Specific Heat of Lutetium Metal Between 0.38 and 4°K†

O. V. LOUNASMAA*

Argonne National Laboratory, Argonne, Illinois

(Received 12 June 1963)

The specific heat of lutetium metal has been measured in a He³ cryostat. Between 0.38 and 4°K (in mJ/mole °K) $C_p = 0.210T^3 + 11.27T + 0.094T^{-2}$. Scatter of individual points from this curve is, except in a few isolated cases, less than 0.5%. The lattice specific heat corresponds to a Debye characteristic temperature $\theta = 210°K$, which is considerably higher than θ's previously assigned to rare earths. The discrepancy is probably due to difficulties in determining θ accurately for those lanthanides which have large magnetic contributions to C_p. On the basis of this and other researches it is suggested that for all trivalent rare earths, θ can be calculated by linear interpolation, as a function of the atomic number, between $\theta = 210°K$ for Lu and $\theta = 142°K$ for La. An accuracy of $\pm 5°K$ may be expected. The present value for the coefficient in the electronic specific heat C_E for Lu and previous measurements on La, Sc, and Y suggest that within $\pm 7\%$ accuracy we may write for all trivalent lanthanides $C_E = 10.5T$. The small T^{-2} term in C_p could be caused by interaction of the nuclear quadrupole moment with the crystalline field gradient or it may be due to long-range exchange-type coupling between the electronic moments of rare-earth impurities in our Lu sample. If the former interpretation is accepted, the electric field gradient, along the symmetry axis, becomes 2.2×10^{24} cm^{-3}.

I. INTRODUCTION

IN continuing our studies [1-5] of the heat capacity of rare-earth metals at low temperatures, we have measured the specific heat C_p of lutetium between 0.38 and 4°K. No previous heat-capacity data are available for this metal in the liquid-helium range; work of Jennings, Miller, and Spedding[6] cover the temperature interval from 15 to 350°K.

The specific heat of most rare-earth metals at low temperatures has four terms: $C_L = AT^3$, the lattice specific heat; $C_E = BT$, the electronic specific heat; C_M, the magnetic specific heat; C_N, the nuclear specific heat. C_M is caused by interatomic exchange interaction between the 4f electronic spins and C_N is, for the most part, due to interaction of the nuclear magnetic moment with the intense magnetic field (several MG) produced by the 4f electrons at the site of the nucleus. Separation of the observed C_p into its four components is thus an interesting, but at the same time a difficult task.

In particular, the nuclear term, which in the first approximation may be written $C_N = DT^{-2}$, seriously interferes with the precise determination of C_E. Usually in metals the electronic term accounts for a major part in the observed C_p below about 2°K and B can, thus, be accurately calculated from measurements between, say, 1 and 4°K, but for many rare earths C_N is considerably larger than or comparable with C_E already at 2°K and is increasing rapidly towards lower tempera-

tures. It is similarly quite hard to separate C_L and C_M. Part of the difficulty here has been that the temperature dependence of C_M has been unknown. Predictions by the simple spin-wave theory, $C_M = CT^{3/2}$ in the ferromagnetic case and $C_M = C'T^3$ in the antiferromagnetic case, are only rather crude approximations.[7] However, theoretical progress has been made in this field quite recently.[8-10]

In some rare-earth metals, anomalous behavior has been observed in C_p between 1 and 4°K,[2,3,5] which further obscures the analysis of results. Such anomalies are most probably caused by magnetic ordering of the trivalent rare-earth ions in the oxide impurity of the samples. Since the entropy of ordering is $2R \ln(2J+1)$ per mole of oxide, even a small impurity (less than 0.1% of oxygen by weight) can have very harmful effects.

For lutetium, the last metal in the rare-earth series, the 4f shell is full and the metal is, thus, nonmagnetic. Consequently, $C_M = 0$ and there can be no magnetic ordering in an oxide impurity. Only a small C_N, due to quadrupole interactions (cf., Sec. IV), is possible. Lutetium thus offers an opportunity for determining C_L and C_E. Since all trivalent rare earths have the same outer electronic configuration and since their crystal structures are rather similar (hcp or a closely related structure), results on lutetium, together with other information available, may be used for estimating C_L and C_E of other trivalent lanthanides. This will be discussed in Sec. IV.

