

Low-temperature heat capacity of electrotransport-purified scandium, yttrium, gadolinium, and lutetium

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The low-temperature heat capacity of electrotransport-purified scandium, yttrium, gadolinium, and lutetium have been measured from 1 to 20 K. The electronic specific-heat constant γ and the Debye temperature Θ_D are determined to be 10.334 ± 0.011 mJ/g-at. K² and 354.3 ± 1.0 K, respectively, for scandium, 7.878 ± 0.004 mJ/g-at. K² and 244.4 ± 0.5 K, respectively, for yttrium, 6.380 ± 0.026 mJ/g-at. K² and 163.4 ± 0.1 K, respectively, for gadolinium, and 8.194 ± 0.016 mJ/g-at. K² and 183.2 ± 0.3 K, respectively, for lutetium. We believe that the above electronic specific-heat constants and Debye temperatures represent the intrinsic values for these four rare-earth metals. The use of the low-temperature heat-capacity results for these metals to evaluate the various contributions to the heat capacities of the magnetic lanthanide metals is examined. The total many-body enhancement factor and its components (the electron-phonon, electron-paramagnon, and spin-wave) are calculated.

I. INTRODUCTION

In the literature, the low-temperature heat-capacity results of rare-earth metals as reported by different investigators are seldom found to be in agreement with one another. This variation is primarily due to impurities, metallic as well as nonmetallic, present in the samples. The presence of minute quantity of magnetic impurities (especially iron) is known to affect the low-temperature heat capacity drastically.¹ Also, the presence of small amounts of hydrogen (of the order of a few ppm by weight) has been shown to cause a large increase in both electronic specific-heat constant γ and Debye temperature Θ_D .² In this paper, the γ and Θ_D values of scandium, yttrium, gadolinium, and lutetium which were purified by solid-state electrotransport are reported. The authors believe that the results given here are the truly intrinsic values for these rare-earth metals.

These values are also of interest to theorists since their values of γ_0 , the electronic specific-heat constant calculated from the bare density of states, are compared to the measured γ values. The comparison of γ_0 and γ helps serve as one check on the reliability of the band-structure calculations. Furthermore, the ratio γ/γ_0 gives the total enhancement factor.

II. EXPERIMENTAL PROCEDURE

A. Electrotransport

The purification of rare-earth metals by solid-state electrotransport has been discussed by Carlson and Schmidt.³ In solid-state electrotransport, the sample, in the shape of a long rod (15 cm \times 0.3 cm in diameter), is heated by internal resistance using a high-density dc electric current under either vacuum or a partial helium atmosphere. Under the electric field, many of the impurities, such as carbon, nitrogen, oxygen, and iron, migrate with the flow

of electrons to the anode end of the rod. Interstitial impurities such as oxygen, nitrogen, and carbon are fast diffusers in rare-earth metals.⁴⁻⁸ Iron group impurities (iron, cobalt, and nickel) are also fast diffusers with approximately the same velocity as carbon. Other impurities such as niobium, tantalum, and tungsten migrate at slower velocities. The rare-earth impurities and other large metallic atoms such as thorium and zirconium are not likely to move under the electric field gradient because of their similarity to the parent metal being purified.

Table I gives the experimental conditions by which scandium, yttrium, gadolinium, and lutetium were electrotransport purified. Chemical analysis of the materials before and after solid-state electrotransport are given in Tables II-V. The absolute error of the sparksource mass spectrographic analysis has been established to be within

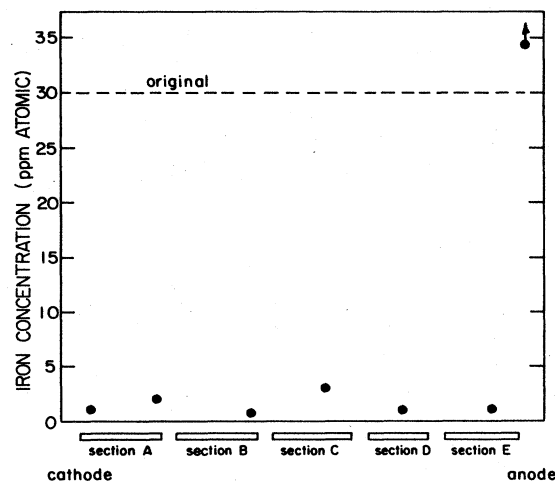


FIG. 1. Profile of Fe concentration along electrotransport-purified scandium sample 3.

TABLE I. Experimental conditions for solid-state electrotransport purification.

