

CBPF-NF-055/85

THE LOW TEMPERATURE CONTRIBUTIONS TO
 β -URANIUM HYDRIDE SPECIFIC HEAT*

by

J.C. FERNANDES¹, M.A. CONTINENTINO^{1§}
and A.P. GUIMARÃES

Centro Brasileiro de Pesquisas Físicas - CNPq/CBPF
Rua Dr. Xavier Sigaud, 150
22290 - Rio de Janeiro, RJ - Brasil

¹Departamento de Física
Universidade Federal Fluminense, CP 296
24210 - Niterói, RJ - Brasil

[§]Present address:
IBM - T.J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598, USA

*Work partially supported by FINEP - Brasil

ABSTRACT

Recent observation of Proton Magnetic Resonance in ferromagnetic β -Uranium Hydride by Barash et al. led us to perform a new analysis of the specific heat data of Flotow and Osborne for this compound. In the temperature region $1.469 \text{ K} \leq T \leq 3.927 \text{ K}$, the specific heat C was found to be given by the expression $C = 29.504 T + 0.099 T^3 \text{ mJ K}^{-1} \text{ mol}^{-1}$ while, for $4.332 \text{ K} \leq T \leq 15.184 \text{ K}$, $C = 28.464 T + 0.157 T^3 + 55.906 \left[T^{3/2} + \frac{4}{5} T_0 T^{1/2} + \frac{4}{15} T_0^2 T^{-1/2} \right] \exp(-T_0/T)$ in the same units, with $T_0 = 79.3 \text{ K}$. This result indicates that the dispersion relation for magnons in this compound has the form $E = k_B T_0 + Dk^2$. The large energy gap ($k_B T_0$) is attributed to the high magneto-crystalline anisotropy arising from the unquenched orbital moment of the uranium ions. To our knowledge this is the first energy gap reported for magnons in an actinide compound.

Key-words: Specific heat; Uranium hydride.

1 INTRODUCTION

Flotow and Osborne¹ performed very accurate measurements of the specific heat of a high purity sample of β -uranium hydride (β -UH₃). They tried to fit their data, for $1.469 \text{ K} \leq T \leq 3.927 \text{ K}$, with the function

$$C = \gamma T + A T^3 + B T^{3/2}; \quad (1)$$

a negative value was obtained for B, which is a physically inconsistent result. Fernandes and Souza² attempted a new analysis of the same data, including a term of the form $C_N T^{-2}$, in order to account for the proton hyperfine interaction. The results of the fitting appear to be very dependent of the sub-set of the experimental points considered while negative values remained for some of these sub-sets. In this way, no conclusion has been reached about the temperature dependence of each internal contribution to the specific heat of β -UH₃.

Recently, the observation of Proton Magnetic Resonance (PMR) in ferromagnetic β -UH₃ by Barash et al.³ showed that the hyperfine contribution to the specific heat of this compound is negligible ($0.006 \text{ T}^{-2} \text{ mJ K}^{-1} \text{ mol}^{-1}$). Besides that, PMR suggests that magneto-crystalline anisotropy in this compound is extremely large since the signal intensity does not appear to suffer any influence of external magnetic fields as intense as 18 kOe. This result is similar to those found for NMR in Tb and Dy metals⁴. The hypothesis of a large anisotropy in β -UH₃ seems reinforced by two observations. Firstly, the PMR frequency as a function of the applied field, in the region of intense

fields, yields a gyromagnetic ratio 0.5% greater than that known for free protons. Secondly, the r.f. power needed for exciting PMR is exceedingly high (≈ 5 kW). These PMR results led us to try a new analysis of Flotow and Osborne data in order to obtain consistent physical results. This is the object of the present study which we will start with a review of some relevant physical properties of β -UH₃.

β -UH₃ is ferromagnetic below a not very well determined temperature T_c . Specific heat measurements by Flotow et al.⁵ give $T_c = 170.7$ K while magnetization measurements by Lin and Kaufmann⁶ and by Henry⁷ give $T_c = 181$ and 168 K respectively. No phase transition or physical anomaly is found below T_c . This pyrophoric hydride conducts electricity almost as well as uranium metal⁸.

