zero, C_N should be small. From our results near 0.4°K we can write $C_N(mJ/mole^oK) \leq 3T⁻²$. This estimate, however, is very rough and a much smaller value is to be expected. For the present purposes we may put $C_N=0$.

An estimate for the specific heat of gadolinium metal between 0.4 and 4°K thus becomes: $C_p(m)/\text{mole}^{\circ}$ K) $= 0.58 T^{3} + 10 T + 5.2 T^{3/2}$. This expression yields the following values (our observed values of *Cp* are included in brackets for comparison): At 1°K , $C_p(mJ/mole^{\circ}\text{K})$ $= 15(170)$; at 2°K , $C_p = 37(260)$; and at 4°K , C_p $= 115(300)$. The excess heat capacity can now be calculated and by assuming that it is associated with the oxide, has been plotted in Fig. 2 the specific heat of Gd₂O₃. (The oxygen content 0.54% in our specimen indicates that 3.6% of the Gd atoms are in the oxide phase.) Points measured directly on an oxide sample by Westrum and Justice¹⁹ (after C_L has been subtracted) are also shown in the figure. The total entropy under the curve is 29.6 J/mole°K as compared with the theoretical value $2R \ln 8 = 34.6 \text{ J/mole}^{\circ}\text{K}$. The excess specific heat (cf. Fig. 2) appears to be removed, not at 5° K as found by Crane,¹³ but at about 80° K. This discrepancy is probably caused by the less reliable analysis of Crane's specimen.

It is clear that meaningful results on the specific heat of gadolinium metal can only be secured with samples

of exceedingly low oxide content. An important step in this direction has been made by Donald, Crane, and Zimmerman²⁰ who have prepared a zone-refined gadolinium sample and measured its heat capacity between 1.4 and 4.6° K. A peak was still observed at 3.1° K but the specific heat was markedly reduced: At 2°K, $C_p(m)/\text{mole}^{\circ}$ K) = 41 and at 4°K, C_p = 79. The latter value, which is considerably smaller than our estimated C_p for gadolinium metal, seems to indicate that the magnetic specific heat cannot be calculated by using the simple spin wave theory. By putting $C_M=0$ our estimate at 4° K becomes $C_p = 77$ in very close agreement with the experimental result quoted above.²⁰ This increases the magnetic entropy of Gd_2O_3 to 32.4 J/mole^oK in good accord with the theoretical value. The close agreement again points to magnetic ordering of the Gd^{3+} ions in Gd_2O_3 as the source of the anomalies. In view of Gooding's¹⁸ calculations the situation with C_M is quite interesting.

2. Ytterbium

Our ytterbium specimen was also prepared by Research Chemicals using vacuum distillation. It had the following impurities: calcium 0.06%, other metals not detected in spectrochemical analysis; hydrogen $0.046\%,$ carbon 0.007 $\%$, nitrogen 0.001 $\%$, oxygen 0.12 $\%$. The sample, a cylindrical ingot 4.9 cm long and 2.8 cm in diameter, weighed 204.697 g $(=1.1829 \text{ moles}).$

The experimental results are listed in Table I and also shown in Fig. 3, where *Cp/T* has been plotted against *T² .* From this figure it is clear that, except for the very lowest temperatures, only *CL* and *CE* are necessary in expressing the specific heat of ytterbium. A least-squares fit of all the experimental points into an equation $C_p = AT^3 + BT$ gave: $A = 1.178 \pm 0.001$, *B* $= 2.92 \pm 0.01$ (C_p in mJ/mole^oK, limits of error are standard deviations only). The upward trend of the points at the low-temperature end seems to suggest a term proportional to T^{-2} in C_p . By writing $C_p = AT^2$ $+BT+DT^{-2}$ the least-squares analysis gave: $A=1.180$ ± 0.001 , $B=2.90\pm 0.01$, $D=0.012\pm 0.003$. In the discussion that follows this latter expression for *Cp* has been adopted. The values of *A* and *B* are in both cases almost the same and their accuracy may be estimated as 0.5 and 1% , respectively. The precision of coefficient D is not better than 30% .