Sample	Time (h)	Temperature (°C)	Pressure (Torr)	Atmosphere	Current density (A/cm ²)
Scandium 1	80	1360	130	He	1300
Scandium 2	500	1275	130	He	700
Scandium 3	1225	1275	130	He	700
Scandium 4	1414	1275	130	He	620
Yttrium	466	1130	2.5×10^{-10}	vacuum	452
Gadolinium	1200	1175	130	He	1225
Lutetium	336	1110	1.6×10^{-10}	vacuum	790

$\pm \times 3$ of the reported value and relative error such as for comparison of the same element in different samples is estimated to be $\pm 50\%$. The carbon contents which were determined by combustion analysis, the oxygen, nitrogen, and hydrogen contents determined by vacuum fusion analysis, and the fluorine contents determined by absorption analysis, are accurate within $\pm 5\%$ at the concentration levels shown in the tables. Figure 1 gives the iron concentration profile in electrotransport-purified scandium, which is typical of the other rare-earth metals purified by solid-state electrotransport. As can be seen from Fig. 1, the iron migrates with the flow of electrons, i.e., from the cathode to the anode end of the specimen. Sam-

ples for heat-capacity measurements are taken from section B, and the right-hand portion (or anode end) of section A (see Fig. 1). The resistance ratios $\Gamma_{4,2} = \rho_{300}/\rho_{4,2}$, before and after solid-state electrotransport, are 32 and 355 for scandium sample 3. For the other metals $\Gamma_{4,2}$ was determined only after electrotransport purification, and the resultant values are 171 for yttrium, 149 and 314 for gadolinium, and 93 for lutetium.

B. Heat capacity

Heat-capacity measurements were carried out over the temperature range of 1–20 K using an isolation heat-pulse-type calorimeter designed for accurate measurement

TABLE II. Mass spectrometric analysis of scandium after solid-state electrotransport (in at. ppm). (All other impurity concentrations were less than 1 at. ppm. H, C, N, O, and F were not analyzed.)

Impurity	Sample (after)			
	1	2 ^a	3 ^b	4
Na	10	1.4	0.2	<0.5
Al	1	0.3	4	9.6
Si	6.6(19) ^c	<4	3	<5
S	<2(20)	<0.2	0.5	<0.7
Cl	6(100)	33	10	4
K	2	3.7	0.7	0.4
Cr	0.2	0.2	1.4	1.5
Fe	0.6(98)	0.4	1.5	2
Ni	3(30)	0.3	1.4	<1
Cu	3(36)	1.3	5	<2
Y	2	6.3	11	8
Zr	<4	0.9	1.1	<1
Nb	<3	0.8	<1	<5
La	7.8	2.3	6	10
Ce	5	<0.3	1	8
Pr	2	<0.2	0.6	1.3
Gd	16	2.6	9	3.5
Dy	1.9	<0.5	0.4	<0.7
Ho	0.47	<0.1	<0.2	1.4
Er	1.4	2.2	0.6	<0.9
Lu	<5.1	<0.4	<0.3	<0.4
Ta	23	<0.4	0.8	400
W	380	8.0	42	180

^aAverage of three analyses taken along the length of the rod.

^bAverage of six analyses taken along the length of the rod.

^cNumbers in parentheses are concentrations before electrotransport purification.

TABLE III. Mass spectrometric analysis of yttrium before and after solid-state electrotransport (in at. ppm). (All other impurity concentrations were less than 1 at. ppm.)

Impurity	Before	After
C	104 ^a	200 ^a
N	13 ^b	10 ^b
O	250 ^b	200 ^b
F	131 ^c	<0.2 ^c
Cl	2	3
Cr	2.1	<0.1
Fe	27	2
Ni	4.6	0.11
Cu	4	0.6
Zr	<3	1
La	5.3	2.7
Ce	2.8	1.5
Pr	8	3.3
Nd	<0.6	1.1
Gd	8.1	3.4
Tb	4.0	1.4
W	20	17

^aBased on combustion.

^bBased on vacuum fusion.

^cBased on absorption.

of small samples (0.5–5 g). A mechanical heat switch allows the addenda (heater, thermometer, and sample holder) and a specimen to cool down to the desired temperature by bringing them into contact with a liquid-helium pot. Good thermal contact between specimen and sample holder is facilitated by a fixed amount (6 mg) of Apiezon N grease. A detailed description of the calorimeter can be found elsewhere.⁹

A germanium resistance thermometer was chosen to measure the temperature. It was calibrated in Ames Laboratory by comparison with two standard germanium resistance thermometers GR618 and GR803. These two standard germanium resistance thermometers were calibrated against a constant-volume gas thermometer at the National Standards Laboratory, Australia, against the Na-

TABLE IV. Mass spectrometric analysis of gadolinium before and after solid-state electrotransport (in at. ppm). (H, C, N, O, and F were not analyzed. All other impurity concentrations were less than 1 at. ppm.)

