

Lattice Heat Capacity of the Rare Earths. Heat Capacities of Yttrium and Lutetium from 15–350°K

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doublet state interaction, we consider a four-electron fragment $H-C'=C''$. There are two structures: the perfect pairing structure ψ_{0s} with the $H-\sigma'$ bond and a $\pi'-\pi''$ bond, and the structure $\psi_{0s'}$ with an $H-\pi''$ bond and a $\sigma'-\pi'$ bond. Here H is a $1s$ orbital on hydrogen, σ' and π' are a sp^2 -hybrid orbital and a pi orbital on carbon C' , and π'' is a pi orbital on carbon C'' . By perturbation theory, the contribution $c_{0s'}$ made by the structure ψ_{0s} is found to be

$$c_{0s'} = \frac{1}{2} \frac{[\sigma', \pi'] - [H, \pi'] + [H, \pi''] - [\sigma', \pi'']}{[H, \sigma'] - [\pi', \pi''] - [\sigma', \pi'] - [H, \pi'']} \quad (A1)$$

where $[A, B]$ is the exchange integral

$$[A, B] = \int A(1)B(2)\mathcal{C}B(1)A(2)d\tau_1d\tau_2. \quad (A2)$$

For the radical in the doublet state resulting from the

removal of the π'' electron, the corresponding coefficient $c_{0d'}$ has the form

$$c_{0d'} = \frac{1}{2} \frac{[\sigma', \pi'] - [H, \pi']}{[H, \sigma'] - [\sigma', \pi']} \quad (A3)$$

As the integrals $[H, \pi']$ and $[\sigma', \pi'']$ are both very small, the only significant difference between the formulas for $c_{0s'}$ and $c_{0d'}$ is the presence of the integral $[\pi', \pi'']$ in the denominator of Eq. (A2). With semi-empirical integrals used previously for the methyl radical¹⁴ ($[H, \sigma'] = -3.92$ ev, $[H, \pi'] = 0.75$ ev, $[\sigma', \pi'] = 1.26$ ev) and the value of -0.90 ev for $[\pi', \pi'']$, we find $c_{0s'} = -0.53$ and $c_{0d'} = -0.065$, in reasonably close agreement. For the corresponding triplet states, the effect of $[\pi', \pi'']$ is to make the coefficient $c_{0t'}$ somewhat larger than $c_{0d'}$, which compensates for the $c_{0s'}$, $c_{0d'}$ difference.

Lattice Heat Capacity of the Rare Earths. Heat Capacities of Yttrium and Lutetium from 15–350°K*

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The heat capacities of lutetium and yttrium have been measured and are found to have the same dependence on a reduced temperature as does that of lanthanum. The lattice heat capacities are given by Θ values of 130.7, 166.0, and 213.7 for La, Lu, and Y and the corresponding electronic heat capacities are given by γ values of 100, 95, and 85×10^{-4} joules/g atom-deg².

INTRODUCTION

IN order to carry out a program directed toward understanding the process of magnetic ordering in the rare-earth metals with the aid of heat capacity measurements, it is necessary to estimate the lattice and electronic contributions to the heat capacity. This estimate has been made with the aid of the heat capacity of lanthanum,^{1,2} but it is desirable to establish whether or not the form of the nonmagnetic heat capacity is the same for all rare-earth metals. Strictly speaking, the only nonmagnetic trivalent rare earths are lanthanum and lutetium, but one would expect that yttrium would have approximately the same bonding parameters and hence a lattice heat capacity

that differs only in temperature scale from that of the rare earths. We have measured the heat capacities of lutetium and yttrium and find that, to the accuracy desired for estimating the form of the magnetic heat capacity of the other rare earths, the lattice parts have the same dependence on a reduced temperature as does the heat capacity of lanthanum.

EXPERIMENTAL

We made use of the same adiabatic calorimeter employed for previous rare-earth samples.³ The sample can was essentially a copy of the can used with terbium which has also been described previously.⁴

The procedures used for the ion exchange separation of the rare-earth salts⁵ and the reduction of the an-

* Contribution No. 892. This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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¹ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

² A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

³ M. Griffel, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **25**, 75 (1956).

⁴ L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. **27**, 909 (1957).

⁵ J. E. Powell and F. H. Spedding, U. S. Atomic Energy Commission Rept. ISC-617 (1955).

TABLE I. Thermodynamic functions of yttrium
joules/(g atom-deg).

