

The Heat Capacity of Gadolinium from 15 to 355°K*

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The heat capacity of gadolinium has been measured over the temperature range 15 to 355°K. An enhanced heat capacity associated with the ferromagnetic transition was observed, with maximum at 18.6°C. The thermodynamic functions were computed and are tabulated for various temperatures. The results are discussed in connection with theories of ferromagnetism.

INTRODUCTION

EXPERIMENTAL investigation of the enhanced heat capacity associated with ferromagnetic transitions is of interest in considering theories of ferromagnetism. Stoner¹ has on a number of occasions discussed the thermodynamics of ferromagnetism and in his collective electron theory² has developed expressions for the magnetic and electronic contributions to the heat capacity. His work has been extended by Wohlfarth.³

Statistical theories by Firgau,⁴ Takagi,⁵ and Weiss⁶ based on the Ising model also lead to expressions for the heat capacity and predict the magnitude of its discontinuity at the Curie temperature.

Of the familiar ferromagnetics, Ni and Fe have been most thoroughly investigated while Co has received less attention.⁷ In this series there is an increased difficulty of accurate work concomitant with the higher Curie temperatures of both Fe and Co and the phase transformations encountered in the case of Fe. Some work has also been done on ferromagnetic compounds such as MnAs,⁸ MnP,⁹ and a Heusler alloy.¹⁰

Gd was the fourth ferromagnetic element to be discovered,¹¹ it has a Curie temperature of only 18.6°C so that the transition falls in a temperature range that is especially suitable for accurate measurement of the heat capacity. We have made such measurements in the temperature interval of 15 to 355°K and have calculated the various thermodynamic functions.

EXPERIMENTAL

The Gd metal was made by reduction with Ca of the anhydrous fluoride. Procedures for the ion exchange separation of the Gd and for the reduction were previously developed in this laboratory.^{12,13} Ten buttons were first made and then recast in a Ta crucible; during this process the excess Ca is distilled off. The Ta is easily stripped or machined off the casting. The final sample, after machining, was in the form of a right circular cylinder 6.58 cm high and 3.67 cm in diameter. It weighed 505.29 g. Spectrographic analysis showed it to contain approximately 0.1 percent Sm, less than 0.1 percent Y, less than 0.3 percent Ta, less than 0.04 percent Ca. Si, Fe, and Mg were present to less than 0.01 percent. Other rare earths were not detected.

The adiabatic calorimeter and experimental techniques were the same as those used in a previous investigation of Th.¹⁴ The 130-ohm heater was of No. 38 constantan wire noninductively wound in a helical groove of a copper shell which fitted tightly into a hole machined along the axis of the Gd cylinder. The latter was suspended as such within the adiabatic shield of the calorimeter. The Pt resistance thermometer was, in turn, slipped into the heater shell. The thermometer has a nominal ice-point resistance of 25 ohms (which was checked just prior to its use) and was calibrated for us by the National Bureau of Standards. A weighed amount of Apiezon T grease was used to insure good thermal contact; this grease may be taken to a higher temperature than can Lubriseal before melting occurs. Leads from the thermometer and from the heater were wrapped around a small ring which fitted into a re-entrant well directly beneath the thermometer; this ring was held to the Gd by small screws.

The heat capacity of the Gd was obtained by subtraction of the heat capacity of the heater-thermometer core and other small parts (such as the ring and the small blocks holding the thermocouples) from the heat capacity of the complete assembly. For this auxiliary determination the heater-thermometer core and other parts were fitted into a thin copper shell having the same inside dimensions as the well in the gadolinium

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¹ E. C. Stoner, *Phil. Mag.* **22**, 81 (1936); *Trans. Roy. Soc. (London)* **A235**, 165 (1936).

² E. C. Stoner, *Proc. Roy. Soc. (London)* **A169**, 339 (1939).

³ E. P. Wohlfarth, *Revs. Modern Phys.* **25**, 211 (1953). This review includes references to relevant previous work.