Impurity	Before	After
Cl	4	2
Cr	1	<0.8
Fe	40	3
Ni	1	<0.08
Cu	4	0.8
Y	2.2	1
Ce	1.2	1
Nd	2	<0.5
Tb	6	8
Lu	4	<1
Ta	6	0.5
W	4	<1

TABLE V. Chemical analysis of lutetium before and after solid-state electrotransport (in at. ppm). (Hydrogen, nitrogen, and oxygen are from vacuum fusion analysis, carbon from combustion method, and all other elements are from mass spectrometry. Impurity not listed is less than 1 at. ppm.)

Impurity	Before	After
H	1050	<175
C	90	100
N	13	ND ^a
O	610	82
Si	<3	0.5
S	0.4	2
Cl	0.6	3
Ti	1	2.6
Fe	10	1
Ni	1	<0.2
Cu	5	<0.03
La	5.8	10
Ce	0.9	1.1
Pr	0.3	1.5
Tb	<0.8	<2
Dy	<2	1
Ta	3.3	4.0
W	20	33

^aND denotes not detected.

tional Bureau of Standards Acoustic scale (1965), and the IPTS-68 (International Practical Temperature Scale—1968) vapor-pressure scale. Temperatures were then corrected to EPT-76 (Echelle Provisoire de Temperature de 1976 entre 0,5 K et 30 K) and are correct to within ± 1 mK.

The heat capacity of the 1965 Calorimetry Conference Standard Copper¹⁰ was measured to serve as a check of the apparatus and experimental technique. A least-squares fit of the copper results give values for γ and Θ_D which deviate by less than 0.3% of the values reported by Osborne *et al.*,¹⁰ Martin,¹¹ and Cetas *et al.*¹² on the same copper standard. This gives credence to the γ and Θ_D values obtained in this study by least-squares fitting the low-temperature heat-capacity results. The error limits reported for the heat-capacity results represent the error in the temperature measurement as well as the error in fitting the data to the standard heat-capacity equation $C/T = \gamma + \beta T^2$.

Atomic weights used in the calculation of heat-capacity results are 44.9559 for scandium, 88.9059 for yttrium, 157.25 for gadolinium, and 174.967 for lutetium.

III. RESULTS

A. Scandium

The low-temperature heat capacity of scandium purified by solid-state electrotransport and the effect of a minute quantity of iron impurities (19 at. ppm) has been noted previously.^{1,13} In this paper, the electronic specific-heat constant γ and the Debye temperature Θ_D of four scandium samples¹⁴ are tabulated in Table VI, together with the values generated by least-squares fitting the combined results of all four samples. Also given in Table VI are the results reported by earlier investigators.

TABLE VI. Heat-capacity results on various scandium samples.

γ (mJ/g-at. K ²)	Θ_D (K)	Temperature range (K)	Fe Concentration (at. ppm)	Reference
10.313±0.008	344.7±0.8	1–20	1.6	sample 1 ^a
10.354±0.004	346.8±0.4	1–20	0.5	sample 2 ^a
10.331±0.005	347.9±1.2	1–20	1.5	sample 3 ^a
10.320±0.009	343.8±1.2	1–20	2	sample 4 ^a
10.334±0.011	345.3±1.0	1–20	0.5→2	a,b
Other results				
11.3±0.1	470±80	1.7–4.2	56	15
10.3				16
10.9±0.1	344±25	0.15–3	60	17
10.66±0.1	359±4	1–23	80	18
10.72±0.3	425±14	1.14–4.2	95	19
10.72±0.05	359±9	0.5–4.2	40	20
7.5±0.8	218±8	3–6		21
	349.4 ^c			22

^aThis study.

^bLeast-squares fitting the combined results of all four electrotransport-purified scandium samples.

^cFrom neutron diffraction.

As can be seen, the γ and Θ_D values reported by others were generally significantly larger than our values, especially Θ_D , except for those reported by Sirota and Kudel'ko,²¹ whose values are anomalously low, and this may be due to their extrapolation from higher temperatures than used in the other studies. Furthermore, in most cases an upturn in the C/T -versus- T^2 plot was observed at the lowest temperature which was probably due to Kondo or spin-glass behavior.¹³ The results reported here show for the first time close agreement among four different samples.