II. EXPERIMENTAL

The heat-capacity measurements were carried out in a He³ cryostat which has been described earlier[2]; only

* Present address: Wihuri Physical Laboratory, University of Turku, Turku, Finland.
[1] O. V. Lounasmaa, Phys. Rev. 126, 1352 (1962).
[2] O. V. Lounasmaa and R. A. Guenther, Phys. Rev. 126, 1357 (1962).
[3] O. V. Lounasmaa and P. R. Roach, Phys. Rev. 128, 622 (1962).
[4] O. V. Lounasmaa, Phys. Rev. 128, 1136 (1962).
[5] O. V. Lounasmaa, Phys. Rev. 129, 2460 (1963).
[6] L. D. Jennings, R. E. Miller, and F. H. Spedding, J. Chem. Phys. 33, 1849 (1960).

[7] J. van Kranendonk and J. H. van Vleck, Rev. Mod. Phys. 30, 1 (1958).
[8] B. R. Cooper, Proc. Phys. Soc. (London) 80, 1225 (1962).
[9] B. R. Cooper, R. J. Elliott, S. J. Nettel, and H. Suhl, Phys. Rev. 127, 57 (1962).
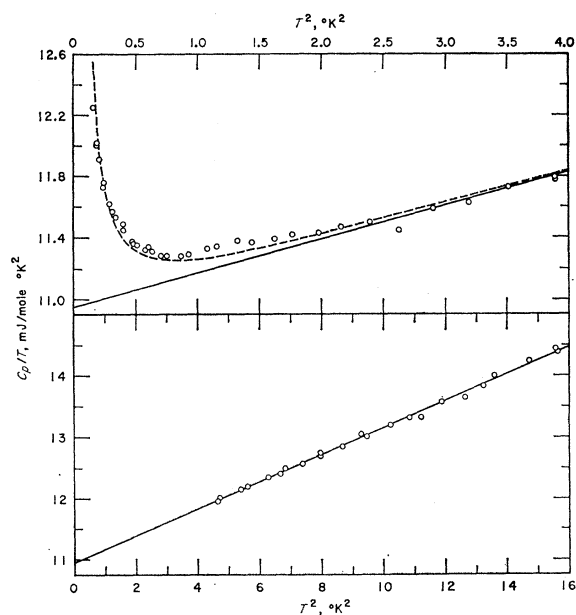[10] A. R. Mackintosh, Phys. Letters 4, 140 (1963).

FIG. 1. The specific heat of lutetium metal. Points are uncorrected for Ta and Lu_2O_3 impurities.

the most important experimental features are related here. He^4 exchange gas was used for cooling the sample down to 4.2°K; the space surrounding the calorimeter was then evacuated by pumping until a mass-spectrometer-type leak detector showed a very small helium reading. For further cooling a mechanical heat switch was employed. In this way, good thermal insulation was achieved when the heat switch was opened 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 in the He^3 pot for 48 h without recondensing. With the heat switch closed the sample was cooled from 4.2 to 0.35°K in about 4 h.

For the heat-capacity measurements a colloidal graphite (Aquadag) thermometer was employed; its construction has been described elsewhere.[2] It is probably useful to mention here that in order to minimize the noise in this thermometer, each time the cryostat is warmed up to room temperature the old carbon film should be removed and a fresh layer of Aquadag painted in its place. The entire operation can be done in about 15 min. The thermometer was calibrated against the vapor pressure of He^4 between 4.15 and 2.2°K, against the vapor pressure of He^3 between 2.2 and 0.75°K, and against a magnetic thermometer (chromium methylamine alum) between 0.75 and 0.34°K. He^4 temperatures were determined according to the T_{58} scale.[11] For He^3 the new 1962 scale[12] was employed; a correction was

made for the 0.5% of He^4 in our He^3 gas. The constants in the susceptibility versus temperature curve for the magnetic thermometer were determined from calibration points between 2.2 and 0.75°K. Altogether about 30 points were measured for the carbon thermometer between 4.15 and 0.34°K.