⁴ U. Firgau, *Ann. Physik* **40**, 295 (1941).

⁵ Y. Takagi, *Proc. Phys. Math. Soc. Japan* **23**, 553 (1941).

⁶ P. R. Weiss, *Phys. Rev.* **74**, 1493 (1948).

⁷ K. K. Kelley, Bureau of Mines Bulletin 476 (U. S. Government Printing Office, Washington, D. C., 1949), presents a comprehensive bibliography. The most accurate work on nickel is that of C. Sykes and H. Wilkinson, *Proc. Phys. Soc. (London)* **50**, 834 (1938).

⁸ L. F. Bates, *Proc. Roy. Soc. (London)* **A117**, 681 (1928).

⁹ B. G. Whitmore, *Phil. Mag.* **7**, 125 (1929).

¹⁰ W. Sucksmith and H. H. Potter, *Proc. Roy. Soc. (London)* **A112**, 157 (1926).

¹¹ Urbain, Weiss, and Trombe, *Compt. rend.* **200**, 2132 (1935).

¹² F. H. Spedding *et al.*, *J. Am. Chem. Soc.* **69**, 2812 (1947).

¹³ F. H. Spedding and A. H. Daane, *J. Am. Chem. Soc.* **74**, 2783 (1952).

¹⁴ M. Griffel and R. E. Skochdopole, *J. Am. Chem. Soc.* **75**, 5250 (1953).

TABLE I. Atomic heat capacity of gadolinium in cal deg⁻¹ (g atom)⁻¹ (experimental points).^a Atomic weight = 156.9. 0°C = 273.16°K.

Mean T °K	Approx. ΔT	C _p	Mean T °K	Approx. ΔT	C _p	Mean T °K	Approx. ΔT	C _p	Mean T °K	Approx. ΔT	C _p
Series I			177.67	4.29	8.258	295.67	2.23	9.216	280.54	2.11	11.858
58.57	4.52	5.268	181.94	4.25	8.324	297.93	2.31	8.878	282.68	2.18	12.119
62.97	4.29	5.542	186.18	4.21	8.394	300.26	2.37	8.637	284.61	1.68	12.384
67.16	4.10	5.792	190.36	4.17	8.466	302.64	2.42	8.457			
71.19	3.97	5.963	194.51	4.13	8.538	305.02	2.46	8.296	286.27	1.65	12.635
75.10	3.85	6.135	198.62	4.09	8.613	307.49	2.49	8.177	287.63	1.08	12.873
78.90	3.75	6.286							288.70	1.06	13.121
			202.69	4.05	8.693	309.97	2.51	8.103	289.74	1.04	13.410
82.59	3.65	6.431	206.72	4.01	8.781	312.49	2.54	8.001	290.66	0.82	13.681
86.21	3.57	6.559	210.87	4.58	8.856	315.03	2.56	7.944	291.47	0.80	13.850
89.75	3.51	6.664	215.42	4.52	8.953	317.59	2.59	7.827			
93.24	3.46	6.754	219.91	4.47	9.048	Series II			292.30	0.87	12.782
96.67	3.41	6.835	224.35	4.41	9.164	15.10	3.59	0.467	293.28	1.08	10.229
100.52	4.29	6.928				18.00	2.22	0.754	294.39	1.15	9.586
			228.74	4.35	9.265	19.96	1.69	0.989	295.85	1.78	9.211
104.78	4.22	7.025	233.08	4.30	9.380	21.51	1.41	1.189	297.95	2.46	8.881
108.97	4.16	7.111	237.36	4.23	9.512	23.45	2.47	1.453	300.43	2.53	8.627
113.10	4.10	7.194	241.57	4.18	9.640	26.05	2.73	1.814	303.90	4.83	8.368
117.18	4.05	7.278	245.74	4.12	9.759	28.66	2.49	2.177	308.78	4.95	8.132
121.21	4.00	7.347	249.83	4.04	9.945	31.30	2.79	2.537	313.75	5.04	7.970
125.19	3.96	7.413				34.28	3.16	2.944	318.80	5.12	7.834
			253.87	3.97	10.108	37.31	2.91	3.326	323.90	5.18	7.731
128.69	3.92	7.475	257.84	3.90	10.299	40.19	2.85	3.654	329.05	5.22	7.666
132.59	3.88	7.539	266.31	3.73	10.748	45.10	3.45	4.175			
136.46	3.85	7.601	273.60	3.56	11.251	48.43	3.20	4.488	334.24	5.26	7.600
140.28	3.81	7.656	279.62	3.39	11.775	51.54	3.02	4.752	339.47	5.31	7.512
144.08	3.78	7.725	282.95	3.28	12.296	54.48	2.87	4.979	344.74	5.37	7.421
147.84	3.74	7.786				62.89	6.44	5.542	Series IV		
			285.41	1.66	12.516				337.33	5.15	7.482
151.57	3.71	7.831	287.05	1.63	12.791	Series III			342.43	5.17	7.454
155.69	4.51	7.897	288.65	1.58	13.148	274.43	2.21	11.284	347.54	5.21	7.378
160.18	4.46	7.974	290.21	1.54	13.565	276.44	1.81	11.474	352.70	5.24	7.323
164.62	4.42	8.047	291.75	1.56	13.383	278.42	2.14	11.637	357.82	5.26	7.287
169.01	4.37	8.122	293.54	2.05	10.048						
173.36	4.33	8.189									