T, °K	C_p	S^0	$(H^0 - H_0^0)/T$	$(-F^0 - H_0^0)/T$
5	0.06	0.064	0.026	0.038
10	0.23	0.150	0.081	0.069
15	0.79	0.322	0.197	0.125
20	1.89	0.693	0.476	0.217
30	5.29	2.063	1.479	0.584
40	8.95	4.121	2.892	1.229
50	12.19	6.478	4.439	2.039
60	14.80	8.953	5.965	2.988
70	16.84	11.398	7.379	4.019
80	18.43	13.757	8.664	5.093
90	19.71	16.006	9.822	6.184
100	20.71	18.136	10.862	7.274
120	22.14	22.054	12.631	9.423
140	23.17	25.541	14.065	11.476
160	23.98	28.686	15.255	13.431
180	24.63	31.547	16.259	15.288
200	25.10	34.169	17.122	17.057
220	25.46	36.577	17.862	18.715
240	25.78	38.805	18.508	20.297
260	26.05	40.880	19.079	21.801
273.15	26.24	42.169	19.422	22.747
280	26.31	42.820	19.587	23.233
298.15	26.52	44.476	20.005	24.471
300	26.54	44.643	20.043	24.640
320	26.74	46.362	20.455	25.907
340	26.92	47.989	20.830	27.159

hydrous fluoride⁶ have been described previously. The metals were vacuum-cast in tantalum crucibles and machined to make a snug fit in the calorimeter can.

Spectrographic analysis showed the yttrium sample to contain impurities of Dy, Gd, Ca, Mg, and Cr but to contain not more than about 0.5% total of these metals. Vacuum fusion showed the sample to contain about 150 ppm carbon, and 250 ppm nitrogen. Chemical analysis completed since taking the heat capacity data showed the sample to contain 0.44% Ta and 0.97% yttrium oxyfluoride. The sample weighed 214.79 g.

Spectrographic analysis showed the lutetium sample to contain small amounts of Y, Sc, Yb, Tm, Ca, Cr, Fe, Cu, Si, and Mg; but to contain not more than about 0.2% total of these metals. Vacuum fusion showed the sample to contain about 100 ppm carbon and 800 ppm nitrogen. Chemical analysis completed since taking the heat capacity data showed the sample to contain 1.62% Ta and 1.97% lutetium oxyfluoride. The sample weighed 455.63 g.

The tantalum and oxyfluoride were detected by dissolving the rare-earth metal with nitric acid and analyzing the insoluble residue. The tantalum was not observed in spectrographic analyses because of interferences and the oxyfluoride gives no detectable lines. We now believe that most of the rare-earth samples whose heat capacities have been measured did contain a significant amount of tantalum. Recent analysis of the terbium and thulium samples used in measurements in

this laboratory showed them to contain small amounts of tantalum but no oxyfluoride.

RESULTS

The results of the individual measurements of $\Delta H/\Delta T$ as a function of the average temperature have been deposited with the Library of Congress.⁷

Smooth curves were drawn through the points and extrapolated to absolute zero using the low-temperature dependence of the Debye temperature of lanthanum as a guide. Representative values which were taken from these curves and corrected for the heat capacity of the tantalum and oxyfluoride impurities are given in Tables I and II. The values of the thermodynamic functions were then calculated by numerical integration and are given in Tables I and II.

Inasmuch as the tantalum and the oxyfluoride form separate phases, it is possible to correct for their presence if the individual heat capacities are known. The heat capacity of tantalum has been measured by Sterett and Wallace.⁸ Unfortunately, no data on the heat capacities of the oxyfluorides exist. The heat capacities of the oxyfluorides were estimated by the

TABLE II. Thermodynamic functions of lutetium
joules/(g atom-deg).

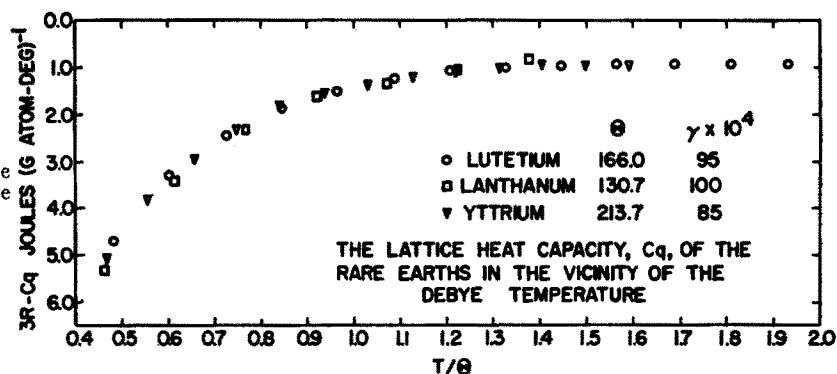
T, °K	C_p	S^0	$(H^0 - H_0^0)/T$	$(-F^0 - H_0^0)/T$
5	0.10	0.063	0.036	0.027
10	0.49	0.225	0.145	0.080
15	1.67	0.607	0.425	0.182
20	3.66	1.346	0.977	0.369
30	8.47	3.746	2.673	1.073
40	12.71	6.793	4.677	2.116
50	15.84	9.973	6.613	3.360
60	18.10	13.072	8.309	4.723
70	19.74	15.993	9.866	6.127
80	20.98	18.712	11.179	7.533
90	21.93	21.241	12.323	8.918
100	22.59	23.587	13.318	10.269
120	23.64	27.802	14.954	12.848
140	24.40	31.506	16.252	15.254
160	24.97	34.802	17.307	17.495
180	25.42	37.769	18.184	19.585
200	25.78	40.457	18.926	21.531
220	26.03	42.936	19.561	23.375
240	26.25	45.210	20.109	25.101
260	26.50	47.322	20.591	26.731
273.15	26.63	48.633	20.739	27.754
280	26.69	49.293	21.020	28.273
298.15	26.85	50.975	21.369	29.606
300	26.88	51.141	21.404	29.737
320	27.04	52.881	21.751	31.130
340	27.17	54.523	22.066	32.457