Most of the rare-earth metals are trivalent with one *3d* and two *6s* electrons in the conduction band. In ytterbium metal, however, the *5d* electron is added to the $4f$ shell which thereby becomes closed. This affects the properties of ytterbium considerably. The metal is soft, its density (7.0 g/cm^3) is considerably lower than the density of its neighbors, thulium (9.3 g/cm^3) and lutetium (9.8 g/cm³), and its crystal structure is face

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²⁰ D. K. Donald, L. T. Crane, and J. E. Zimmerman, J. Chem. (to be published).

centered cubic rather than the normal hexagonal close packed. As might be expected, the specific heat of ytterbium is also rather different from the C_p of the other higher rare earths. Its lattice specific heat corresponds to a Debye $\theta = 118.1^{\circ}$ K as compared with the usual value $\theta \sim 160^{\circ}K$; its electronic specific heat $C_E(m)/\text{mole}^\circ K$ = 2.90 $\times T$ is much smaller than C_E $\sim 10\times T$ as observed for trivalent rare earths. The removal of the *5d* electron from the conduction band thus considerably reduces the density of states at the Fermi level.

Since ytterbium is nonmagnetic $C_M=0$. The small T^{-2} term could be caused by a fraction f of the ytterbium ions being in the paramagnetic ${}^2F_{7/2}$ state with 13 electrons in the $4f$ shell. Bleaney's²¹ calculations show that our observed result may be explained by magnetic interactions between these ions if $f=0.1\%$. The T^{-2} term could also be due to long-range exchange-type coupling between the electronic moments of rare earth impurities in our ytterbium sample. This is probably a more likely explanation. Such impurities were not found

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

$T({}^{\circ}{\rm K})$	C_p	$T({}^{\circ}{\rm K})$	C_p	
Run I			Run II	
0.4275	1.418	0.3697	1.305	
0.4428	1.451	0.3864	1.341	
0.4651	1.510	0.4051	1.368	
0.4959	1.603	0.4268	1.412	
0.5355	1.734	0.4514	1.476	
0.5823	1.907	0.4781	1.554	
0.6350	2.123	0.5058	1.638	
0.6915	2.376	0.5360	1.746	
0.7494	2.654	0.5688	1.860	
0.8090	2.966	0.6043	2.012	
0.8727	3.311	0.6422	2.171	
0.9403	3.711	0.6811	2.328	
1.0109	4.170	0.7217	2,528	
1.0848	4.665	0.7652	2.736	
1.1615	5.236	0.8123	2.977	
1.2422	5.877	0.8645	3.260	
1.3283	6.629	0.9226	3.607	
1.4200	7.468	0.9850	3.990	
1.5201	8.542	1.0518	4.431	
1.6343	9.871	1.1238	4.941	
1.7626	11.586	1.2044	5.563	
1.9097	13.724	1.2924	6.296	
2.0682	16.407	1.3909	7.188	
2.2351	19.622	1.4957	8.277	
2.4120	23.460	1.6309	9.827	
2.6012	28.000	1.7562	11.387	
2.7992	34.028	1.9045	13.635	
3.0023	40.886	2.0815	16,621	
3.2097	48.643	2.2782	20.498	
3.4197	57.253	2.4883	25.335	
3.6341	67.595	2.7076	31.218	
3.8576	78.375	2.9215	38.017	
		3.1315	45.610	
		3.3404	53,958	
		3.5487	63.249	
		3.7656	73.805	
		3.9959	86.267	

FIG. 3. The specific heat of ytterbium metal. \bullet , run I; \Box , run II.

in spectrochemical analysis but the limits of detection are for rare-earth metals quite high (Tb 0.4% ; Ce, Pr, Nd, Sm 0.2%; others 0.1% or better). Lock²² has measured the magnetic susceptibility of ytterbium metal between 1.3 and 80°K. According to his interpretation the results show that although most of the atoms are in the nonmagnetic *^lS* state, one atom in 260 is in the paramagnetic ²*F*_{7/2} state. Lock's calculation, however, rests on the assumption that all contributions to the susceptibility, other than that of the $4f$ electrons, are the same in ytterbium as in lanthanum, and this seems impossible since they have different crystal structures. A more likely explanation is again that the observed paramagnetism is due to a small trace of neighboring lighter rare earth elements. Lock dismissed this possibility because an analysis of his sample showed only very small amounts of other rare earths. However, methods of detecting these metals have only very recently become reliable.

