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THE CERIUM MAGNESIUM NITRATE TEMPERATURE SCALE FROM NUCLEAR ORIENTATION

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Lawrence Radiation Laboratory
Berkeley, California

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ERRATUM

Cerium Magnesium Nitrate Temperature Scale from Nuclear Orientation, R. B. Frankel, D. A. Shirley, and N. J. Stone [Phys. Rev. 140, A1020 (1965)]. Table I on page A1022 contains errors in the first 8 entries of each of the first two columns. The first eight rows should read:

$(\frac{H}{T})_{initial}$ kG°K^{-1}	$(\frac{S}{R})_{calc}$	$\frac{1}{T^*_s}$	$(\frac{1}{T})_{DR}$	$(\frac{1}{T})_{FSS}$
0.8	0.692	20	20	20
1.6	0.688	40	40	40
2.5	0.682	60	60	60
3.3	0.673	80	80	80
4.2	0.661	100	100	100
5.0	0.647	120	120	120
5.9	0.631	140	140	140
6.8	0.611	160	160	160

We thank Dr. R. P. Hudson for calling our attention to the erroneous values. These errors were completely unrelated to the research reported in our paper, but arose from a computational mistake. These entries were given simply to indicate that our data for T >.006°K agree with the DR scale, although they do not stringently test it. None of our conclusions are altered.

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R. B. Frankel, D. A. Shirley, and N. J. Stone

April 1965

THE CERIUM MAGNESIUM NITRATE TEMPERATURE SCALE FROM NUCLEAR ORIENTATION*

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Berkeley, California

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ABSTRACT

Systematic deviations were found below 0.003° K in the temperature dependence of nuclear orientation of Ce^{137m} in cerous magnesium nitrate, using the temperature scale proposed by Daniels and Robinson. The temperature scale below 0.006° K was redetermined using a new method: nuclear orientation. This has the advantage over the γ-ray heating method of high sensitivity at the lowest temperature. The most striking result is that a value of 1/T of 520, rather than the previously accepted 324, is obtained by demagnetization from initial conditions of 18.8 kG deg^{-1}. The useful absolute temperature range is thus extended by at least 60% in 1/T. Auxiliary experiments on oriented Pm^{144} gave similar results and provided independent confirmation both of the inadequacy of the old temperature scale and of the validity of the new one.

I. INTRODUCTION

Cerium magnesium nitrate CMN is unique among paramagnetic working substances in that it may be demagnetized adiabatically from helium bath temperatures (~1° K) and commonly available magnetic fields of ~20 kG to an absolute temperature at least a factor of three lower than that attainable with the second best pure paramagnetic salt, chromium potassium sulfate. The lowest attainable temperatures to which a specimen may be cooled are thus made available by the use of CMN.[1] In 1952 Daniels and Robinson (DR) reported[2] a T-T^* correlation for CMN. Here T^* is the magnetic temperature, defined from the susceptibility by fitting Curie's Law at high temperatures. They discovered the very convenient feature of CMN that $T = T^*$ to very low temperatures (within 1% at 0.006° K). This property has led to the use of CMN as a thermometer in many experiments in the 0.01° K range.

At the lowest temperatures DR found it desirable to employ an "integral heat" method of calorimetry because of the low heat capacity of CMN. This led to a less reliable T-T^* correlation at these temperatures. Nonetheless, the DR scale has been in use for 13 years. DeKlerk[3] reinterpreted the DR data, concluding that $T = 1/400$, rather than $T = 1/324$, was the lowest available temperature. Hudson, Kalser, and Radford have remeasured the T-T^* correlation by similar techniques, finding that the lowest temperature is in the 0.001-0.002° K region.[4]

Although CMN has often been used as a thermometer down to $T \cong 1/150$, it has been used in its lowest temperature range only for nuclear orientation experiments (including the parity experiment).[5] In some of these the measured quantities were not temperature-sensitive at the lowest temperatures. In others discrepancies were observed but were not attributed to the DR temperature scale. In two earlier studies in this Laboratory, for example,

irregularities in the temperature dependence of γ-ray angular distributions were noted.[6,7] With the availability of the new Berkeley 88-inch cyclotron we have been able to restudy the more promising case, Ce^{137m}, in much greater detail. We have found that the DR temperature scale for CMN is very much in error in the lower range, as is deKlerk's modification. In particular, temperatures as low as 1.9 mdeg, rather than 3.1 mdeg, are easily reached.

