which are consistent with the observed de Haas–van Alphen frequencies. Further experiments or calculations which can distinguish between this model and the circular one proposed by Watts are necessary. It should be noticed in Fig. 2 that there is a waist on the almost triangular cigar. This is also consistent with the de Haas–van Alphen data. The larger cross-sectional area is about 2% greater than that of the waist. The corresponding experimental results predict 3%.

Specific Heat of Thulium Metal Between 0.38 and 3.9°K*

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The specific heat C_p of thulium metal has been measured in a He³ cryostat. Between 0.38 and 3.9°K $C_p = 2.839T^3 + 17.94T + 23.43T^{-2} - 1.79T^{-3} - 0.066T^{-4}$ (in mJ/mole °K). The last three terms represent the nuclear specific heat C_N. On the basis of earlier estimates, we put $C_L = 0.243T^3$ and $C_E = 10.5T$ for the lattice and electronic specific heats, respectively. According to the simple spin-wave theory, the magnetic specific heat C_M is proportional to T^3 for a ferrimagnetic metal; experimentally one finds $C_M = 6.2T^{5/2}$ for thulium, which has a rather complicated ferrimagnetic structure. Further, there seems to be no evidence in C_M for an exponential factor, to be expected because of magnetic anisotropy. All conclusions on C_M are tentative, however, until data at temperatures between 4 and 20°K become available. C_N does not fit to the simple picture as given by Bleaney either. Since $I = \frac{1}{2}$ for the only stable thulium isotope Tm¹⁶⁹, quadrupole interactions are zero and there are only two nuclear energy levels, their separation being determined by the magnetic hyperfine constant a'. This would give a nuclear specific heat with even powers of T only, with a' determining the values of the coefficients. The observed C_N cannot be fitted into an equation of this type which indicates that other interactions, probably nuclear exchange interactions, are present. Formally, the experimental situation may be expressed by writing $a' = a_0 - b/T$, instead of treating a' as a constant. Our results are in good agreement with recent Mössbauer data by Kalvius et al. who found 22.9 for the coefficient of the T^{-2} term.

I. INTRODUCTION

AT low temperatures, the specific heat of rare-earth metals has four components which, depending on circumstances, can be separated totally or partially from each other. These are the lattice specific heat $C_L = AT^3$, the electronic specific heat $C_E = BT$, the magnetic specific heat C_M, and the nuclear specific heat C_N. In the higher lanthanides, C_M is primarily caused by exchange interaction between the $4f$ electronic spins. At 4.2°K and below, thulium has a unique ferrimagnetic structure, to be described in some detail later (cf. Sec. IV.B).[1] It is interesting to see how well the magnetic specific heat follows the prediction, $C_M = CT^3$, of the simple spin-wave theory.[2]

C_N is due to splitting of the nuclear spin states by interaction with the $4f$ electrons. By far the largest contribution to C_N comes from the magnetic field pro-

duced by the orbital angular momentum of the $4f$ electrons. The resulting nuclear specific heat has the familiar appearance of a Schottky curve with its maximum somewhere below 0.1°K. Above the maximum, C_N may be expressed in inverse powers of T, the leading term being proportional to T^{-2}.

According to the above discussion the total specific heat of thulium becomes

$$C_p = AT^3 + BT + C_M + C_N, \quad (1)$$

where A and B are constants.

The present measurements on thulium are a part of our research program for studying the heat capacities of rare-earth metals between 0.4 and 4°K,[3–10] with particular emphasis on C_N. The specific heat of thulium has previously been measured by Jennings, Hill, and

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Spedding[11] between 15 and 360°K and by Dreyfus, Goodman, Lacaze, and Trolliet[12] between 0.5 and 4°K. The former data do not extend to low enough temperatures for determining C_N. Measurements by Dreyfus *et al.* are published as a brief research note only and detailed comparisons are thus impossible; this is unfortunate in view of the interesting behavior observed for C_N in the present research (cf. Sec. IV.C).