B. Yttrium

The low-temperature heat capacity of electrotransport-purified yttrium is shown in Fig. 2. The values for γ and Θ_D are tabulated in Table VII, and compared to results reported by other investigators. It should be pointed out that the values reported by Wells *et al.*²³ also made on an electrotransport-purified yttrium sample; however, the sample measured in the present investigation has much lower gaseous impurities (10 ppm atomic N and 200 ppm atomic O versus 200 and 480 ppm, respectively, in the Wells *et al.* sample), lower metallic impurities (14 ppm rare-earth impurities versus 25 ppm), and therefore higher overall purity. We believe, however, that the thermometry of Wells *et al.* is questionable and is probably the main reason for the discrepancy rather than the difference in sample purity. Furthermore, apparently Wells *et al.* did not check their apparatus by measuring a standard substance, so it is difficult if not impossible to distinguish between differences in sample purities and systematic errors. This is more evident when a comparison is made with their gadolinium and lutetium heat-capacity results.

As is evident, the literature values for γ and Θ_D are significantly larger than those obtained in our study of

electrotransport-purified yttrium. In this case we believe the higher γ and Θ_D values are probably due to hydrogen impurities in the yttrium sample used by other investigators. This belief is based on our results obtained for a series of lutetium alloys containing hydrogen.² However, the influence of iron impurities in the other yttrium samples cannot be absolutely ruled out at this time. But the absence of an upturn at low temperatures in the C/T -versus- T^2 plot is a good evidence that iron impurities, if present, are not interacting with one another.

The present Θ_D value obtained from heat-capacity measurement is in excellent agreement with that obtained from neutron inelastic scattering studies, but is in poor agreement ($\sim 5\%$ smaller) with the Θ_D value calculated from elastic constant measurements. However, it should

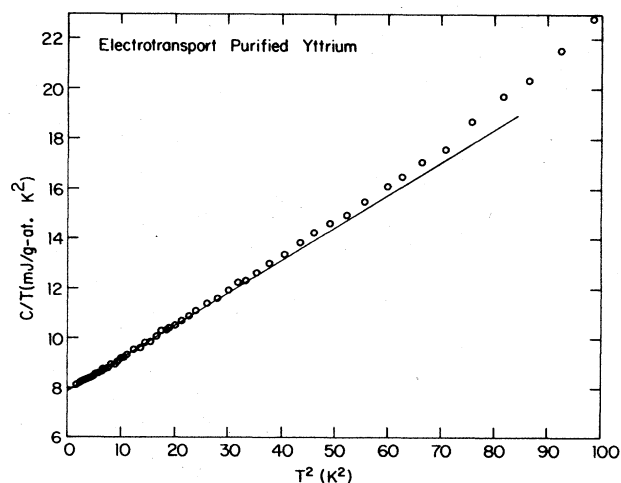


FIG. 2. Heat-capacity results of electrotransport-purified yttrium. Solid line is least-squares fit of result from 1 to 5 K.

TABLE VII. Heat-capacity results for yttrium.

γ (mJ/g-at. K ²)	Θ_D (K)	Reference
7.878±0.004	244.4±0.5	this study
Other results		
8.2±0.1	248±3	23
8.75±1	276	24
9.4	232	25
10.5	330	26
10	235	27
10.2	300±10	15
	258 ^a	28
	245 ^b	29

^aFrom elastic constant measurement.

^bFrom neutron scattering measurement.

be pointed out that the elastic constant measurements were made ~25 years ago and on a much lower purity material. This could easily account for the difference.

C. Gadolinium

The low-temperature heat capacity of electrotransport-purified gadolinium is shown in Fig. 3, where it is seen that the C/T -versus- T^2 plot follows a straight line from $T=1$ K to $T=7.5$ K. The γ and Θ_D values are obtained by least-squares fitting the data from the linear portion of Fig. 3, and are tabulated in Table VIII together with results by earlier investigators.³⁰⁻³⁴

The present results differ considerably from those reported by Wells *et al.*³⁰ on a gadolinium sample that was also electrotransport purified in that their heat-capacity results in a C/T -versus- T^2 plot exhibited some curvature between 1.5 to 5 K. Their Gd sample had a resistance ratio of 160 and the overall purity was given to be greater than 99.95 at. %. Wells *et al.*³⁰ fitted their results to the equation

$$C/T = \gamma + \beta T^2 + \alpha T^{n-1}, \quad (1)$$

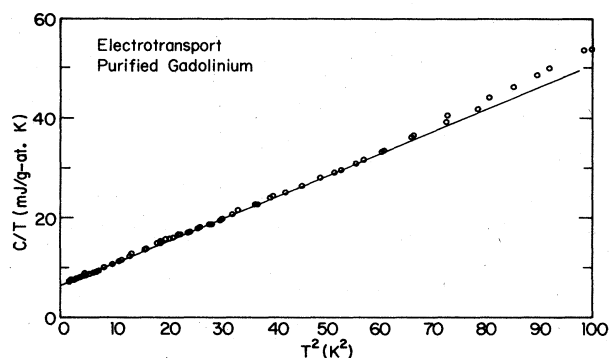


FIG. 3. Heat-capacity results of electrotransport-purified gadolinium. Solid line gives least-squares fit of result from 1 to 7 K.