III. RESULTS

Our lutetium metal was purchased from Research Chemicals, Inc. (Division of Nuclear Corporation of America). It was vacuum distilled by the manufacturer, then remelted in a vacuum and cast into a tantalum crucible. Next, the tantalum was machined off and the sample turned down to a cylinder 0.7 cm long and 2.8 cm in diameter; its weight was 40.644 g (=0.23229 moles). The spectrographic laboratory at Argonne found the following metallic impurities (weight %): Fe, 0.01%; Gd, 0.03%; Mo, 0.01%; Nd, 0.05%; and Ta, 1.4%. These analyses are uncertain by a factor of 2 except in the case of Ta for which the precision is ±10%. The Ta result was obtained by a very careful densitometric analysis. Of nonmetallic impurities the Argonne chemical laboratory found: H, 0.03%; N, 0.021%; O, 0.17%; C, 0.020% and F, 0.017%. The accuracy is about 10%.

The experimental specific-heat results are listed in Table I and the points are also plotted as C_p/T versus T^2 in Fig 1. All calculations were performed by an IBM-704 digital computer.[13] The results in Table I and Fig. 1 have been corrected for curvature (due to finite temperature increments when measuring C_p).

TABLE I. Specific heat (in mJ/mole °K) of lutetium metal. Experimental Results.[a]

T (°K)	C_p	T (°K)	C_p	T (°K)	C_p
Run I		2.5844	32.05	1.5477	17.79
0.3873	4.83	2.8222	35.79	1.7032	19.75
0.4348	5.23	3.0781	40.04	1.8739	21.98
0.4937	5.79	3.3489	44.62	Run V[b]	
0.5618	6.50	3.6372	50.35	2.6123	32.64
0.6377	7.33	3.9535	56.93	2.8211	35.94
0.7177	8.14	Run III		3.0450	39.75
0.7987	9.04	0.4029	4.94	3.2930	43.85
Run II		0.4300	5.16	3.5538	48.50
0.6973	7.92	0.4618	5.50	3.8370	54.66
0.7806	8.85	0.4989	5.87	Run VI	
0.8668	9.78	0.5413	6.29	1.9744	23.29
0.9638	10.88	0.5862	6.76	2.1581	25.80
1.0771	12.21	0.6360	7.28	2.3245	28.22
1.2004	13.65	0.6949	7.90	2.5054	30.91
1.3301	15.19	0.7640	8.65	2.7166	34.11
1.4704	16.87	0.8422	9.50	2.9483	37.84
1.6214	18.57	0.9321	10.52	3.1990	42.21
1.7855	20.77	1.0357	11.73	3.4458	46.81
1.9723	23.23	1.1512	13.10	3.6863	51.65
2.1699	26.04	1.2753	14.53	3.9443	56.99
2.3696	28.88	1.4063	16.07		

[a] Not corrected for Ta and Lu_2O_3 impurities.
[b] External interference during Run IV.

[11] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. 64A, 1 (1960).
[12] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, Los Alamos Scientific Laboratory Report No. 2701, 1962 (unpublished).

[13] P. R. Roach, Argonne National Laboratory Technical Report No. 6497, 1962 (unpublished).

Corrections for the tantalum and oxygen impurities, to be discussed below, are not included here.

After a heating period (about 1 min) the sample came to equilibrium in less than 2 sec. The heat leak to the calorimeter was never more and normally considerably less than 1% of the heat input during heating periods. A correction for this was made in the customary manner by assuming linear drifts. The scatter of the points (cf., Fig. 1) from a smooth curve, with a few isolated exceptions, is about 0.5%. This is somewhat more than has usually been found in our experiments and is caused by the rather small total heat capacity of lutetium.