β -UH₃ is a well defined stoichiometric compound. Its crystallographic structure, as studied by Rundle⁹, is shown in Figure 1. The structure is cubic with eight formula units per unit cell. The uranium ions occupy the two non-equivalent sites of β -W (A15) lattice. The 24 hydrogen ions are all equivalent. Each one is found inside a tetrahedron of uranium ions. In turn, each uranium ion is found at the center of an icosahedron of hydrogens. For the uranium ion shown schematically at the center of the cube in Figure 1, the vertices of the surrounding icosahedron are the six pairs of hydrogens on the lines joining the six pairs of uranium ions on the opposite faces of the cube. The smallest distance between uranium ions is 3.316 \AA . The lattice constant is 6.631 \AA .

Henry's magnetization measurements⁷ of powdered β -UH₃ in

dicating $n_f = 1.18 \pm 0.03 \mu_B \equiv \mu_{\text{total}}$ where n_f is the apparent saturation magnetization per uranium ion in Bohr magneton units. Neutron diffraction studies¹⁰ led to $n_f = 1.39 \mu_B \equiv \mu_{5f}$ and PMR measurements³ give $n_f = 1.45 \pm 0.1 \mu_B \equiv \mu_{\text{PMR}}$. The quantity $\Delta\mu = \mu_{\text{total}} - \mu_{5f}$ is a measure of the conduction electrons polarization¹¹. The result $\mu_{5f} \approx \mu_{\text{PMR}}$ reinforces the idea of an electronic configuration for hydrogen in $\beta\text{-UH}_3$ similar to that of atomic helium². For such a configuration, protons should be screened against conduction electrons.

Wilkinson et al.¹², in further neutron diffraction studies, established that the lattice ordering is of simple ferromagnetic type and pointed out that the magnetic form factor has strong orbital moment characteristics.

Magnetization, as well as PMR measurements, indicate strong anisotropy fields. Henry's work⁷ shows that the magnetization of $\beta\text{-UH}_3$, for liquid helium temperature range, increases rather slowly as a function of applied field, approaching an asymptote at 60 kOe. Lin and Kaufmann⁶ conclude that the high coercive force measured in $\beta\text{-UH}_3$ is accounted for by the high magneto-crystalline anisotropy.

2 ANALYSIS OF THE SPECIFIC HEAT DATA

The tabulated data of Flotow and Osborne¹ consist of 35 points in the region $1.469 \text{ K} \leq T \leq 22.650 \text{ K}$. For fitting purposes we have taken from this ensemble two groups of points: 15 in the region $1.469 \text{ K} \leq T \leq 3.927 \text{ K}$ (lower temperature re-

gion) and 15 points in the region $4.332 \text{ K} \leq T \leq 15.184 \text{ K}$ (higher temperature region). The remaining 5 points have not been considered for fitting calculations. Such division is justified since the Debye temperature θ_D may change in the whole region causing a change in the lattice contribution coefficient. This is the case of metallic uranium¹³ and of the non-magnetic rare earths¹⁴. Also, if the magnetic anisotropy field is exceptionally intense, magnons will not contribute to the specific heat in the lower temperature region as is the case of metallic Tb¹⁵ and Dy¹⁶.

2.1 Least squares fits in the lower temperature region

The function chosen for fitting the experimental data in this region was:

$$C = \gamma T + A T^3 + C_M. \quad (2)$$

The first term accounts for the conduction electrons, the second one for the lattice and the last for the magnon contribution to the molar specific heat C . The hyperfine contribution has been neglected since it is exceedingly small. As C_M we have tried two different functions: $B T^n$ and $B T^{3/2} \exp(-T_0/T)$, where B was to be fitted while n and T_0 were previously chosen. In the region $n < 1$ the three coefficients γ , A and B were found to be positive. For $1 < n < 3$ B was found negative. For $3 < n \leq 3.5$ the coefficient A turned out to be negative. For $n = 1$ and $n = 3$ we have identical situations: Eq.2 is reduced to only two terms which were found both positive. The second expression taken as C_M led to negative values for B if $0 \leq T \leq 4.5 \text{ K}$. However, the

modulus of B decreased continuously as T_0 was increased.