⁷ A copy of these results in tabular form may be had by requesting Document No. 6320 from the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C., and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress, Washington, D. C.

⁸ K. F. Sterrett and W. F. Wallace, J. Am. Chem. Soc. **80**, 3176 (1958).

⁶ A. H. Daane and F. H. Spedding, J. Electrochem. Soc. **100**, 442 (1953).

FIG. 1. Lattice heat capacity C_q of the rare earths in the vicinity of the Debye temperature.



following approximation, suggested by the work of Hofmann *et al.*⁹

$$C_x = n[f_D(\Theta_r/T) + f_D(\Theta_o/T) + f_D(\Theta_f/T)],$$

where C_x is the approximate heat capacity of the compound, n is the number of moles of the compound present, $f_D(\Theta/T)$ is the Debye function; and Θ_r , Θ_o , and Θ_f are estimated Debye temperatures for the rare earth, oxygen, and fluorine atoms, respectively. The Debye temperature of the rare-earth atoms was assumed to be that found for each metal in these measurements. The Debye temperatures for the oxygen and fluorine atoms were estimated by roughly averaging values found for these atoms in several compounds by Hofmann *et al.*⁹ The values used were 1000 and 650 for oxygen and fluorine, respectively. On treating the samples as mixtures of three phases, rare-earth metal, tantalum, and rare-earth oxyfluoride, the results were corrected for the presence of the tantalum and oxyfluoride impurities.

The net corrections to yttrium for the tantalum and oxyfluoride impurities varied from 0 to 0.6% of the heat capacity. The net corrections to lutetium varied from 0 to 1.3% of the heat capacity, except at temperatures below 25°K where the corrections increased to about 2%. We have estimated that these corrections for impurities are correct to 10–15% of their values. Most of the error is due to the uncertainty in the heat capacity values used for the oxyfluorides. This would mean that the corrected results could still be in error by as much as 0.1–0.2% due to the tantalum and oxyfluoride impurities.

We estimate the precision of our results from the scatter of points about the smooth curves. For yttrium this scatter did not amount to more than about 0.2% at temperatures from 30° to 300°K except for six points which were within 0.3% of the smooth curve. For lutetium the scatter did not amount to more than about 0.1% in the range 30° to 300°K except for two points which were within 0.2% of the smooth curve. The precision for both samples dropped to 0.3% at

20°K and 2% at 15°K and also dropped to 0.3% at 350°K due to increased difficulty in maintaining adiabatic conditions.

The accuracy for the data is thought to be about the same as the precision for the actual sample used. We estimate then that the error in heat capacity of either sample would not exceed about 0.3% above 30°K of which 0.1–0.2% arises from the uncertainty in the corrections for impurities. The error in the entropy at room temperature of either sample should not exceed 0.25 joules/g atom-deg of which 0.10 arises from the uncertainty in the extrapolation below 13°K. The error in the enthalpies of either sample should not exceed 0.25% above 100°K. The absolute accuracy of the results would of course be dependent upon purity conditions not corrected.

DISCUSSION

In order to reduce the results for lanthanum, lutetium, and yttrium to the same form, it is necessary to

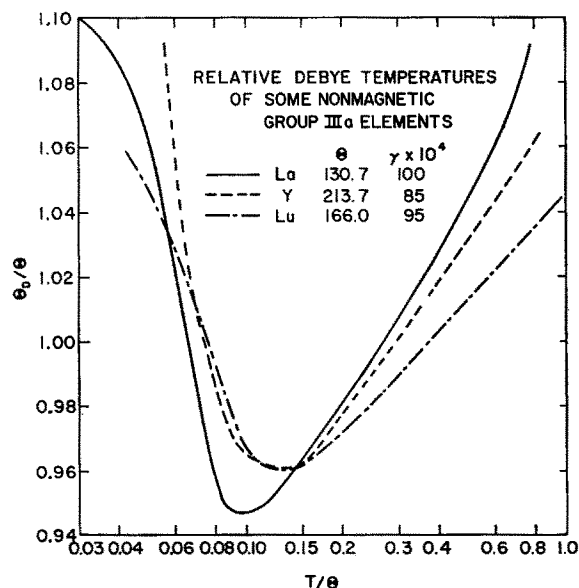


FIG. 2. Relative Debye temperatures of some nonmagnetic group IIIa elements.