TABLE VIII. Heat-capacity results for gadolinium.

γ (mJ/g-at. K ²)	Θ_D (K)	Reference
6.380±0.026	163.4±0.1	this study
Other results		
3.7 ^a	187 ^a	30
10.5 ^{b,c}	195 ^{b,c}	31
6.27	159	32
	184 ^d	33
	182.2 ^d	34

^aFitted to Eq. (1) with $n=1.75$.

^bFitted to Eq. (1) with $n=2.7$.

^cSample contained Gd₂O₃ which ordered magnetically at ~3 K.

^dFrom elastic constant measurement.

where the third term on the right-hand side represents the magnetic contribution to the heat capacity. They obtained a reasonable fit to their data for $n=1.75$.

Attempts to fit the present data to Eq. (1) always gives a negative value for α over any temperature interval between 1 and 7 K. Thus it is concluded that there is no magnetic contribution to heat capacity over the temperature range of 1 to 7 K unless $n=3$ (see Sec. IV B). Calculation by Rao and Narayana Murty³⁵ showed that the magnetic contribution to heat capacity is negligible below 15 K.

The γ and Θ_D values in the present investigation are considerably smaller than those reported by Lounasmaa and Sundström,³¹ but their results showed a magnetic ordering at ~3 K due to the presence of Gd₂O₃ in their sample. Our γ value agrees well with that determined by Hill³² on some electrotransport-purified gadolinium supplied by the authors. Our Θ_D value is considerably smaller (12%) than that obtained from elastic constant measurements.

D. Lutetium

The low-temperature heat capacity of electrotransport-purified lutetium has also been previously reported.² The results are tabulated in Table IX together with the results

TABLE IX. Heat-capacity results for lutetium.

γ (mJ/g-at. K ²)	Θ_D (K)	Reference
8.194±0.016	183.2±0.3	this study
Other results		
8.30±0.08	185±1	36
6.8±0.1	205±3	23
8.937±0.009	196	37
11.27±0.11	210	38
	184.5 ^a	39

^aFrom elastic constant measurement.

of other investigators. Since a minute quantity of hydrogen is known to have a dramatic effect on the γ and Θ_D values of Lu,² one must take into consideration the effect of this and other impurities in comparing the present results with that obtained on another electrotransport-purified Lu,²³ and on a well-characterized Lu sample.³⁶ The Lu sample measured by Taylor *et al.*³⁶ contains 816 at. ppm H (versus <175 ppm for the sample reported here), 104 ppm N (versus 0 ppm), 2188 ppm O (versus 82 ppm), 35 ppm Fe (versus 1 ppm), and 25 ppm Gd (versus <0.7 ppm). The electrotransport-purified Lu sample measured by Wells *et al.*²³ contained 350 ppm N, 680 ppm O, and 90 ppm rare-earth impurities (hydrogen concentration was not given).

The agreement between the present result and that reported by Taylor *et al.*³⁶ is good—the γ and Θ_D values for the present investigation are smaller by 1%. However, our γ value is 17% larger than that reported by Wells *et al.*,²³ while our Θ_D value is 12% smaller. The large discrepancy might be due to their thermometry. Our Θ_D value also agrees well with that obtained from elastic constant measurement.³⁹

IV. DISCUSSION

Knowledge of the intrinsic values of the electronic specific-heat constants and Debye temperatures of metals are important to theorists, and a comparison of their theoretical values to experiment is an important guide in testing the reliability of their methods and approaches. In the case of magnetic lanthanides the values of the non-magnetic rare-earth metals have been used to estimate the magnetic contribution to the heat capacity. Various averaging procedures have been used to estimate the γ and Θ_D values for the particular magnetic lanthanide from the known values, generally of La and/or Lu. This approach is examined in the next two subsections. In the third subsection we discuss the total enhancement factor and the partitioning of it into its components. Finally, in the fourth subsection we comment on the effect that sample purity improvements may have on γ and Θ_D .