We have constructed a temperature scale based on the nuclear orientation measurements. This is the first temperature scale for a pure paramagnetic salt based on nuclear orientation, and we accordingly discuss this technique in Sec. II. Results are given in Sec. III. The new scale is discussed and related to prospective cooling experiments in Sec. IV.

II. TEMPERATURE SCALE DETERMINATIONS FOR CMN

A. Gamma-Ray Heating

In adiabatic demagnetization experiments it is essential to know the absolute temperature, T, in terms of easily measurable quantities. One such quantity is the entropy, S, which is the same after as before demagnetization. The entropy before demagnetization may be directly measured, or, if the partition function of the salt is accurately known, calculated from the initial magnetic field and temperature. To the extent that the lattice entropy is negligible, S is a function of $(H/T)_i$. On demagnetization from each value of $(H/T)_i$ a magnetic temperature $T^* = C/\chi$ is reached. Here χ is the magnetic susceptibility and C is the Curie Law constant, evaluated from the susceptibility at higher temperatures. Since T^* is shape-dependent, it is more useful to tabulate $T^{\circledast}$, the magnetic temperature of a spherical sample.[8] An absolute temperature also corresponds to each $(H/T)_i$, and the relation of these temperatures is called the T-$T^{\circledast}$ correlation.

In the method of γ-ray heating the heat input Q and entropy are correlated by heating the demagnetized sample through absorption of γ radiation. The susceptibility is measured and $T^{\circledast}$ is treated as an independent variable. The temperature is obtained as

$$T = dQ/dS = (dQ/dT^{*})/(dS/dT^{*}) \ . \qquad (1)$$

A major weakness of the method is that the data must be differentiated. This is especially harmful at the lowest temperatures.

Another problem that arises in CMN is that $T^{\circledast}$ becomes an insensitive parameter, varying only slowly with T. It is then advisable to use $(H/T)_i$ directly as the independent variable, demagnetizing from different fields into the region where $T^{\circledast}$ doesn't vary and heating into the sensitive region.

This "integral heat" method has the disadvantage that in heating the specimen through a considerable temperature interval at the lowest temperatures heat leak corrections are particularly difficult to make. Differentiation of the resulting "integral heat" taken as a function of S is thus extremely open to systematic error.

Daniels and Robinson fitted their Q(S) data with a straight line, thus requiring the temperature to be constant for a range of entropy. This is shown to be clearly in error by the nuclear orientation results below. DeKlerk, by neglecting the lowest points, i.e., those with greatest uncertainty, refitted the data, obtaining a different, but as we shall show below, still incorrect temperature scale. The difference of the two scales, and the experimental difficulty of the method have argued for several years for a redetermination of the CMN temperature scale below 0.006° K by a more suitable technique.

Hudson, Kalser, and Radford[4] have published preliminary accounts of a redetermination of the temperature scale by essentially the same method. We cannot compare their data in detail with ours as yet, but we note that they also find very low temperatures, in the 0.001 to 0.002° K region.

B. Nuclear Orientation: A New Method

Nuclear orientation has been used for thermometry for at least nine years,[9] but it has not been used before to determine a temperature scale for a paramagnetic salt. To be applicable this method requires an isotope that goes isomorphously into the lattice, with a well-known decay scheme, a large γ-ray anisotropy which does not reach a saturation value in the available temperature range, and a spin Hamiltonian whose form is known. Cerium-137m provides a happy combination of these qualities. The decay scheme is the sequence 11/2- (M4) 3/2+ and there are no intermediate states involved. A large anisotropy had been observed in earlier experiments.[7] The spin Hamiltonian is