II. EXPERIMENTAL

The heat capacity measurements were carried out in a He^3 cryostat which has been described earlier[4]; only 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 24 h.

For the heat capacity measurements, a colloidal graphite (Aquadag) thermometer was employed; its construction has been described elsewhere.[4,8] 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 (chrominum methylamine alum salt) between 0.75 and 0.35°K. He^4 temperatures were determined according to the T_{58} scale.[13] For He^3 the 1962 Los Alamos scale[14] was employed; a correction was made for the 0.6% 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 0.35°K.

III. RESULTS

Our thulium 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 0.9 cm

long and 2.7 cm in diameter; its weight was 49.902 g (=0.29539 mole). The spectrographic laboratory at Argonne found the following metallic impurities (weight %): Al, 0.03%; Cr, 0.003%; Fe, 0.01%; K, 0.01%; Mg, 0.005%; Mn, 0.01%; Na, 0.02%, Ta, 0.12%; Ti, 0.01%. 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, 0.0006%; N, 0.20%; O, 0.10%; F, 0.024%; C, 0.014%. The accuracy is about 10%.

The experimental specific heat results are listed in Table I and the points are also plotted into Fig. 1. All

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

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
Run I		2.6331	101.5	Run III	
0.3876	129.6	2.8513	119.7	1.0345	42.04
0.4304	110.1	3.0789	140.9	1.1744	41.92
0.4808	92.70	3.3205	167.8	1.3213	43.54
0.5405	78.06	3.5976	199.1	1.4803	46.24
0.6114	65.71	3.9122	241.7	1.6372	50.29
0.6949	56.08			1.7819	54.75
0.7916	48.96	Run II		1.9211	60.12
0.8996	44.46	0.3799	133.6	2.0550	66.33
1.0157	42.26	0.4155	116.2	2.1880	72.38
1.1468	41.85	0.4572	100.2	2.3306	80.92
1.2877	43.24	0.5111	84.73	2.4937	91.61
1.4233	45.37	0.5746	71.73	2.6947	106.8
1.5598	48.40	0.6495	60.86	2.9315	126.8
1.6952	52.48	0.7359	52.63	3.1984	151.9
1.8286	57.04	0.8341	46.87	3.4993	187.5
1.9666	62.44	0.9428	43.44	3.8202	226.6
2.1092	69.19	1.0690	41.96		
2.2622	77.53	1.2077	42.49		
2.4347	88.37	1.3524	44.19		

calculations were performed by an IBM-704 digital computer.[15] The results have been corrected for curvature due to finite temperature increments when measuring C_p. The size of these increments may be computed from the separation of successive points in Table I.

After a heating period (about 1 min), the sample came to equilibrium in less than 2 sec at all temperatures. The heat leak to the calorimeter was always less than 0.2% of the corresponding heat input during heating periods. A correction for this was made in the customary manner by assuming linear drifts. The scatter of the points belonging to the same run from a smooth curve is about 0.3% (cf. Fig. 2). The heating current was measured with a Rubicon No. 2781 potentiometer and timed with an electronic timer using a tuning-fork frequency standard. The potentiometer was cross checked against a Rubicon No. 2773 double potentiometer, the timer compared with radio signals over a 24-h period, and standard cells and standard resistors cali-

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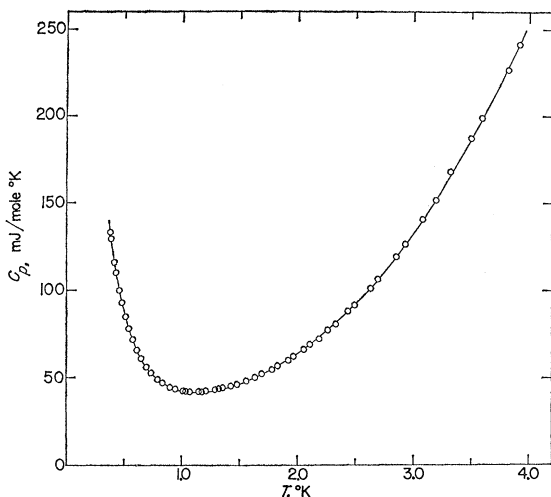
FIG. 1. The specific heat of thulium metal. Solid curve corresponds to equation $C_p = 2.839T^3 + 17.94T + 23.43T^{-2} - 1.79T^{-3} - 0.066T^{-4}$ (C_p in mJ/mole °K).