A. Electronic specific-heat constant

One of the difficulties in estimating the electronic specific-heat constant for the magnetic lanthanides is that there is a crystal structure change across the series from double hcp (dhcp) for the light lanthanides to hcp for the heavy ones, this is not considering the fcc phases of La

and Ce and the nine-layer Sm structure as part of this analysis. Assuming one knew how to correct for the difference in crystal structures, there is no reason to expect γ to vary as a linear function across the series. Band-structure calculations⁴⁰ suggest that γ does not vary smoothly along the series, but peaks and valleys could be expected in a plot of γ versus the atomic number. This is also evident in the experimentally determined γ values for electrotransport-purified Gd, Tb,⁴¹ and Lu, all of which have the hcp structure. For the magnetic lanthanides Gd and Tb the magnetic contribution to the heat capacity below 5 K is negligible or quite small and reliable γ values can be derived from the experimental data. The γ values for these three metals (Gd, Tb, and Lu) are 6.38, 3.71,⁴¹ and 8.19 mJ/g-at. K², respectively. Thus we believe that any attempt to estimate the electronic contribution to the heat capacity of the magnetic lanthanide metals from the known, reliably determined γ values of the other members of this series is wrong. And any such attempt to extract the magnetic contribution using such estimated electronic contributions could lead to serious errors and the wrong conclusions regarding the magnetic heat capacities of the lanthanide metals. Difficulties in estimating the Debye temperature, see below, compound the problem.

B. Debye temperature

There are two ways to estimate the Debye temperature of the magnetic lanthanides. One is to use a plot of Θ_D versus the atomic number Z , which appears to give a straight line.⁴² The other method is to use the Lindemann equation,⁴³ which relates Θ_D to the melting point T_m , atomic mass M , and atomic volume V of a substance by the equation

$$\Theta_D = K \left[\frac{T_m}{M} \right]^{1/2} \left[\frac{1}{V} \right]^{1/3}, \quad (2)$$

where K is a constant approximately equal to 145. Values of T_m , M , V ,⁴⁴ and Θ_D determined from low-temperature heat capacity are tabulated in Table X, together with the value of K calculated from the Lindemann equation. The results of Pan *et al.*⁴⁵ for electrotransport-purified dhcp (β) La are also included in this analysis. The average value of $K = 141.9$ for these five electrotransport-purified rare-earth metals agrees well with the average value reported for all metals $K = 145 \pm 32$.⁴² As seen in Table X the Lindemann constant K varies considerably ($\sim 10\%$) for these closely related metals. Thus it would appear

TABLE X. Parameters for Lindemann equation.

Element	T_m (K)	Θ_D (K)	M (g/mol)	V (cm ³ /mol)	K	Θ_D^a (K)
Sc	1814	345.3	44.9559	15.039	134.2	365
Y	1795	244.4	88.9059	19.893	147.4	235
La	1191	150.0 ^b	138.9055	22.602	144.8	147
Gd	1586	163.4	157.25	19.903	139.4	166
Lu	1936	183.2	174.967	17.779	143.7	181

^aDebye temperature calculated from Lindemann equation using the average value for $K = 141.9$.

^bAfter Pan *et al.* (Ref. 45).

TABLE XI. Electronic density of states and enhancement factors.

Metal	$N(E_F)^a$ (states/atom eV spin)	$N_0(E_F)$	Year of publication	Reference	λ_{total}	$\lambda_{e\text{-ph}}$	λ_{spin}	λ_{sw}
Sc	2.192	1.17	1976	58	0.87	0.30	0.57	
		0.97	1976	59	1.26	0.30	0.96	
		1.18	1977	60	0.86	0.30	0.56	
		1.09	1980	61	1.01	0.30	0.71	
		0.73	1980	62	2.01	0.30	1.71	
		0.79	1982	63	1.78	0.30	1.48	
Y	1.671	1.00	1968	64	0.67	0.30	0.37	
		0.80	1977	60	1.09	0.30	0.79	
		0.92	1980	65	0.82	0.30	0.52	
		1.00	1982	63	0.67	0.30	0.37	
		0.96	1983	66	0.74	0.30	0.44	
La (dhcp)	2.004	0.71	1968	67	1.81	0.76	1.05	
Gd	1.353	0.90	1964	68	0.50	0.30		0.20
		1.05	1968	69	0.29	0.30		0
		0.84	1974	70	0.60	0.30		0.30
		0.40	1979	71	2.35	0.30		2.05
		1.00	1982	49	0.35	0.30		0.05
		0.44	1983	50	2.04	0.30		1.74
Lu	1.738	0.94	1968	69	0.86	0.31	0.55	
		0.87	1982	72	0.99	0.31	0.68	
		0.87	1984	57	0.99	0.31	0.68	

^aCalculated from electronic specific-heat constant γ .

that the Lindemann equation is probably not too reliable for estimating the unknown Θ_D , even if the Θ_D value for Gd is excluded in calculating the proportionality constant K .