⁹ J. A. Hofmann, A. Paskin, K. J. Tauer, and R. J. Weiss, *J. Phys. Chem. Solids* **1**, 45 (1956).

determine a parameter, similar to the Debye temperature, which defines a reduced temperature scale for each element. Because of its utility when dealing with the magnetic rare earths, we have chosen this parameter, Θ , as that value of the Debye temperature which yields a Debye entropy equal to the experimental lattice entropy near room temperature. Because the heat capacity is practically its classical value near room temperature, the exact temperature at which the match is made is not critical. If, instead of the entropy, the enthalpy were used, the value of Θ would be increased by about 3%, but the consistency of the results would not be modified appreciably.

Before evaluating Θ , it is necessary to establish the contribution of the conduction electrons to the heat capacity. We assume that this contribution has the form: $C = \gamma T$. Since very low temperature results are not yet available, we evaluate γ in the following way. We make the preliminary estimate that the electronic contribution is the same as it is in lanthanum and are thus able to make a first approximation to the value of Θ . We then choose a new value of γ so that the lattice heat capacity, C_θ , of La, Lu, and Y is the same function of T/Θ at temperatures near and above Θ , where the contribution of γT is appreciable. That we get good agreement over a wide range of temperature as

shown in Fig. 1 encourages us to believe that this method is valid.

Thus, having chosen a corrected value for γ , we can calculate the final value of Θ . It is then convenient to depict the lattice heat capacity by plotting Θ_D/Θ , against T/Θ , as shown in Fig. 2. Here Θ_D is the Debye temperature which yields the actual value of the lattice heat capacity at any temperature. This value may then be determined from tables of $C(\Theta_D/T)$.¹⁰ The values of Θ and γ which were used are given in the tables incorporated with the figures.

If one's primary interest is in the entropy near room temperature, the bulk of the information is contained in the curves of Fig. 2 in the range of T/Θ of 0.1 to 0.5, as the contribution at the lower temperatures is small and the contribution at higher temperatures is nearly independent of Θ . If attention is focused on the enthalpy, the important range is even smaller. It may be appreciated then, in view of the fact that a 2% difference among the curves of Fig. 2 means only a 6% difference in the heat capacity at low temperatures and less at higher temperatures, that the lattice heat capacity of La, Lu, and Y may be well described by a single function of a reduced temperature.

¹⁰ Landolt-Bornstein, *Physikalische-Chemische Tabellen*, *Erste Ergänzungsband* (Julius Springer, Berlin, 1927), p. 705.

Temperature Variation of the Linewidth in Nonresonant Microwave Absorption*

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(Received July 22, 1960)

The linewidth parameter $\Delta\nu/p$ for nonresonant microwave absorption in CH_3Cl and in CHCl_2F has been determined at five temperatures between 10° and 150°C from cavity measurements of dielectric dispersion in the gases as a function of pressure at a frequency of 402 Mc. The linewidth is found to be proportional to $T^{-1.5}$, as opposed to the $T^{-1.0}$ dependence predicted by Anderson's theory of collision broadening.

INTRODUCTION

AT all but the lowest pressures, the width of spectral lines in the microwave region is determined by collision broadening due to the effects of intermolecular collisions in the gas. The phenomenon is of general interest in that it inherently contains information about molecular force fields out to distances considerably greater than can be studied by kinetic theory methods. The line half-width $\Delta\nu$ is directly proportional to gas pressure, and the linewidth parameter $\Delta\nu/p$ is characteristic of the colliding molecules.

* This work has been supported by Office of Naval Research. The results were reported in part at the 1960 spring meeting of the American Physical Society, Washington, D. C., April, 1960.

Anderson's quantum mechanical treatment of pressure broadening¹ has been successful in treating both self-broadening in ammonia and the broadening of ammonia lines by foreign gases. Anderson's theory predicts that the line-broadening constant should vary as $T^{-1.0}$ in the case of dipole-dipole interactions and as a lower power of temperature, down to a limit of $T^{-0.5}$, for shorter range forces.

Anderson's theory has not been successful² in the prediction of the magnitude of the linewidth parameter

¹ P. W. Anderson, *Phys. Rev.* **75**, 1450L (1949); **76**, 647 (1949); **80**, 511 (1950).

² G. Birnbaum, Ph.D. dissertation, George Washington University, 1956.