The heating current was measured with a Rubicon No. 2781 potentiometer and timed with an electronic timer using a tuning fork frequency standard. Possible systematic errors here are thus negligible. The electrical leads between the He^4 bath and the calorimeter were made of lead-covered constantan and were superconducting below 7°K. It was observed, however, that if a heating current larger than about 2 mA was used the leads became normal. Since this "critical" current is very much smaller than would be expected (when immersed in liquid helium the same leads carried a current of about 100 mA in the superconducting state), it is likely that the superconducting lead coating had tiny cracks, which the current was forced to cross by flowing through the constantan core of the wire. In a vacuum, heat thus generated could not be carried away sufficiently fast at currents larger than 2 mA and superconductivity was destroyed by a too high temperature of the leads. The maximum heating current used in the present experiments, 0.5 mA, was well below the "critical", value. However, due to small but largely unknown heating effects in the leads, the effective heater resistance ($R_H = 362.13 + 0.03T$ Ω) is uncertain by not more than 0.1%.

The heat capacity of the empty calorimeter ($C = 0.0090T^3 + 0.116T$ mJ/°K) was known from an earlier experiment; it was 4% at 0.5°K and 8% at 4°K of the heat capacity of the sample. Possible uncertainties here cannot cause systematic errors larger than 0.2% in the final results.

As is usual in low-temperature calorimetry, the largest errors in C_p are probably caused by the resistance versus temperature formula adopted for the carbon thermometer. The equation used was

$$1/T = a/R^{5/2} + b/R + c + dR^{1/2} + eR + fR^2 \\ + g/(\ln R)^{1/2} + h \ln R, \quad (1)$$

where the constants $a, \cdots, h$ were determined by the method of least squares. Deviations of the calibration points from Eq. (1) were, with a few exceptions, less than 1 mdeg over the whole temperature range. The calculated temperature above 0.75°K is, thus, probably within 1 mdeg of the temperature defined by the He^3 and He^4 scales.[12,11] Additional errors of about 2 mdeg may arise from uncertainties in the calibration against the magnetic thermometer below 0.75°K.

After considering all the sources of errors mentioned above, the accuracy of the present results is estimated as 0.6% between 1 and 4°K and 2% at 0.4°K.

The only sizeable impurities in our lutetium sample were 1.4% of tantalum and 0.17% of oxygen. The latter, on the basis of observations on this and other rare earths, was in the form of sesquioxide, Lu$_2$O$_3$. Tantalum probably migrated into our sample when the molten lutetium metal was cast into a tantalum crucible. The diffusion rate could have been rather high since the melting point of lutetium is 1652°C. Fortunately, it appears that most of the tantalum precipitates out of the lutetium lattice.[6] Microphotographs of our sample were made and they clearly showed two minority phases present, one presumably Lu$_2$O$_3$, the other Ta. A correction for these can, thus, be made by subtracting the heat capacity of impurities and by adjusting the number of moles of sample to correspond to pure lutetium metal only. An oxygen content of 0.17% means that 1.3% of the lutetium atoms were in the sesquioxide phase. The specific heat of Lu$_2$O$_3$ was assumed to be (in mJ/mole°K) $C_p = 0.26T^3$; the result was estimated on the basis of measurements by Westrum between 7 and 20°K.[14] The correction is small and can be applied with confidence only because there are no magnetic contributions to the heat capacity of Lu$_2$O$_3$. For tantalum (a superconductor) the specific heat can be expressed with $\sim 5\%$ accuracy by $C_p = 1.09T^3$ (in mJ/mole°K).[15]

From Fig. 1 it is clear that, except for the lowest temperatures, only C_L and C_E are necessary in expressing the specific heat of lutetium. A least-squares fit of all the experimental points (Table I) into the equation $C_p = AT^3 + BT + DT^{-2}$ gave $A = 0.220 \pm 0.001$, $B = 10.95 \pm 0.01$, $D = 0.091 \pm 0.004$ (C_p in mJ/mole°K, limits of error are standard deviations only). A term proportional to T^{-2} is necessary for representing the upward trend of C_p/T at the lowest temperatures. After correcting for the Ta and Lu$_2$O$_3$ impurities, the specific heat of lutetium metal becomes (in mJ/mole°K)

$$C_p = 0.210T^3 + 11.27T + 0.094T^{-2}. \quad (2)$$

Uncertainties in the impurity corrections will increase the earlier error estimates by about 0.3%. After taking this into account, the limits of error for the coefficients in Eq. (2) are: 3% for A, 1% for B, and 10% for D.