^a Corrections for slope are included in Table II.

cylinder. Subtraction of the heat capacity of the weighed shell using the data of Giaque and Meads¹⁵ (confirmed by our own redetermination) gave the net heat capacity of the remainder. The thermochemical calorie is taken as 4.1840 absolute j.

In this work there occurred a difficulty which we did not previously encounter in the case of Cu or Th. This difficulty was associated with the poor thermal conductivity of gadolinium. As a result, for our rates of heating (which ranged from 0.15 to 0.45 deg per min), the temperature at the surface of the Gd was not uniform. It therefore was necessary to make an extensive series of investigations of the temperature distribution on the surface during a heating and of the heat leakage modulus between the Gd and the adiabatic shield. This work showed that by optimum placement of the thermocouples the shield could be controlled to the mean surface temperature of the cylinder. Under these conditions the corrections were made negligible; in the most unfavorable circumstances actually encountered the corrections would have been small.

¹⁵ W. F. Giaque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

RESULTS

The results of our measurements are given in Table I and are shown in Fig. 1. The values of C_p in Table II were taken from large smoothed curves. Four series of measurements were made. Series I extended from 58 to 317°K, series II from 15 to 63°K, series III extended from 274 to 345°K and series IV from 337 to 358°K. The experimental points lie within 0.1 percent of the smoothed curve with most points much closer than this. Because of the decreasing sensitivity of the thermometer the accuracy is limited to 1 percent at 20°K; 0.3 percent at 30°K. Above 35°K, the accuracy is believed to be 0.1 percent.

In Table III are listed the entropy, the enthalpy, and the Gibbs function. The extrapolation below 15°K was by means of a Debye function with $\theta = 152$.

DISCUSSION

The quantitative interpretation of heat capacity data for ferromagnetics is still very rudimentary, and experiments of this type may, in time, serve as a guide for further modification of theory. Nevertheless, it seems worthwhile to examine our results in light of existing theoretical schemes. We are interested in comparing (a) the "magnetic" entropy with its theoretical value,

(b) the heat capacity associated with the energy of magnetization with its value predicted from magnetization data alone, and (c) the discontinuity of the heat capacity at the Curie point with theoretical predictions.

The measured heat capacity at constant pressure C_p , regarded as the sum of several contributing factors, may be written as

$$C_p = C_q + C_m + C_e + \delta C. \quad (1)$$

In this equation C_q , C_m , and C_e are, respectively, the lattice, the magnetic, and the electronic contributions; and δC , the dilatation term, is the difference between the heat capacities at constant pressure and constant volume. Such a decomposition, admittedly not rigorous, may form the basis for discussion since to a first approximation the several terms are independent. Both C_m and C_e are electronic in origin but are treated as distinct.