A plot of Θ_D versus Z shows that Gd falls below the straight line drawn through the La and Lu points, and if we include the Θ_D of Tb determined by Ikeda *et al.*⁴¹ one finds that this point lies above this straight line. This suggests that this approach may not be too reliable either for estimating unknown Θ_D values. But the problem may actually lie with the Θ_D values for Gd and Tb, i.e., there may be a magnetic contribution which has been ignored in deriving these Θ_D 's. This point is discussed below for the Gd case.

In the analysis of the heat-capacity results for Gd, a value of $\Theta_D = 163.4$ K is obtained when the heat capacity contains only the electronic and lattice contribution. If magnetic anisotropy is absent, Lounasmaa and Sundström³¹ predicted a T^3 behavior for the magnetic contribution to heat capacity in Gd. If one were to include a T^3 term for magnetic heat capacity in our analysis, then the value of Θ_D would be increased. In Table X the mean value of K for La and Lu is 144.25; this translates to a Θ_D of 169 K for Gd. This difference of $\Theta_D = 169$ and 163.4 K could be due to a magnetic contribution to heat capacity that has a T^3 dependency.

It has been pointed out³⁴ that sample purity can affect elastic constants, and therefore the value of Debye temperature calculated from elastic constant measurements. For example, Greiner *et al.*⁴⁶ found that the addition of

0.063 at. % carbon to thorium raises the Debye temperature by ~ 3 K. The addition of oxygen to vanadium⁴⁷ also increases the elastic constants, and hence the value of Debye temperature calculated from elastic constant measurement. The addition of oxygen to niobium⁴⁸ produced first a slight initial softening of the lattice, followed by a hardening. Since the elastic constant measurements for Gd were performed ten or more years ago and on samples with lower overall impurity, this might explain the large difference ($\sim 12\%$) in the value of Θ_D determined from elastic constant measurements and the present investigation on an electrotransport-purified sample. A new measurement on electrotransport-purified Gd single crystals would be helpful in clarifying this situation.

C. Enhancement factor

Due to the periodic potential of the lattice, and various direct and indirect interactions, the experimentally determined electronic specific-heat constant γ is different from the "free-electron" value γ_0 . This difference can be expressed by the equation

$$\frac{\gamma}{\gamma_0} = 1 + \lambda_{\text{total}} = \frac{N(E_F)}{N_0(E_F)}, \quad (3)$$

with

$$\lambda_{\text{total}} = \lambda_{e\text{-ph}} + \lambda_{\text{spin}}, \quad (4)$$

where λ_{total} is the total enhancement factor due to

electron-phonon enhancement λ_{e-ph} and electron-paramagnon (or spin fluctuation) enhancement λ_{spin} . γ_0 is calculated from the bare density of states at the Fermi level, $N_0(E_F)$, obtained from theoretical band calculations.

In the past few years Eagles⁴⁹ and Fulde and Jenson⁵⁰ suggested that there is also an enhancement due to the spin waves, λ_{SW} , in the magnetic lanthanide metals, i.e.,

$$\lambda_{total} = \lambda_{e-ph} + \lambda_{SW} \quad (5)$$

For scandium $\lambda_{e-ph} = 0.30$ as determined separately by Knapp and Jones,⁵¹ and Ross *et al.*⁵² For yttrium, $\lambda_{e-ph} = 0.30$.⁵¹ For lanthanum λ_{e-ph} has been determined to be 0.75,⁵³ 0.77,⁵⁴ and 0.85.⁵⁵ For lutetium $\lambda_{e-ph} = 0.31$.^{53,56} For gadolinium we have assumed it to be 0.30, the same as for the other rare-earth metals, except lanthanum. The density of states and the various enhancement factors are tabulated in Table XI by using the experimental value of $N(E_F)$, as calculated from our measured γ values, and the different theoretical band structures for the rare-earth metals to estimate λ_{total} .

An examination of Table XI shows a general trend in that the theoretical density of states values for these metals become smaller with time. This is especially evident for scandium and gadolinium (except for one recent value) where there is a significant difference between the first calculated values and the most recent ones. Presumably the most recent calculations are the more correct ones because of advances in theory and computational techniques and power. In the case of gadolinium the old values are based on a paramagnetic calculation, while some of the newer values are based on a ferromagnetic calculation.