IV. DISCUSSION

Coefficient $A = 0.210$ mJ/mole°K^4 in C_L corresponds to a Debye characteristic temperature $\theta = 210$°K for lutetium. Measurements of the velocity of sound by Smith, Carlson, and Spedding[16] at room temperature

[14] E. F. Westrum (private communication).
[15] D. White, C. Chou, and H. L. Johnston, Phys. Rev. 109, 797 (1958).
[16] J. F. Smith, C. E. Carlson, and F. H. Spedding, J. Metals 9, 1212 (1957).

TABLE II. The Debye characteristic temperature θ
(in °K) of rare-earth metals.

	Low temp.[a] θ	"Average"[b] θ
Lanthanum	142[c]	132
Cerium	147	
Praseodymium	152	
Neodymium	157	
Promethium	162	
Samarium	166	150
Europium[d]		
Gadolinium	176	152
Terbium	181	158
Dysprosium	186	158
Holmium	191	161
Erbium	195	163
Thulium	200	167
Ytterbium	118[e]	
Lutetium	210[f]	166

[a] Linear interpolation between values for La and Lu.
[b] Based on heat capacity measurements between 15 and 300°K by Spedding *et al.* For complete list of references see Ref. 17, p. 38.
[c] From Ref. 18.
[d] Metal is divalent.
[e] From Ref. 5. Metal is divalent.
[f] From present measurements.

indicate that for all trivalent rare earths θ's follow a straight line when plotted against the atomic number.[17] In view of this, with some justification and probably within an accuracy of ± 5°K the low-temperature Debye θ's of all trivalent lanthanides can be calculated by linear interpolation from heat capacity measurements by Berman, Zemansky, and Boorse[18] on lanthanum and by us on lutetium; results are listed in Table II.

θ's given in Table II are considerably higher for higher rare earths than the "average" θ's calculated by Spedding and his co-workers at the Iowa State University from heat-capacity measurements between 15 and 300°K (cf., Table II). Part of the discrepancy is due to a dip in the θ versus T curve at intermediate temperatures,[6] part is probably caused by difficulties in separating the various contributions to the heat capacity. For instance, it appears that at least in several cases Spedding *et al.* adopted for C_E a value ($C_E = 6.7T$ mJ/mole°K) which is too low. If this is corrected, the "average" θ's would tend to increase.

From their measurements between 15 and 350°K Jennings, Miller, and Spedding[6] deduced $\theta = 166$°K for lutetium. In calculating this "average" θ the value $B = 9.5$ mJ/mole°K^2 was used. Even after allowing for variations of θ with temperature the discrepancy between our low temperature $\theta = 210$°K and the "average" θ is somewhat large. No explanation can be offered at present.

Owing to complications caused by C_M, the low-temperature lattice specific heats can be determined

accurately only for lanthanum, ytterbium, and lutetium, for which $C_M = 0$. Reliable comparisons with interpolated values in the first column of Table II can thus not be made. In some cases, notably for terbium and dysprosium, a comparison may be attempted. For these metals C_M is proportional to $\exp(-E_g/kT)$,[8] with $E_g \cong 20-30$°K. The magnetic specific heat should thus be quite small below 4°K. For Tb Lounasmaa and Roach[3] deduced $\theta = 150$°K and for Dy Dreyfus, Goodman, Trolliet, and Weil[19] found $\theta = 207$°K. Neither of these values agree particularly well with those listed in the first column of Table II. For Dy, different investigators have obtained specific heat results which disagree at 4°K by several hundred percent.[2] The discrepancies are most likely caused by impurities, either directly, for instance, by magnetic ordering of Dy^{3+} ions in the Dy_2O_3 impurity, or indirectly by lowering the energy gap E_g at the minimum of the spin-wave spectrum. The high value of θ found by Dreyfus *et al.*[19] for Dy, corresponding to low C_L, cannot be explained in this way. If adopted, it would seem to indicate that the low temperature θ is approximately the same for the higher rare earths. This is unlikely since the atomic distances become smaller towards the heavier members of the lanthanide series. The bonding strength between atoms is at the same time increased, which in turn increases θ. At the present time, the most reliable low-temperature Debye θ's for rare-earth metals seem to be those given in the first column of Table II.