The above results led us to conclude that the function which represents the specific heat of β -UH₃ in the region $1.469 \text{ K} \leq T \leq 3.927 \text{ K}$ is:

$$C = (29.504 \pm 0.010)T + (0.099 \pm 0.001) T^3 \quad (3)$$

where C is given in $\text{mJ K}^{-1} \text{ mol}^{-1}$. The possibilities $n < 1$ and $n > 3.5$ have not been considered since there is no theoretical justification for them.

Eq.3 fits the experimental points with a standard deviation of 0.1% for an individual point and a maximum deviation of 0.3%. Above results for γ and A change less than 0.1% and 4% respectively for whatever sub-set of experimental points considered in this temperature region, down to a minimum of 8 points.

The physical interpretation of Eq.3 may be guessed with the aid of Figure 2. This figure shows both the graphical extrapolation of the function given by Eq.3 and the experimental points obtained in the higher temperature region and above. It is clear from this figure, unless some contribution of the lower temperature region suffers an unexpected increase, that there is an added new contribution for the β -UH₃ specific heat in the higher temperature region. We tried to identify this new contribution as due to magnons of a highly anisotropic material. As we shall see below, such interpretation seems to be consistent. In this way, the terms in T and T^3 represent only the conduction electrons and the lattice contributions respectively.

2.2 Fits in the higher temperature region

For a cubic crystal having simple ferromagnetic order, the dispersion relation for magnons is

$$E = g \mu_B H_A + D k^2 \quad (4)$$

provided the spontaneous magnetization meets two conditions: it is small in face of the anisotropy field H_A and it lies either along the (1,0,0) or the (1,1,1) directions¹⁷. In Eq.4 g , μ_B , D and k stand for the gyromagnetic ratio, the electronic Bohr magneton, the spin wave stiffness and the wave number respectively.

If Eq.4 is valid, the relative magnetization and the volumetric specific heat are given, respectively, by

$$\frac{M_0 - M(T)}{M_0} = \frac{g\mu_B}{M_0} \left(\frac{k_B T}{4\pi D} \right)^{3/2} F\left(\frac{3}{2}, \frac{T}{T_0}\right) \quad (5)$$

and

$$C_M^V = \frac{15}{4} k_B \left(\frac{k_B T}{4\pi D} \right)^{3/2} \left[F\left(\frac{5}{2}, \frac{T}{T_0}\right) + \frac{4}{5} \frac{T_0}{T} F\left(\frac{3}{2}, \frac{T}{T_0}\right) + \frac{4}{15} \left(\frac{T_0}{T}\right)^2 F\left(\frac{1}{2}, \frac{T}{T_0}\right) \right] \quad (6)$$

where

$$T_0 = g\mu_B H_A / k_B \quad (7)$$

and

$$F(s, x) = \sum_{p=1}^{\infty} p^{-s} \exp(-p/x). \quad (8)$$

The symbol k_B stands for the Boltzmann constant. The expressions 5 and 6 have been first obtained by Kouvel and Brooks¹⁸.

To fit the specific heat data in the higher temperature region we have again used Eq.2 taking as C_M a simplified version of Eq.6. Since C_M must be negligible in the frontier between the two temperature regions in order to be continuous, we may expect that all terms in the summation appearing in Eq.8 may be neglected in face of the first. For this reason, the trial function taken as C_M in the higher temperature region is:

$$C_M = B \left[T^{3/2} + \frac{4}{5} T_0 T^{1/2} + \frac{4}{15} T_0^2 T^{-1/2} \right] \exp(-T_0/T) \quad (9)$$

The results of the fit of Eq.2 to the experimental points lying in the higher temperature region, with C_M given by Eq.9, appear in Table I. It must be remarked that four parameters have been simultaneously fitted. The standard deviation for an individual point is 0.1% if the fifteen points of this temperature region are considered. Table I shows that the lower points in higher temperature region led to large values for T_0 . This fact justifies the approximation used in Eq.6. It may be verified also, from the results in Eq.3 and in Table I, that each individual contribution to the specific heat fulfils satisfactorily the continuity requirement in the frontier between the two temperature regions. The exception is the lattice con

tribution whose coefficient A is 50% greater in the higher temperature region. This change indicates that the average of θ_D in this region is 14% smaller than that in the lower temperature region. A decrease of 10% in θ_D , for the same temperature regions, is found for uranium metal¹³.