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y) \qquad (2)$$

with B >> A. The angular distribution of the M4 γ ray from oriented Ce^{137m} in CMN is thus[7] given by

$$W(\theta,T) = 1 - 0.889\, B_2 P_2(\cos\theta) + 0.443\, B_4 P_4(\cos\theta) \qquad (3)$$

The orientation parameters B_2 and B_4 may be calculated from Eq. (2) in the usual way,[10] in terms of $\beta = B/2kT$. By fitting the data to a theoretical curve

in the region above 0.006° K we derived $B = 0.0060\ cm^{-1}$. As in this region $T=T^{\circledast}$, we used temperatures calculated from susceptibility measurements using the DR temperature scale. With this value of B the theoretical $W(\theta,T)$ curve is then used to deduce temperatures from gamma-ray ansiotropies observed in the region below $1/T = 150$. As usual the anisotropies observed were corrected for finite detector solid angle and for source decay.

Three separate Ce^{137m} experiments were performed using different crystal samples. One of these was spherical; for the other two T^{*} was corrected to $T^{\circledast}$ using estimated demagnetizing factors. The three sets of data were in excellent agreement.

As a precaution against unknown systematic errors in the Ce^{137m} work, additional experiments were performed on Pm^{144} in CMN. The spin Hamiltonian for Pm is completely different, being of the form[11]

$$\mathcal{H} = P[I_z^{\ 2} - \tfrac{1}{3}I(I+1)] \ . \qquad (4)$$

Pm^{3+} is non-magnetic and it would not be expected to participate in any possible collective transitions involving the magnetic Ce^{3+} ions in CMN. The results are discussed in Sec. III and are completely consistent with the temperature scale deduced from the Ce^{137m} data.

Nuclear orientation and the older technique have a complimentary function in determining an unknown temperature scale. In the higher temperature range the γ-ray heating method is reliable and, as in this case, is sometimes necessary to make possible measurement of the nuclear orientation parameters. However, as the temperature decreases, systematic errors in the heating method become much larger as discussed above, whereas the observed gamma-ray anisotropies increase, making the nuclear orientation technique far more accurate in this region.

III. RESULTS

In Fig. 1 we have plotted W(0) for the 255-keV γ-ray of Ce^{137m}, oriented in CMN, against $1/T_{DR}$, using Daniels and Robinson's temperature scale. The dramatic departure of the data from a fitted theoretical curve at $1/T_{DR} \sim 300$ suggests that the temperature scale is in error or that the Hamiltonian suddenly becomes inadequate at this temperature. The latter possibility could be the case if CMN became antiferromagnetic at $1/T = 300$, for example. However, it is easily shown that antiferromagnetic ordering in the plane perpendicular to the crystalline c axis would lead to a decrease in nuclear orientation, while an increase is observed. An error in the temperature scale is thus indicated.

A new temperature scale was established by fitting the nuclear orientation data for Ce^{137m} to the Hamiltonian in Eq. (2) for $T > 1/150^{\circ}$ K, to determine B, and using this theoretical curve for the lower temperatures. In Table I the resulting temperatures are tabulated against H_i/T_i and $T^{\circledast}$; T_{DR} is included for comparison. Figure 2 shows the Ce^{137m} data fitted to the theoretical curve for $B = 0.0060\ cm^{-1}$, indicating the lowest temperature reached to be $1/T = 520 \pm 15$. Figure 3 shows our suggested T-$T^{\circledast}$ relation with the DR scale and deKlerk's version.

It is fortunate that for Ce^{137m} the constant coefficient of the $P_4(\cos\theta)$ term in $W(\theta,T)$ is large, as below $\sim 0.0022^{\circ}$ K the $P_2(\cos\theta)$ term is close to its maximum value, and the temperature sensitivity relies largely on variation of B_4. At $1/T = 500$ the coefficient of P_4 is $+0.215 \pm 0.010$. If, for example, the temperature were really 1/700, this coefficient would be +0.268.

The relation between W(0) and $W(\pi/2)$ is sensitive to changes in the nuclear spin Hamiltonian. In Fig. 4 the theoretical curve for pure M4 radiation and planar alignment is compared with the experimental data. The agreement is excellent and in particular no discontinuity is observed in the $1/T = 300$ region.