Our value of 11.27 mJ/mole°K^2 for the coefficient B in the electronic specific heat of lutetium may be compared with the following experimental results, all calculated from heat capacity measurements below 4°K: $B = 10.1$ for La,[18] 12.1 for Sm,[1] 9.05 for Tb,[3] 9.5 for Dy,[2] 10.3 for Sc,[20] and 10.2 for Y.[20] (The last two metals are not true rare earths but are, together with the lanthanides, in column IIIb of the periodic table.) The values given for Sm, Tb, and Dy are not too reliable because C_N is interfering in these cases with the precise determination of C_E. Dreyfus, Goodman, Lacaze, and Trolliet[21] have found for several rare earths larger values of B: 19 for Pr, 26 for Ho, 13 for Er, and 21.5 for Tm. However, since the large magnetic specific heat was ignored in the analysis, these numbers appear to be too high.

The electronic structure of rare-earth atoms outside a xenon core is $(4f^n, 5s^2, 5p^6, 6s^2, 5d^1)$, where the value of n increases from 0 for lanthanum to 14 for lutetium. The outer electron configuration of these metals is thus the same; they are normally trivalent with the $6s$ and $5d$ electrons in the conduction band. As a first approximation one might assume that C_E is the same for all

[17] K. A. Gschneidner, *Rare-Earth Alloys* (D. Van Nostrand Company, New York, 1961), pp. 37 and 38.
[18] A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

[19] B. Dreyfus, B. B. Goodman, G. Trolliet, and L. Weil, Compt. Rend. **253**, 1085 (1961).
[20] H. Montgomery and G. P. Pells, Proc. Phys. Soc. (London) **78**, 622 (1961); and H. Montgomery (private communication).
[21] B. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, Compt. Rend. **253**, 1764 (1961).

trivalent lanthanides and Sc and Y, and according to experimental results on La, Lu, Sc ,and Y this assumption is valid within $\pm 7\%$ if the average B for these metals, 10.5 mJ/mole°K^2, is chosen.

However, magnetic ordering of the localized $4f$ electrons can have an effect on the conduction electrons. Mackintosh[22] has shown that the magnetic periodicity along the c axis, which, in general, is incommensurate with the periodicity of the hcp lattice, will introduce extra planes of energy discontinuity into the Brillouin zone structure. Since the magnetic arrangement differs considerably from one rare earth to another, differences are also expected in B. At the present time, theoretical calculations are not yet available for estimating the size of this effect. It would be of considerable interest to study experimentally the possible changes in B. For sufficient accuracy, however, the other contributions to C_p must be small below 2°K. This condition can be fulfilled only by some of the lanthanides. The orbital angular momentum of the $4f$ electrons is zero for La, Eu, Gd, Yb, and Lu because the $4f$ shell is either empty, half-full, or full. A small or zero C_N would thus be expected for these metals. Eu and Yb are divalent and a very different B has been observed.[23,5] In the case of Gd impurity effects are particularly troublesome.[5] For Ce, $C_N = 0$ because the metal has only even-even stable isotopes, but an anomaly in C_p near 1°K makes an accurate analysis impossible.[23]

For all rare earths with an even atomic number C_N can be made zero by making measurements on a sample with even-even isotopes only. Experiments of this kind could be done on Nd, Sm, Gd, Dy, and Er. Of these, Gd is less profitable for reasons already discussed and Nd because C_M is large even at 0.5°K.[24] This leaves Sm, Dy, and Er as possible candidates for measurements with isotopically pure samples. The main difficulty in these experiments is, of course, in obtaining sufficiently large quantites (at least 1 g) of the required isotopes. Results of measurements, together with values of B for La and Lu, would be sufficient for establishing some of the details about the changes in C_E from one rare earth to another.

After new results have now become available for estimating C_L and C_E of all trivalent rare earths with higher precision than before, it should be possible to determine C_M for these metals quite accurately. This is particularly interesting in view of recent theoretical progress on C_M. For studying the magnetic specific heat further it would be most desirable to make measurements of C_p in the largely neglected temperature region from 4 to 15°K.