The Figure 2 shows the C versus T curve calculated from those parameters obtained in the case all the fifteen points in the higher temperature region have been considered for fitting. It may be verified that this function fits very well not only the experimental points considered for calculations but also those, above 15.184 K, which became a test for the fitting.

Other functions such $BT^n \exp(-T_0/T)$, where $n=1.5, 2$ and 3 , have been tried as C_M in the higher temperature region. The values obtained for T_0 lie all above 30 K. The correspondent functions for C fit very well the experimental points which lie inside this region, but they do not fit as accurately as that with C_M given by Eq.9 the remaining points above 15.184 K. We believe that this criterion is good for choosing the correct function. Due to the large energy gap, the number of magnons is sufficiently low to ensure the validity of spin wave theory well above 20 K in β - UH_3 . The deviation of the experimental points from the full line, which appears in Figure 2 above 19 K, is very probably due to changes in θ_D and in H_A and not to a breakdown of the validity of spin wave theory.

The function BT^n does not lead to any fitting in the higher temperature region if the same precision requirements, as those imposed to the other mentioned functions, are maintained.

3 DISCUSSION OF THE RESULTS

The results obtained from the computer fits give us the density of electronic states at the Fermi level, $n(E_F)$, the Debye temperature θ_D and the magnetic parameters D and T_0 for β - UH_3 .

In the low temperature region we get $n(E_F) = 12.6/$ atom eV if we consider only the uranium ions. If we consider also the hydrogen ions this number is obviously divided by four. Probably the hydrogen ions do not furnish electrons to the Fermi sea since, as we have mentioned in §1, $\mu_{\text{PMR}} \approx \mu_{\text{total}}$. Therefore, the above number seems to be the correct one. For uranium metal and US the values of γ are 9.88 and 23.38 $\text{mJ K}^{-2} \text{mol}^{-1}$ respectively^{13,20}.

For θ_D the situation is complicated due to the structure of the primitive cell. However, as the ionic masses are quite different, the acoustical branch of the dispersion relation for phonons depends only on the uranium mass. For this reason we may assume, in a first approximation, that there are only uranium ions in the crystal. Within this picture we get $\theta_D = 270$ K in the lower temperature region. The value of θ_D is 222 K for uranium metal¹³ and 190 K for US²⁰.

To obtain D we must equate the product of the constant terms in front of the brackets in Eq.6 to the B coefficient in Eq.9 divided by the molar volume v . Thus

$$\frac{D}{k_B} = \frac{1}{4\pi} \left[\frac{15}{4} \cdot \frac{k_B \cdot v}{B} \right]^{2/3} \quad (10)$$

For β - UH_3 , $v = 22.07 \text{ cm}^3 \text{ mol}^{-1}$ since its density⁹ is 10.92 g cm^{-3} . Taking for B the value obtained in the case the fifteen points are considered for fitting (see Table I), we get $D/k_B = 0.60 \cdot 10^{-14} \text{ K cm}^2$. The correspondent values for Gd ¹⁹ and US are $0.33 \cdot 10^{-13}$ and $1.1 \cdot 10^{-13}$ respectively, in the same units. The last value has been calculated from results by Westrum et al.²⁰.

The value obtained for T_0 in β - UH_3 , 79.3 K , is large if compared to the correspondent values for the strongly anisotropic ferromagnets Tb and Dy which are 23.5 and 31 K respectively¹⁴. However, such a comparison may not be meaningful since the function taken as C_M for fitting the specific heat data in these rare earths was $BT^{3/2} \exp(-T_0/T)$ and not that given by Eq.9.