To obtain a completely independent check of these measurements we aligned Pm^{144} in CMN, and studied the anisotropies of the 615 and 695 keV gamma rays using Ge(Li) and NaI(Tl) detectors. The results are more detailed and accurate than those reported by Grant and Shirley. Again the "hook" in the temperature-dependence curve was apparent (Fig. 5) using T_{DR}. However, the new scale allowed a smooth fit (Fig. 6). Although there is considerable uncertainty in the nuclear parameters involved in this decay,[6] and a detailed discussion would be out of place in this paper, the fact that with physically reasonable parameters a fit is obtained at all temperatures at least shows that the new temperature scale contains no serious irregularities. A full analysis of this experiment will be published separately.

IV. DISCUSSION

The new CMN temperature scale extends the available range of absolute temperature to below 0.002° K. Considerably lower temperatures may be reached by using larger $(H/T)_i$ or by magnetic dilution, and nuclear orientation clearly offers the possibility of determining these temperatures accurately. This temperature region should be useful in connection with searches for very low temperature transitions in superconductors[12,13] and in He^3.[14,15] It is especially important for the He^3 problem that there be no spurious irregularities in the temperature scale. One further aspect of temperature scale determinations should be mentioned. A temperature scale is only useful if it can be reproduced with ease and reliability. It is difficult to grow large clear CMN crystals. The crystals used in this work were not perfectly clear, though they were grown from a solution of

many times recrystalized material. This might have an effect on their thermal properties. On the other hand our T^* vs $(H/T)_i$ data agree well with those of Daniels and Robinson and were very reproducible using different crystals. The scale reported here seems clearly preferable to those previously available, and the usefulness of nuclear orientation in determining temperature scales in this region seems established.

FOOTNOTES AND REFERENCES

*This work was supported by the U S. Atomic Energy Commission.

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1. Of course, the temperature range may be extended down still further by magnetic dilution of CMN or several other salts. For those experiments in which this extension of technique is feasible (dilute) CMN would presumably still be the best working substance.

   Lower spin temperatures are attainable by nuclear demagnetization, but until now this has not proved to be a useful cooling technique because the nuclear spins do not achieve equilibrium with the lattice.

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Table I. $1/T^{\otimes}$-$1/T$ correlation for CMN. According to Daniels and Robinson (DR) and this work (FSS).

$(H/T)_{initial}^{kG^{o}K^{-1}}$	$(S/R)_{calc.}$	$1/T^{\otimes}$	$(1/T)_{DR}$	$(1/T)_{FSS}$
1.0	.691	20	20	20
1.9	.686	40	40	40
2.9	.678	60	60	60
3.8	.667	80	80	80
4.6	.654	100	100	100
5.4	.640	120	120	120
6.2	.625	140	140	140
6.9	.610	160	160	160
7.8	.590	180	182	181
8.75	.567	200	223	210
9.2	.555	210	231	221
9.7	,543	220	249	232
10.2	.529	230	266	249
10.8	.513	240	284	266
11.4	.497	250	300	287
12.1	.477	260	312.5	305
12.8	.459	270	319	322
13.5	.439	280	322.5	358
14.2	.420	290	324	383
15.5	.384	300	324	430
18.0	.321	310	324	500
18.8	.303	312	324	520

FIGURE CAPTIONS

Fig. 1. Normalized intensity along the crystalline c axis of the 255-keV γ ray following the decay of Ce^{137m} oriented in CMN vs 1/T on the Daniels and Robinson scale. The theoretical curve was fitted for $T > 1/150$ by adjusting B in Eq. (2) with $H_x = H_y = H_z = 0$. Departure of the data from this curve for $T < 1/300$ indicates an error in the temperature scale. Different symbols denote different samples.

Fig. 2. Normalized intensity along the crystalline c axis of the Ce^{137m} 255-keV γ-ray vs 1/T using the new temperature scale for CMN. This scale was derived by fitting these data to the theoretical curve.