brated against NBS certified equipment. 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. As described in another paper,[8] it is likely that the coating had tiny cracks at which a small amount of heat was generated. Due to this, there might be an error of 0.1% in the effective heater resistance ($R_H = 362.13 + 0.03T$ Ω).

The heat capacity of the empty calorimeter ($C_{cal} = 0.0090T^3 + 0.116T$ mJ/°K) was known from an earlier experiment; it was never more than 1.2% of the heat capacity of the sample. Possible uncertainties here can cause only errors smaller than 0.1% in the final results.

As is usual in low-temperature calorimetry, the largest errors in C_p are probably due to calibration of the carbon thermometer. The scatter of the calibration points was, with a few exceptions, less than 1 mdeg. The calculated temperature is thus probably within 1 mdeg of the temperature defined by the He^4 and He^3 scales.[13,14] Uncertainties of about 2 mdeg may arise from the extrapolation of the magnetic thermometer calibration below 0.75°K.

The three runs and the thermomenter calibrations were made during the same experiment without warming the sample above 4.2°K in the meantime. Largest discrepancies between runs occur in C_p at 2.0°K where they are about 0.5%.

After considering all the sources of errors and the discrepancies 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 observed specific heat points from Table I, over the entire temperature range from 0.38 to 3.9°K, were fitted, after assuming $C_N = DT^{-2} - FT^{-4}$ ($F = D^2/R$, cf.

Sec. IV.C) and $C_M = CT^3$, to Eq. (1) by the method of least squares. The result was (C_p in mJ/mole °K):

$$C_p = 2.74T^3 + 19.2T + 19.15T^{-2} - 0.044T^{-4}. \qquad (2)$$

However, as may be seen from Fig. 2, deviations of the measured points from this curve are fairly large at low temperatures. This indicates that a term proportional to T^{-3} must be taken into account when expressing C_N (for a discussion on the temperature dependence of C_N, see Sec. IV.C). By writing $C_N = DT^{-2} - ET^{-3} - FT^{-4}$ the least-squares result was

$$C_p = 2.839T^3 + 17.94T + 23.43T^{-2}$$
$$- 1.79T^{-3} - 0.066T^{-4}. \qquad (3)$$

Standard deviations of the first four coefficients are 0.012, 0.12, 0.26, and 0.11. Equation (3) gives a reasonably good fit to the experimental points over the entire temperature range from 0.38 to 3.9°K (cf. Fig. 1); maximum deviations in $\Delta C/C$ are 1.9% at 1.3°K. Figure 2 shows that the fit is much better than with Eq. (2).

IV. DISCUSSION

A. The Lattice and Electronic Heat Capacities

Since the temperature dependence of C_M is uncertain, we must assume that the first term in (3) is due to C_L and C_M, the second term to C_E and C_M, and the last three terms to C_N. It is thus impossible to separate C_L and C_E from C_M without additional information.

On the basis of considerations described in an earlier paper,[8] we estimate that the lattice heat capacity of thulium should correspond to a Debye characteristic temperature $\theta = 200°K$ giving $C_L = 0.243T^3$, and that $C_E = 10.5T$ (C_L and C_E in mJ/mole °K). The major contribution to the first term in Eq. (3) thus comes
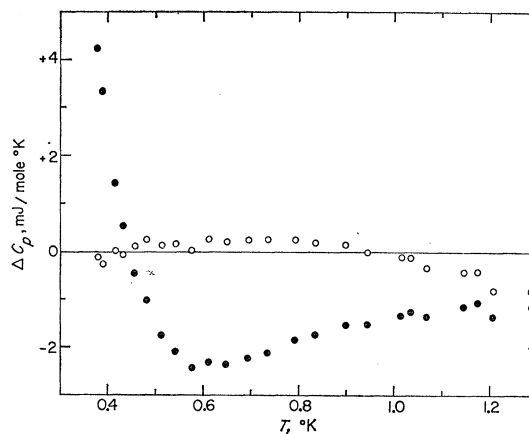