From electron paramagnetic resonance measurements on trivalent ytterbium garnets, where the metal atoms are in the ${}^{2}F_{7/2}$ state, Bleaney²³ has deduced $D=16$ mJ°K/mole as compared with our very much smaller value $D=0.012$.

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21 B. Bleaney (to be published).

²² J. M. Lock, Proc. Phys. Soc. (London) **B70,** 476 (1957).

²³ B. Bleaney, **J.** Phys. **Soc. Japan 17, Suppl. B-I,** 435 (1962).

municating their experimental results prior to publication and to Professor B. Bleaney and Dr. R. W. Hill for discussions on the origin of the T^{-2} term in ytterbium. He is also indebted to Conrad Littig for mathematical

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Ionized-impurity Scattering Mobility of Electrons in Silicon

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A quantitative, partly empirical formula for the ionized-impurity scattering mobility of electrons in silicon, derived earlier by Long and Myers from an analysis of resistivity and Hall effect data, is compared with a theoretical formula of Samoilovich, Korenblit, and Dakhovskii for this mobility, which enables one for the first time to calculate its magnitude from the known conduction band parameters of silicon. Very good quantitative agreement between the two formulas is found.

THE first detailed calculations of anisotropic electron scattering by ionized impurities in materials like *n*-type silicon and germanium have recently been HE first detailed calculations of anisotropic electron scattering by ionized impurities in materials published by Samoilovich, Korenblit, and Dakhovskii.¹ Their calculations proceed from essentially the same assumptions on which well-known earlier theories of impurity scattering were based, but they have extended the situation to account for anisotropy in the scattering.^{1,2} The explicitly stated assumptions in the SKD theory are:

(a) The energy ϵ vs wave number k relationship has the anisotropic form

$$
\epsilon = \sum_{i=1}^{3} \frac{h^2 k_i^2}{2m_i}, \quad m_1 = m_2 < m_3. \tag{1}
$$

In *n-type* silicon the effective mass parameters determined by cyclotron resonance are $m_1 = (0.192 \pm 0.001) m_0$ and $m_3 = (0.90 \pm 0.02)m_0$, where m_0 is the free-electron mass.³ The *m* value is well established, but other cyclotron resonance experiments have given $m_3 = (0.98 \pm 0.04) m_0$, although the $m_3 = 0.90 m_0$ value is probably the better. The mass anisotropy is the cause of the scattering anisotropy according to the SKD calculations.

(b) No magnetic field exists (this actually means that the field must not affect the scattering probability).

(c) The impurity potential *V* has the form

$$
V = (q^2/\kappa r)e^{-r/a},\tag{2}
$$

where κ is the dielectric constant $(\kappa = 11.7$ for Si), *q* the 3 electronic charge, *r* a radius from the ionized impurity center, and *a* the screening radius.

(d) The Born approximation applies.

1 The SKD results are expressed in terms of relaxationtime tensor components $\tau_1 = \tau_2 < \tau_3$, where the subscripts refer to the directions in the constant-energy spheroids defined by Eq. (1) .

The rigorous validity of some of the explicit and implicit assumptions in the theory is questionable for doping levels in silicon and germanium high enough to give easily observable impurity scattering,⁴ and yet the earlier mobility formulas resulting from these assumptions (e.g., the Brooks-Herring formula) have been) shown to give a very good functional description of mobility data, at least in *n*-type silicon.^{5,6} In applying the earlier formulas to the data, however, the effective mass appearing in them had to be treated as a parameter 0 to be determined empirically, since it was not clear exactly how to calculate its value from the known anisot tropic mass parameters. The SKD results now provide a means for making such a calculation, and the purpose s of this note is to do so for *n-type* silicon and then to compare the resulting impurity scattering mobility formula with the quantitative formula determined empirically in previous studies.^{5,6}

In earlier work we found by analysis of resistivity and Hall effect vs temperature data that the impurity scattering electron mobility μ_I in Si samples with doping levels up to nearly 10¹⁶ atoms per cm³ is well described

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dix of this paper gives a corrected quantitative expression for the ionized-impurity scattering mobility of electrons in Si which is believed to be more accurate than the expression given in reference 5.