Our results represent qualitatively the same type of behavior evidenced by Fe and Ni. The rise from the low-temperature side starts much earlier than would be expected; the discontinuity has a pronounced knee on the high-temperature side. For an extended range the heat capacity remains appreciably higher than would be expected from a combination of lattice and electronic terms.

We have calculated C_q under the assumption that it may be represented by a single Debye curve. In obtaining a value of Θ_D from our measurements at the lowest temperatures we should take account of the electronic heat capacity. If $C_p \sim C_p = \gamma T + AT^3$, then a plot of C_p/T vs T^2 permits evaluation of γ . This method is of use only in the T^3 region and its application to our three lowest points leads to values of γ which are certainly too high. Until accurate measurements at lower temperatures are available, we are constrained to assume that the γ coefficient of Gd is the same as that of La, namely 16×10^{-4} .¹⁶ After subtraction of the electronic contribution from each of the first three entries in Table II, we calculate Θ_D as 152, 150, and 148. We

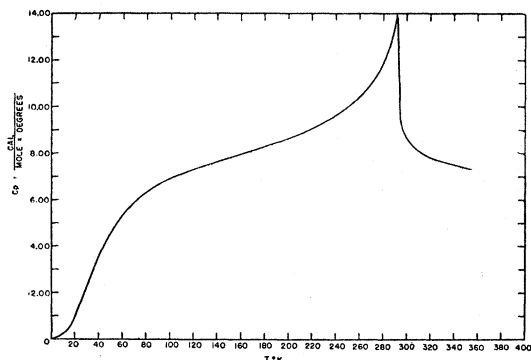


Fig. 1. Heat capacity of gadolinium at constant pressure.

¹⁶ Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

TABLE II. Heat capacity of gadolinium in cal deg⁻¹ (g atom)⁻¹. Atomic weight = 156.9. 0°C = 273.16°K.

T°K	C _p	C _q	T°K	C _p	C _q
15.0	0.456	0.435	190	8.458	5.775
20	0.995	0.936	195	8.547	5.784
25	1.664	1.542	200	8.641	5.793
30	2.363	2.151	205	8.738	5.801
35	3.035	2.704	210	8.842	5.808
40	3.632	3.180	215	8.944	5.815
45	4.160	3.579	220	9.051	5.822
50	4.627	3.911	225	9.170	5.828
55	5.012	4.186	230	9.299	5.833
60	5.361	4.414	235	9.440	5.839
65	5.670	4.604	240	9.592	5.844
70	5.922	4.763	245	9.757	5.848
75	6.134	4.902	250	9.953	5.853
80	6.337	5.010	255	10.168	5.857
85	6.520	5.108	260	10.408	5.861
90	6.670	5.191	265	10.673	5.865
95	6.796	5.263	270	10.979	5.868
100	6.914	5.326	275	11.349	5.871
105	7.026	5.381	280	11.802	5.875
110	7.134	5.429	285	12.446	5.878
115	7.235	5.471	290	13.468	5.880
120	7.329	5.509	295	9.402	5.883
125	7.417	5.543	300	8.667	5.886
130	7.499	5.573	305	8.316	5.888
135	7.577	5.601	310	8.086	5.891
140	7.655	5.624	315	7.926	5.893
145	7.734	5.647	320	7.805	5.895
150	7.813	5.667	325	7.715	5.897
155	7.893	5.685	330	7.650	5.899
160	7.973	5.701	335	7.586	5.901
165	8.054	5.716	340	7.499	5.902
170	8.135	5.730	345	7.415	5.904
175	8.215	5.743	350	7.350	5.906
180	8.293	5.754	355	7.309	5.907
185	8.374	5.765			

adopt the value 152, which is considerably above the value 132 which may be regarded as characteristic for La.¹⁶ The values of C_q ¹⁷ entered in Table II were found by use of the tables of Beattie. The total lattice contribution to the entropy at 360°K is $S_{360} - S_0 = 13.115$ cal/M deg. With our previous assumption as to the coefficient γ and the linearity with T of the electronic heat capacity, we calculate that its contribution to the entropy at 360°K is 0.576 cal/M deg. Hence the sum of the lattice and electronic contributions to the entropy is 13.691 cal/deg g atom.