FIG. 2. Deviations ΔC_p of the experimental specific heat points from the expressions $C_p = 2.74T^3 + 19.2T + 19.15T^{-2} - 0.044T^{-4}$ [filled circles, Eq. (2)] and $C_p = 2.839T^3 + 17.94T + 23.43T^{-2} - 1.79T^{-3} - 0.066T^{-4}$ [open circles, Eq. (3)]. $\Delta C_p = C_p$(calc.) $- C_p$(exp) (in mJ/mole °K).

from C_M. The precision of these values is estimated as 5% for θ and 7% for C_E.[8]

B. The Magnetic Heat Capacity

The magnetic susceptibility of polycrystalline thulium has been studied by Rhodes, Legvold, and Spedding[16] and by Davis and Bozorth.[17] A Néel point was observed at about 56°K and a Curie point at 22°K. According to Jennings, Hill, and Spedding[11] the heat capacity shows a pronounced peak at the Néel point but no anomalous behavior was noted at the Curie point.

The magnetic structure of thulium has been determined by Koehler, Cable, Wollan, and Wilkinson[1] by using neutron diffraction techniques. At 4.2°K, where saturation has very nearly been reached, thulium has an antiphase domain-type structure in which four layers of atoms with their magnetic moments pointing in the direction of the positive c axis are followed by three layers of atoms with their moments in the opposite direction. The low-temperature magnetic structure of thulium is thus ferrimagnetic. Each atom has an ordered magnetic moment of 7 μ_B, and the ferrimagnetic structure has thus a net moment of 1 μ_B per atom.

According to the simple spin-wave theory,[2] the magnetic specific heat of a ferrimagnetic metal, at temperatures well below the Curie point, may be written $C_M = CT^3$, where C is a constant. Niira[18] and Cooper[19] have shown, however, that in metals with magnetic anisotropy there is an energy gap E_g at the bottom of the spin-wave spectrum. Due to this, $C_M = CT^{3/2} \exp(-E_g/kT)$ for a ferromagnetic metal and $C_M = CT^3 \exp(-E_g/kT)$ for a ferri- or antiferromagnetic metal.[20] More complicated formulas have also been proposed.[19] The physical reason for E_g is that it always takes a finite energy to turn a spin against the anisotropy field. Energy gaps of the order of $E_g/k = 20-30°$K have been predicted for dysprosium[19] and for terbium.[5]

We have tried to fit the magnetic specific heat of thulium, calculated from the relation (in mJ/mole °K; C_p is the measured specific heat) $C_M = C_p - 0.243T^3 - 10.5T - 23.43T^{-2} + 1.79T^{-3} + 0.066T^{-4}$, to the above formula for C_M. The best agreement was obtained without an exponential term and with C_M proportional to $T^{5/2}$ instead of T^3. The magnetic specific heat has been plotted into Fig. 3; the straight line corresponds to equation (C_M in mJ/mole °K).

$$C_M = 6.2T^{5/2}. \qquad (4)$$

Above 2.2°K, where C_M is more than 60% of the total C_p, the agreement is quite good; at lower temperatures C_M is small in proportion to the other contributions and the relative precision with which it can be deter-