We may acquire confidence in the values we have obtained for T_0 and D if some known value of the relative decrease of magnetization with temperature is recovered by Eq.5 with these values replaced in it. Under the same approximation used for obtaining Eq.9, Eq.5 becomes:

$$\frac{M_0 - M(T)}{M_0} = \frac{1}{N S} \left(\frac{k_B T}{4\pi D} \right)^{3/2} \exp(-T_0/T), \quad (11)$$

where N is the number of spins per unit volume and $1/NS$ replaces the factor $g \mu_B/M_0$. For $S=1$, which is a likely spin value per uranium ion in β - UH_3 , Eq.11 gives $(M_0 - M(40 \text{ K}))/M_0 = 6\%$. This result is consistent with experimental observations⁷. The values obtained for T_0 and D are, therefore, reliable. Eq.11, which is a result of spin wave theory, may be applied

up to 40 K in β - UH_3 since the relative decrease of magnetization at this temperature is small.

Of course, it would be desirable to obtain D and T_0 independently, i.e., through a fit of Eq.11 to the experimental curve of magnetization versus temperature. Unfortunately, an accurate version of this curve is not available below 80 K.

To conclude, a qualitative justification for the existence of a large magneto-crystalline anisotropy in β - UH_3 must be given. As the symmetry around a uranium ion in β - UH_3 is the highest attainable in a crystal (see § 1), we may expect that its orbital moment is only slightly quenched. This fact is confirmed by neutron diffraction studies¹². Consequently, a large magneto-crystalline anisotropy arising from the unquenched orbital moment of uranium may be expected in ferromagnetic β - UH_3 .

HEADINGS OF THE FIGURES LEGENDS AND TABLE

FIGURE 1

Crystal structure of β -UH₃. ○ Uranium ions ● Hydrogen ions.
Not all hydrogen ions are shown.

FIGURE 2

● Flotow and Osborne specific heat measurements in β -UH₃.
Full line: Graphical representation of the function

$$C = \gamma T + A T^3 + B \left[T^{3/2} + \frac{4}{5} T_0 T^{1/2} + \frac{4}{15} T_0^2 T^{-1/2} \right] \exp (-T_0/T)$$

with values of γ , A, B and T given at the top of Table I.

Dashed Line: Graphical representation of the function.

$$C = 29.504 T + 0.099 T^3$$

which fits the specific heat measurements of Flotow and Osborne¹
in β -UH₃ in the region $1.469 \text{ K} \leq T \leq 3.927 \text{ K}$.

TABLE I

Results of least squares fits of Flotow and Osborne specific
heat measurements¹ in β -UH₃ to the function

$$C = \gamma T + A T^3 + B \left[T^{3/2} + \frac{4}{5} T_0 T^{1/2} + \frac{4}{15} T_0^2 T^{-1/2} \right] \exp (-T_0/T).$$