The dilatation correction is made uncertain by lack of data over the complete range of temperature. The isothermal compressibility κ has been determined by Bridgman,¹⁸ at room temperature it is 25×10^{-7} cm²/kg. The coefficient of volume expansion β from -195°C to 300°C may be inferred from the work of Trombe and Foex¹⁹ which indicates that from -150°C to the Curie temperature the linear expansion coefficient is zero. Hence, application of the usual expression $C_p - C_v$

¹⁷ J. A. Beattie, J. Math. and Phys. **6**, 1 (1926).

¹⁸ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **82**, 99 (1953).

¹⁹ F. Trombe and M. Foex, Compt. rend. **235**, 42 (1952).

TABLE III. Thermodynamic functions of gadolinium.

$T^{\circ}\text{K}$	$S - S_0^{\circ}$ Cal/g atom deg	$(H^{\circ} - H_0^{\circ})/T$ Cal/g atom deg	$-(F^{\circ} - H_0^{\circ})/T$ Cal/g atom deg
15	0.155	0.116	0.039
50	2.797	1.875	0.922
100	6.880	3.948	2.932
150	9.867	5.098	4.769
200	11.770	5.878	5.892
250	13.820	6.545	7.275
293	15.610	7.246	8.364
298.16	15.774	7.284	8.490
300	15.828	7.293	8.535
360	17.238	7.364	9.874

$=T\upsilon\beta^2/\kappa$ shows that over the range mentioned the correction is negligible. Over the interval of 16 to 100°C, the linear expansion coefficient is constant and approximately equal to 8.3×10^{-6} deg⁻¹. At 25°C, we may thus take $\beta = 25 \times 10^{-6}$ deg⁻¹ and $\kappa = 25 \times 10^{-7}$ cm²/kg and find that C_v is about 0.034 cal/M deg less than C_p . The correction for other temperatures above 25°C may be assumed to vary by the factor $T/298$.

We may now inquire as to the entropy associated with the magnetic heat capacity. In the case of Gd both the saturation moment and the paramagnetic susceptibility variation may be accounted for by the same carrier as in the "ideal" magnetically dilute Gd salts.²⁰ The spectroscopic state of the trivalent ion is $^8S_{7/2}$, representing a parallel alignment of the seven electrons in the 4*f* shell. Hence, the entropy associated with the complete ordering of the spins is $R \ln 8$ or 4.132 cal/M deg. We may neglect the entropy associated with the dilatation, and from the calculations presented above the magnetic entropy at 360°K is 3.547 cal/deg g atom. This is 0.585 below the value $R \ln 8$. It should be remarked that even above 360°K there probably remains an appreciable magnetic contribution so that, especially in view of the uncertainties associated with Θ_D and γ , the discrepancy is not disturbing.

In the formal Weiss treatment, which postulates the existence of an internal field of magnitude $N\rho\sigma$, the internal energy per g associated with the intrinsic magnetization is $U = -\frac{1}{2}N\rho\sigma^2$. Assuming a constant density, the corresponding heat capacity is $C_m = -\frac{1}{2}AN\rho/J \times (\partial\sigma^2/\partial T)$. In these equations, σ is the intrinsic magnetization per g at temperature T , ρ is the density, N is the Weiss molecular field coefficient (not necessarily independent of T), J is the Joule mechanical equivalent of heat, and A is the atomic weight. From measurements of the paramagnetic susceptibility above the Curie temperature, it is possible to estimate $N\rho$. With the additional knowledge of $\partial\sigma^2/\partial T$ at various temperatures, it is then possible to evaluate the corresponding heat capacities and compare them with our more directly obtained values.