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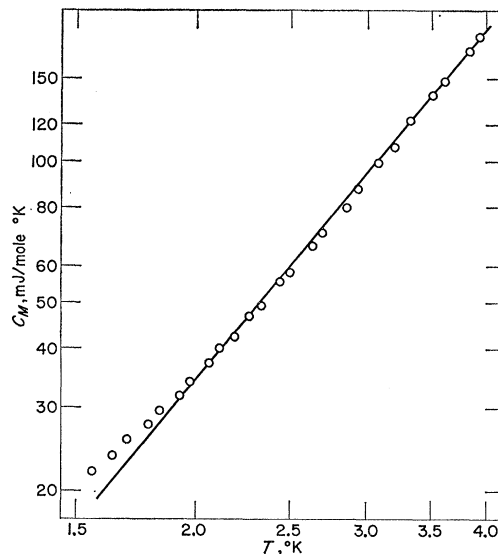[20] A. R. Mackintosh, Phys. Letters 4. 140 (1963).

FIG. 3. The magnetic specific heat of thulium. The straight line corresponds to equation $C_M = 6.2T^{5/2}$ (C_M in mJ/mole °K).

mined becomes poor. Of course, the weak points in our calculation are the assumptions made about the size of C_L and C_E. By writing $C_E = 17.94T$ [cf. Eq. (3)], C_M would be proportional to T^3. It seems unlikely, however, that the electronic specific heat is much larger for thulium than for the other trivalent lanthanides.[8] Of course, by subtracting C_L, C_E, and C_N from C_p in Eq. (3), we get $C_M = 2.596T^3 + 7.44T$. This relation for C_M has, however, no theoretical basis.

Before drawing any definite conclusions about the temperature dependence of C_M, measurements of C_p should be made at higher temperatures, especially between 4 and 20°K. This would allow us to decide whether or not an exponential factor is necessary in expressing C_M. At the moment one can only say that such a factor does not seem to be very important.

Measurements by Dreyfus et al.[12] gave $C_p = 0.949T^3 + 21.5T + 27T^{-2}$ (C_p in mJ/mole °K). Their data agree with ours at 1.5°K, are higher at lower temperatures and lower above 1.5°K; at 4°K the difference is 40%. Large discrepencies between specific heat results of different investigators are quite common between 2 and 4°K for rare-earth metals.[3–5,9] The disagreement is usually attributed to impurities which, even in small concentrations, might significantly alter the energy gap E_g at the bottom of the spin-wave spectrum.[4,5,19] There is some difficulty with this explanation here since the exponential factor in C_M seems to be absent or its effect is small in thulium. Another possibility is magnetic ordering in an impurity which, even in quantities of 0.1% of the sample, will cause large contributions to the observed specific heat, provided a magnetic transformation occurs in the impurity in or near the temperature range under investigation.[7]

C. The Nuclear Heat Capacity

Bleaney[21] has discussed the nuclear specific heat of rare-earth metals in detail. The splitting of the nuclear energy levels is given in general by the Hamiltonian

$$\mathfrak{IC}=a'i+P[i^2-\tfrac{1}{3}I(I+1)]-\tfrac{1}{2}\sum_{j\neq k} 2(\mathbf{I}_j\cdot \mathbf{K}_{jk}\cdot \mathbf{I}_k),\quad (5)$$

where the first two terms represent magnetic hyperfine and electric quadrupole interactions between the nucleus and its own electrons (usually by far the biggest interaction is due to the $4f$ electrons) and the third is exchange interaction between neighboring nuclei. Since $I=\tfrac{1}{2}$ for the only stable thulium isotope Tm^{169}, there are only two nuclear energy levels, corresponding to $i=+\tfrac{1}{2}$, $-\tfrac{1}{2}$ in (5), and quadrupole interactions are identically $=0$. The magnetic hyperfine constant a' varies as $\langle J_z\rangle$, which measures the electronic magnetization. At temperatures below $2°K$, where C_N is appreciable when compared with the other contributions to C_p, complete electronic magnetization is usually assumed and $\langle J_z\rangle$ is replaced by $J(=6$ for Tm^{3+} ions) and thus $a'=$ const.