For scandium one sees that it is a strongly enhanced metal with λ_{total} nearly equal to 2. The large enhancement primarily comes from spin fluctuations, which can be quenched by high magnetic fields (> 5 T).⁷³ According to the calculations lanthanum also appears to have a rather large λ_{spin} which is rather surprising in view of its good superconducting properties ($T_c \approx 4.9$ K). More likely, however, is that the theoretical $N_0(E_F)$ value is too low (which is just the opposite of the trends observed earlier). The enhancements for yttrium and lutetium are significantly smaller than those of the other metals listed in Table XI.

The case of gadolinium is quite interesting since the total enhancement is quite large, $\lambda_{total} > 2$. This large enhancement is probably due to the spin waves of the 4f electrons.^{50,71}

Since there is considerable scatter in the various enhancement values (other than λ_{e-ph}), the following are recommended as the best values for λ_{total} and λ_{spin} : Sc—1.90 and 1.60, respectively; Y—0.74 and 0.44, respectively; and Lu—0.99 and 0.68, respectively. For Gd we chose 2.20 for λ_{total} and 1.90 for λ_{SW} .

D. Consequences of further improvement of sample purity

Today we are able to prepare rare-earth metals ~ 99.9 at. % pure with respect to all of the elements in the Periodic Table, and if one ignores the interstitial elements the purities approach 99.999 at. %. Although the impurity levels today are 1 to 2 orders of magnitude lower than

they were 10–15 years ago, they are still high compared to the low levels attained in the noble metals for example. One wonders what the effect of decreasing the impurity levels would have on the reported γ and Θ_D values, especially since we have in principle the ability to prepare 99.99% to 99.999% pure rare-earth metals.⁷⁴ Of course, the answer will only be known after samples of 99.99 at. % pure have been measured. But recent results over the past few years, as discussed below, indicate that we have probably measured the intrinsic γ and Θ_D values for these metals.

The impurities which are most likely to have appreciable effects on γ and Θ_D are the magnetic elements: Cr, Mn, Fe, Co, Ni, and the lanthanides which have unpaired 4f electrons, and the interstitial impurity H. H impurity levels > 300 at. ppm are known to cause measurable shifts in both γ and Θ_D in Lu,² and these H levels probably do the same in the lanthanides from Dy to Tm, and Sc and Y. For the other lanthanide elements in the H solid solubility is too low at $T < 10$ K and no effect is expected, since the H is not dissolved in the matrix metal. For Sc and Y, H impurity levels below this limit (~ 7 and ~ 3.5 wt. ppm, respectively) are easily attained, especially since we have been able to do it in Lu where this limit is ~ 2 wt. ppm. (Note the lower limit of H detectability is 1 wt. ppm.)

The magnetic lanthanide elements present no problem since the total impurity levels of these metals are usually below 10 at. ppm, as routinely prepared at the Ames Laboratory. The magnetic transition metals also present no problem in the rare-earth metals since the transition metals can easily be removed by electrotransport purification to levels of < 2 at. ppm. Sc metal is probably the most sensitive rare earth to transition-metal impurities because of its high spin-fluctuation enhancement factor, and we^{1,13} have shown that Fe impurity levels of somewhere between 2 and 19 at. ppm are necessary to have a measurable effect on γ and Θ_D .

Thus if impurity levels of these critical elements (H, magnetic transition metals and magnetic lanthanides) are sufficiently low, i.e., < 1 at. ppm each, one should be measuring the intrinsic γ and Θ_D of the rare-earth metals provided other impurity levels are not high (< 100 at. ppm for any one individual element and collectively < 1000 at. ppm). Indeed our measurements on four different Sc samples (Table VI), where the standard deviation in γ is 0.1% and Θ_D is 0.3%, or the difference between the highest and lowest value is 0.4% for γ and 1.2% for Θ_D , strongly support this contention. Additional support is also found in the comparison of the unpublished results of Hill on electrotransport-purified Gd with our values (Table VIII)—a 1.7% difference in γ and a 2.5% difference in Θ_D . These differences could easily be accounted for by the fact that the data have been measured at two different laboratories, by different investigators using slightly different techniques over different temperature ranges.

Thus we conclude that further improvements in the sample impurity levels will not result in any significant changes in the γ and Θ_D reported here for Sc, Y, Gd, and Lu. That is, we believe that the values given here in

Tables VI–IX are the intrinsic values within an estimated error limit of $\pm 2\%$.

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