We finally have to discuss the small T^{-2} term in C_p. The ground state of Lu^{3+} ion is $^1S_0$ and, thus, the usual

magnetic and quadrupole interactions responsible for C_p are absent. However, in substances with less than cubic symmetry the electric field gradients of the crystal will interact with the nuclear electric quadrupole moment. In lutetium this type of interaction might be relatively strong, since the quadrupole moments of both stable lutetium isotopes, Lu^{175} and Lu^{176}, are large, 5.6×10^{-24} and 8×10^{-24} cm^2,[25] respectively. In the first approximation, the nuclear specific heat due to this type of interaction with an axially symmetric field gradient becomes[26]

$$C_N = (R/45)P^2I(I+1)(2I+3)(2I-1)T^{-2}, \qquad (3)$$

where R is the gas constant, $P = 3e^2qQ/4kI(2I-1)$ the quadrupole coupling constant, and I the nuclear spin. Q is the nuclear quadrupole moment, e the electron charge, q the magnitude of the electric-field gradient in the direction of the c axis, and k the Boltzmann constant. By taking into account the relative abundances and the nuclear spins of the two lutetium isotopes (Lu^{175}: 97.5%, $I = \frac{7}{2}$; Lu^{176}: 2.5%, $I = 7$) and our experimental result $C_N = 0.094T^{-2}$ we obtain from Eq. (3) $q = 2.2 \times 10^{24}$ cm^{-3}. This electric-field gradient is about two orders of magnitude larger than the value calculated by de Wette,[27] using a point-ion model, for an hcp lattice with the axial ratio $(c/a = 1.5846)$ of lutetium metal. It is thus clear that the crystal field causes considerable distortion of the closed electronic shells and this, in turn, produces a field gradient at the nucleus. The effect is called antishielding. Edmonds[28] has investigated three lanthanum salts by NMR and finds crystal-field gradients about 20 times larger than those calculated by a simple theory. In a metal the antishielding should be somewhat bigger. The remaining discrepancy between our observed q for lutetium and the theoretical value by de Wette[27] is probably due to the point-charge model. Electric-field gradients of similar magnitude as deduced by us for lutetium have been found for other metals from an analysis of low-temperature heat-capacity measurements. Phillips[29] obtained for bismuth (rhombohedral lattice) $q = 1.83 \times 10^{24}$ cm^{-3} and Keesom and Bryant[30] found for rhenium (hcp lattice) $q = 2.9 \times 10^{24}$ cm^{-3}.

Using our experimental value for q the quadrupole coupling constant of Lu^{175} becomes $P = 0.00072$°K $= 15$Mc/sec.

It is also possible that the T^{-2} term is caused by long-range exchange-type coupling between the electronic moments of rare earth impurities in our lutetium sample. C_N could also be a combination of quadrupole and

[22] A. R. Mackintosh, Phys. Rev. Letters **9**, 90 (1962).
[23] O. V. Lounasmaa, Phys. Rev. (to be published).
[24] O. V. Lounasmaa, Phys. Rev. **133**, A211 (1963).

[25] A. Steudel, Z. Physik **152**, 599 (1958).
[26] B. Bleaney, J. Appl. Phys. **34**, 1024 (1963).
[27] F. W. de Wette, Phys. Rev. **123**, 103 (1961).
[28] D. T. Edmonds, Phys. Rev. Letters **10**, 129 (1963).
[29] N. E. Phillips, Phys. Rev. **118**, 644 (1960).
[30] P. H. Keesom and C. A. Bryant, Phys. Rev. Letters **2**, 260 (1959).

impurity effects; the above values of q and P must thus be considered as upper limits. A small "nuclear" term found in the specific heat of ytterbium[5] was attributed to impurities since the crystal structure of this metal is cubic and quadrupole interactions with the crystalline field are thus identically zero.