Kriessman and McGuire²¹ have reported that the

²⁰ L. Pauling, Proc. Natl. Acad. Sci. U. S. **39**, 551 (1953).

²¹ C. J. Kriessman and T. R. McGuire, Phys. Rev. **90**, 374 (1953).

molar paramagnetic susceptibility may be represented as $\chi_m = 8.21/T - 25.5$, T being in °C. The Curie constant per g is then 0.0524, and the effective magneton number $\mu_{\text{eff}} = (3\kappa C_m/\beta^2 N)^{\frac{1}{2}}$ is 8.15, corresponding closely to a spin of 7/2. On the basis of the Weiss theory the g susceptibility is given by the expression $\chi = C/(T - \theta) = C/(T - N\rho C)$, so that $N\rho$ is 5.70×10^3 . Values of $\partial\sigma^2/\partial T$ in the range from 8 to 14°C may be estimated from the work of Elliott, Legvold, and Spedding.²² From their curve we estimate that $\partial\sigma^2/\partial T$ at 8, 10, and 14°C is, respectively, -230, -290, and -507, so that from the equation $C_m = -(AN\rho/2J)(\partial\sigma^2/\partial T)$ we would predict the magnetic heat capacities 4.9, 6.1, and 10.8 cal/M deg. These may be compared with 5.60, 5.85, and 6.46 on the basis of Eq. (1).

The next item to be considered is the discontinuity in the heat capacity. Since the initially abrupt drop on the high-temperature side glides into a more gradual decrease, it is customary to extrapolate back from that side and take the discontinuity as the difference between the maximum heat capacity and the extrapolated point. Such a procedure yields for the discontinuity a value of about 7 cal/M deg, which is very similar to that found in the case of Fe, and about 3.5 times that found for Ni. But whereas the Weiss theory²³ comes close to agreement with experiment for both Ni and Fe, there is no such agreement for Gd. The same must be said for the statistical theories of Fircgau,⁴ Takagi,⁵ and Weiss⁶ which are based on the Ising model and are essentially equivalent. For simple cubic, body-centered cubic, or face-centered cubic lattices, the discontinuity in the heat capacity is found to be

$$\Delta C = \frac{3R}{8} \frac{Z^2(Z-2)}{Z-1} \left(\ln \frac{Z}{Z-2} \right)^2 \text{ cal/M deg,}$$

where Z is the number of nearest neighbors. We may assume that the value would not be essentially different for hexagonal closest packing. For $Z = 12$, the discontinuity is 3.24 cal/M deg, assigning one spin per atom. There seems no way to fit this to the case of Gd.

We may add a further comment on our choice of $\Theta_D = 152^\circ$ which is necessitated by the fact that the ratio of the heat capacity of Gd to that of La at 15°K is only 0.584 and cannot be much altered by any reasonable alternative choice of γ . The rare-earth metals would be expected to have characteristic temperatures which would be close together and show a monotonic variation in keeping with the increasing atomic weight

²² Elliott, Legvold, and Spedding, Phys. Rev. **91**, 28 (1953). Their curve of σ_0, τ^2 versus T was obtained by extrapolation to zero field of lines of constant magnetization in an $H-T$ plot. Unfortunately, the behavior of Gd is such that magnetic isothermals do not have a lengthy straight-line portion close to zero field such as is characteristic of Ni. This factor introduces some uncertainty into the extrapolation.

²³ For development of the equations see R. Becker and W. Döring, *Ferromagnetismus* (Julius Springer, Berlin, 1939), p. 67.

and the generally decreasing atomic volume. We may speculate as to whether the tighter binding in the case of Gd is primarily to be associated with its ferromagnetism. A determination of the characteristic temperature of Lu will thus be of interest.