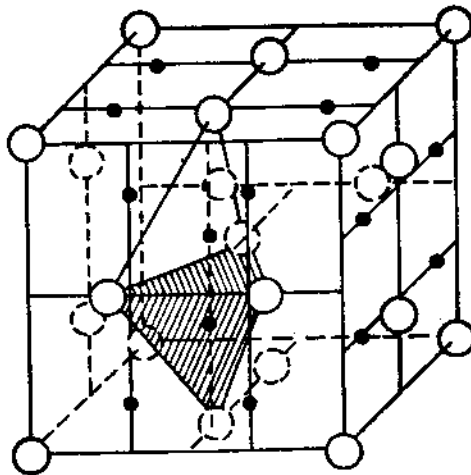


Figure 1

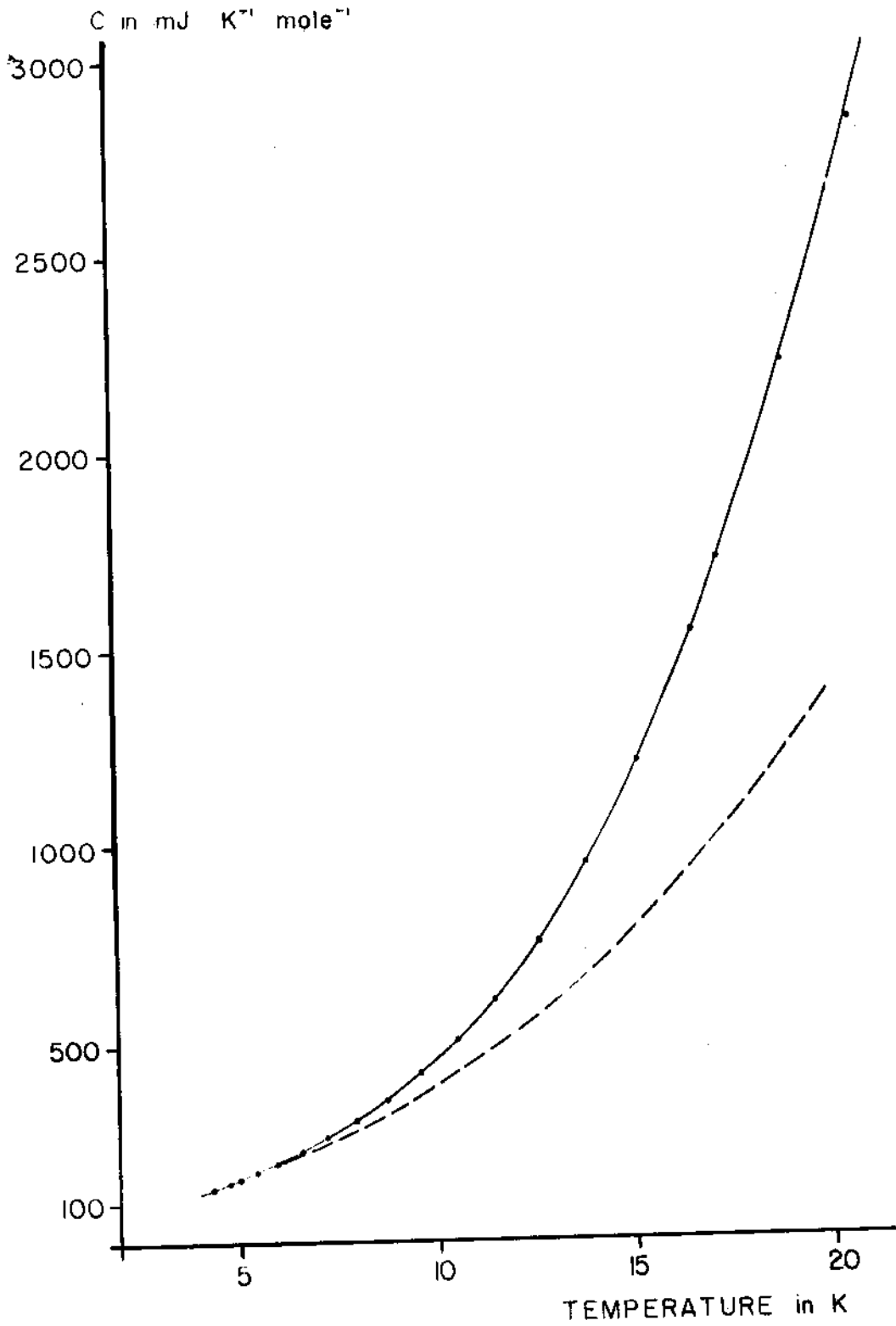


Figure 2

Number of points considered	γ	A	B	T_0
Temperature range (K)	$\text{mJ K}^{-2} \text{ mol}^{-1}$	$\text{mJ K}^{-4} \text{ mol}^{-1}$	$\text{mJ K}^{-5/2} \text{ mol}^{-1}$	K
$4.332 \leq T \leq 15.184$	28.464 ± 0.001	0.157 ± 0.000	55.906 ± 0.006	79.254 ± 0.002
$6.540 \leq T \leq 15.184$	28.266 ± 0.003	0.161 ± 0.000	57.678 ± 0.022	80.817 ± 0.008
$4.332 \leq T \leq 9.615$	28.691 ± 0.002	0.149 ± 0.000	27.262 ± 0.045	65.586 ± 0.020

TABLE I

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