Ising Model and Self-Avoiding Walks on Hypercubical Lattices and "High-Density" Expansions

MICHAEL E. FISHER AND DAVID S. GAUNT

Wheatstone Physics Laboratory, King's College, London W.C.2, England

(Received 17 July 1963)

The high-temperature expansions of the partition function Z and susceptibility χ of the Ising model and the number of self-avoiding walks c_n and polygons p_n are obtained exactly up to the eleventh order (in "bonds" or "steps") for the general d-dimensional simple hypercubical lattices. Exact expansions of $\ln Z$ and χ in powers of $1/q$ where $q=2d$, and $1/\sigma$ where $\sigma=2d-1$, for $T>T_0$ are derived up to the fifth order. The zero-order terms are the Bragg–Williams and Bethe approximations, respectively. The Ising critical point is found to have the expansion

$$\theta_c = kT_c/2dJ = 1 - q^{-1} - 1\tfrac{1}{3}q^{-2} - 4\tfrac{1}{3}q^{-3} - 21\frac{34}{45}q^{-4} - 133\frac{14}{15}q^{-5} - \cdots,$$

while for self-avoiding walks

$$\mu = \lim_{n\to\infty} |c_n|^{1/n} = \sigma[1 - \sigma^{-2} - 2\sigma^{-3} - 11\sigma^{-4} - 62\sigma^{-5} - \cdots].$$

Numerical extrapolation yields accurate estimates for θ_c and μ when $d=2$ to 6 and indicates that χ diverges as $(T-T_c)^{-[1+\delta(d)]}$ where

$$3/\delta(d) \simeq 4, 12, 32\pm 1, 80\pm 2, 188\pm 12, \cdots \quad (d=2,3\cdots),$$

and that $c_n \approx A n^\alpha \mu^n$ $(n\to\infty)$ with

$$1/\alpha(d) \simeq 3, 6, 14\pm 0.3, 32\pm 1.5, 72\pm 7, \cdots.$$

1. INTRODUCTION

AN interesting conclusion that has emerged from the study of phase transitions in lattice systems is that the nature of the singularities characterizing the transition point are chiefly dependent on the dimensionality of the lattice. Thus, one-dimensional systems (with finite ranged forces) show no transitions, while all two-dimensional Ising models (at least those with nearest-neighbor interactions) have logarithmically divergent specific heats at T_c.[1-3] More strikingly, it has been shown that the ferromagnetic susceptibility of the Ising model diverges at the critical point as

$$\chi(T) \approx C/(T-T_c)^{1+\delta}, \tag{1.1}$$

where $\delta = \tfrac{3}{4}$ in two dimensions[4] and $\delta = \tfrac{1}{4}$ in three

dimensions.[5-8] Approximate theories of the mean-field type always predict $\delta = 0$.[3] Intuitive considerations, however, do suggest that $\delta(d)$ should decrease with dimension and approach this mean-field value as $d \to \infty$. This line of thought is supported by the recent development[9-11] of schemes for expanding the partition functions of interacting systems in inverse powers of a 'coordination parameter' z which is probably best regarded as a measure of the range of the interaction.[12,13]

[1] L. Onsager, Phys. Rev. **65**, 117 (1944).

[2] R. M. F. Houtappel, Physica **16**, 425 (1950); G. H. Wannier, Phys. Rev. **79**, 357 (1950); I. Syozi, Progr. Theoret. Phys. (Kyoto) **6**, 306 (1951).

[3] C. Domb, Advan. Phys. **9**, Nos. 34 and 35 (1960). This is an important review of work on the Ising model.

[4] M. E. Fisher, Physica **25**, 321 (1959).

[5] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).

[6] C. Domb and M. F. Sykes, J. Math. Phys. **2**, 52 (1961).

[7] G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961).

[8] For the Heisenberg model in three dimensions, the index δ is apparently $\tfrac{1}{3}$, see C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

[9] R. Brout, Phys. Rev. **118**, 1009 (1960); *ibid*. **122**, 469 (1961).

[10] G. Horwitz and H. B. Callen, Phys. Rev. **124**, 1757 (1961).

[11] R. B. Stinchcombe, G. Horwitz, F. Englert, and R. Brout, Phys. Rev. **130**, 155 (1963).

[12] G. A. Baker, Jr., Phys. Rev. **126**, 2071 (1962); *ibid*. **130**, 1406 (1963).

[13] A. F. J. Siegert (to be published) and in *Statistical Physics*, 1962 Brandeis Lectures (W. A. Benjamin, Inc., New York, 1963).