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The Isotope Effect in Superconductivity

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The isotope effect in superconductors is usually summarized by giving the observed values of p in the equation $M^p T_c = \text{constant}$, where M is the isotopic mass and T_c the superconducting transition temperature. Fröhlich predicted the value $p=1/2$, but the measurements in some instances show deviations from this prediction. An explanation of the deviation of p from $1/2$ is offered based on an analog of Wien's displacement law applicable to the vibration spectrum of real crystal lattices. The departure of p from the value $1/2$ is attributed to the departure of the frequency spectrum from a simple power law. For many superconducting elements, p may be estimated from specific heat data, when such data are available to the desired degree of accuracy. A value of p is calculated for Sn which is in good agreement with some of the experiments. The large value 0.73 observed for Pb is shown to be reasonable. The values of p for the other superconducting elements are discussed. It is concluded that the observed deviations of p from $1/2$ are not necessarily in conflict with the theories of Fröhlich and Bardeen.

INTRODUCTION

THE various isotopes of a superconducting element have different transition temperatures T_c . This is the isotope effect discovered simultaneously by Maxwell of the National Bureau of Standards¹ and by Reynolds, Serin, Wright, and Nesbitt of Rutgers University.² Shortly after the discovery, the Rutgers group showed that the data of the mercury isotopes could be correlated by the formula $M^{1/2} T_c = \text{constant}$, where M is the isotopic mass.^{3,4} Since then, it has become customary to represent the data in the form⁵

$$M^p T_c = \text{constant}, \quad (1)$$

and to express the experimental results in terms of the power p . Actually, the range of M and T_c is so small that one observes more nearly the equivalent relation,

$$p = -\frac{M d T_c}{T_c d M} = -\frac{d \log T_c}{d \log M}, \quad (2)$$

arising from a plot of T_c versus M , or of $\log T_c$ versus $\log M$.

Measurements have been made of the isotope effect

¹ E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950).

² Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).

³ Serin, Reynolds, and Nesbitt, Phys. Rev. **78**, 813 (1950); **80**, 761 (1950).

⁴ Serin, Reynolds, and Nesbitt, Phys. Rev. **84**, 691 (1951).

⁵ Herzfeld, Maxwell, Scott, Phys. Rev. **79**, 911 (1950).

for Sn, Pb, Hg, and Tl.^{4,6-11} A review of the data to the end of 1952 can be found in an article by Maxwell.¹² The results seem to indicate that p is close to $\frac{1}{2}$ for some metals, with, however, significant departures, particularly for Pb. The observed values of p are shown in Table I taken from Maxwell's review article.¹²

At the time that the data were being collected which led to the discovery of the isotope effect, Fröhlich¹³ was developing a theory of superconductivity which attributed the cause of superconductivity to the interaction of the electrons with the phonon field. The theory was developed for the temperature 0°K and led to a threshold magnetic field H_0 proportional to $M^{-1/2}$. From this, one surmises that $T_c \propto M^{-1/2}$ from the fairly well established correlation $H_0 \propto T_c$. Thus, one can take Fröhlich's theory as having predicted the isotope effect. Bardeen also proposed a similar theory at about the same time. A review of both theories has been given by Bardeen.¹⁴ Neither theory has been developed to the extent required to include significant departures from the $\frac{1}{2}$ power law.

⁶ E. Maxwell, Phys. Rev. **86**, 735 (1952).

⁷ Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

⁸ Reynolds, Serin, and Lohman, Phys. Rev. **86**, 162 (1952).

⁹ Allen, Dawton, Bär, Mendelssohn, and Olsen, Nature **166**, 1071 (1950).

¹⁰ M. Olsen, Nature **168**, 245 (1951).

¹¹ E. Maxwell and O. S. Lutes, Jr., Phys. Rev. **86**, 649 (1952).

¹² E. Maxwell, Phys. Today **5**, No. 12, 14 (1952).

¹³ H. Fröhlich, Phys. Rev. **79**, 845 (1950).

¹⁴ J. Bardeen, Revs. Modern Phys. **23**, 261 (1951).