Once the nuclear energy levels are known, C_N can be calculated from the partition function in the usual way and, by expanding the nuclear specific heat in inverse powers of T, we obtain [cf. Eq. (3)]

$$C_N=DT^{-2}-ET^{-3}-FT^{-4}+\cdots,\quad (6)$$

where

$$D/R=\tfrac{1}{3}(a')^2I(I+1)$$
$$+(4/9)I^2(I+1)^2\sum_{jk}(K_x^2+K_y^2+K_z^2)_{jk},\quad (7)$$

$$E/R=(4/9)(a')^2\sum_{jk}(K_{jk})_z I^2(I+1)^2,\quad (8)$$

$$F/R=(1/30)(a')^4 I(I+1)(2I^2+2I+1)\quad (9)$$

($P=0$, R is the gas constant, magnetic field is assumed in z direction, some higher terms in $\mathbf{K}$ have been ignored).

According to Bleaney's[21] estimates, contributions from the nuclear exchange interaction should be relatively small. However, if we put $\mathbf{K}=0$ only even powers of T appear in (6) and $(I=\tfrac{1}{2})$

$$F=(3D^2/10R)(2I^2+2I+1)/(I^2+I)=D^2/R.\quad (10)$$

By assuming $D=19.15$ mJ $°K/$mole [cf. Eq. (2)], we get $F=0.044$ mJ $°K^3/$mole. Even at $0.4°K$, the T^{-4} term accounts only for 1.5% of the total C_N. By ignoring relation (10) and by letting all the coefficients in (2) be free in the least-squares analysis, we obtain a considerably larger value of F (C_p in mJ/mole $°K$):

$$C_p=2.82T^3+18.2T+21.6T^{-2}-0.49T^{-4}.\quad (11)$$

This equation fits to the measured points almost as well

as (3). Our experimental accuracy is not sufficient to decide whether the "residual" C_N is proportional to T^{-3} or to T^{-4}.

In any case, the observed C_p below $1°K$ forces us to assume that other interactions, besides the magnetic hyperfine term, have a fairly large effect in the value of C_N. Due to the peculiar magnetic structure of thulium, the nuclear exchange interaction, acting through the spin waves, might be unusually large in this metal. We shall adopt Eq. (3) for representing the specific heat of thulium; this choice was made since it is impossible to explain the large T^{-4} term in (11) on theoretical grounds. In these two relations the coefficient of the T^{-2} term differs by 8%. On the basis of this and our earlier error estimates (cf. Sec. III), we put $D=23.4\pm1$ mJ $°K/$mole. If the temperature dependence of C_N in Eq. (3) and the ratio $F/D=D/R$ [cf. Eq. (10)] can be assumed correct, the limits of error in D would be ±0.5 mJ $°K/$mole.

Dreyfus et al.[12] have calculated from their specific heat data $D=27\pm3$ mJ $°K/$mole without taking higher terms in C_N into account. Since their measurements have been published as a smoothed curve only, it is impossible to reanalyze them. However, inclusion of higher terms would tend to increase D. From atomic beam experiments on neutral thulium atoms by Ritter,[22] Bleaney[21] has derived $D=26.9$ mJ $°K/$mole, which is in good agreement with the result by Dreyfus et al. However, recent Mössbauer measurements by Kalvius, Kienle, Eicher, Wiedemann, and Schüler[23] on thulium metal gave, at $5°K$, the splitting of the ground state as $9.04\cdot10^{-6}$ eV, which corresponds to $D=22.9$ mJ $°K/$mole. If electronic magnetization was not complete at $5°K$, this value would tend to increase towards lower temperatures; this effect cannot be larger than about 0.5%.[23]

The present specific heat measurements are thus in good agreement with the Mössbauer data.[23] The observed temperature dependence of C_N remains a puzzle. Formally one can write for thulium, in the temperature range studied, $a'=a_0-b/T$, whatever the reason may be. Here a_0 and b are constants. By extending the measurements to still lower temperatures, more would be learned about the nature of the interactions, in particular, one could see whether cooperative effects are present.

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