Fig. 3. Comparison of several T-$T^{\otimes}$ correlations for CMN. Curve A: $T=T^{\otimes}$. Curve B: Daniels and Robinson. Curve C: deKlerk. Curve D: Present work. The hook in curve B is clearly responsible for the hooks in Figs. 1 and 5.

Fig. 4. Comparison of normalized 255-keV γ-ray intensity, from Ce^{137m} oriented in CMN, at 0° and 90° from the crystalline c axis. Dashed line is for a pure $P_2(\cos\theta)$ distribution.

Fig. 5. Temperature dependence of normalized intensity along the crystalline axis of the 615 and 695 γ rays following the decay of Pm^{144} oriented vs CMN, using Daniels and Robinson's temperature scale, with a theoretical curve derived from Eq. (4). Again the spurious hook below $T = 1/300$ is evident.

Fig. 6. Normalized gamma-ray intensity data for Pm^{144}, from Fig. 5, plotted against 1/T, but using the new CMN temperature scale. Good agreement with the theoretical curve is evident. This serves as an independent check on the new temperature scale.

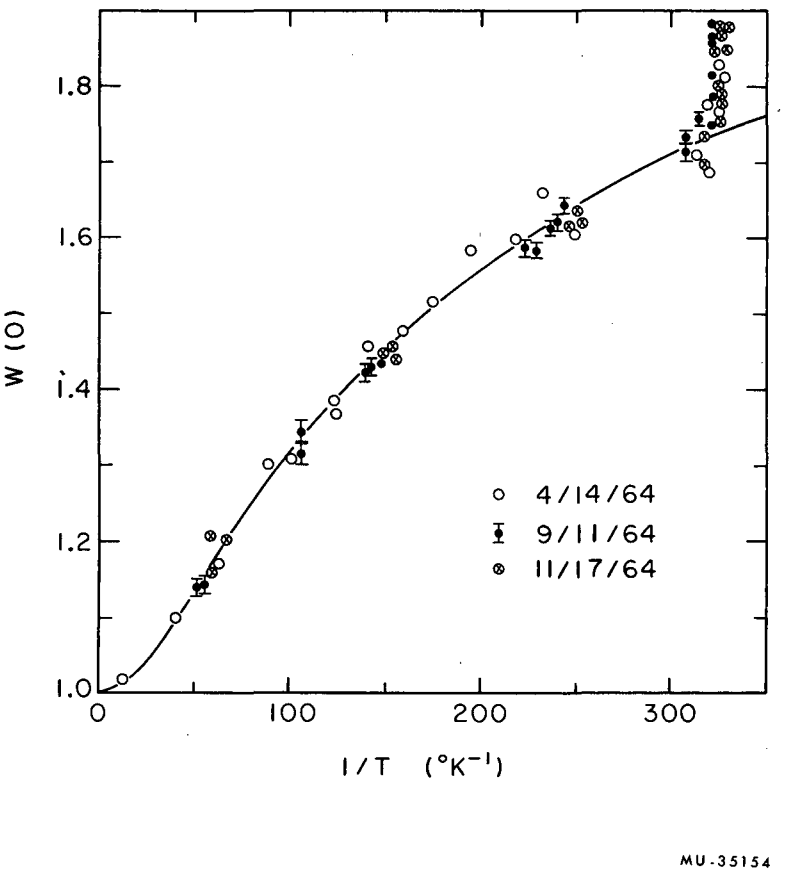

Fig. 1

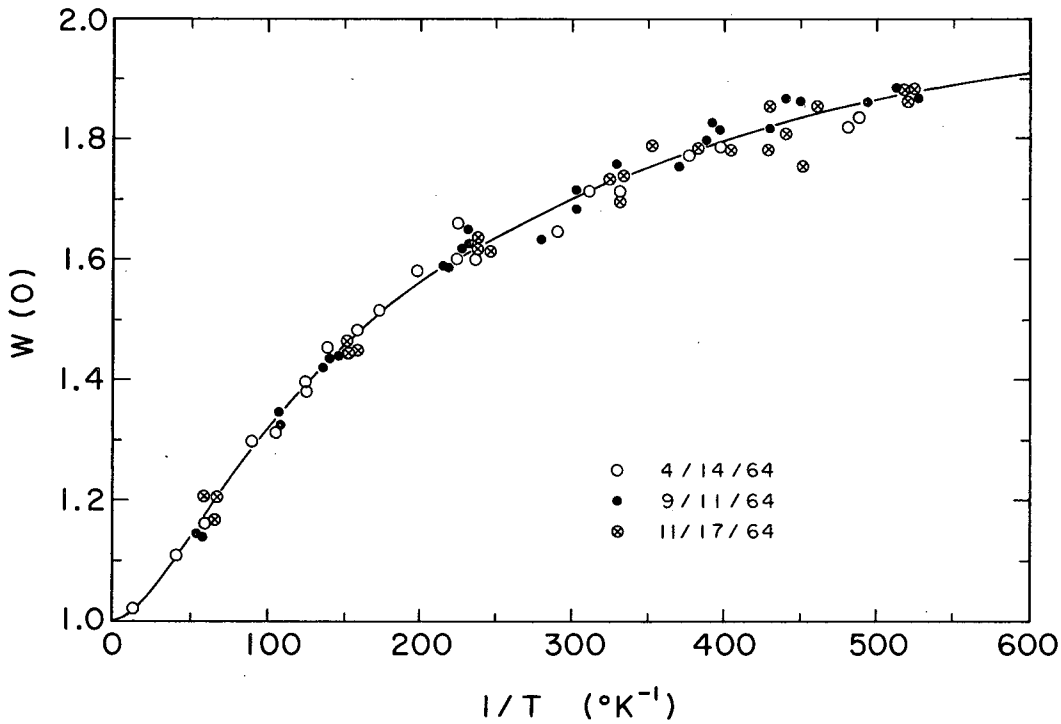

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Fig. 2

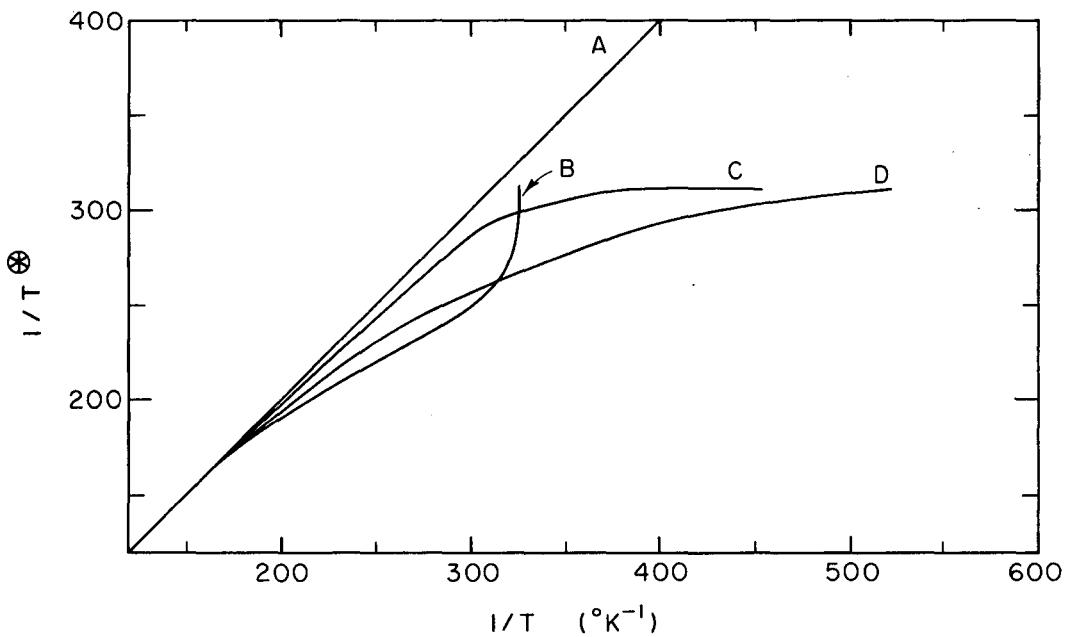

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Fig. 3

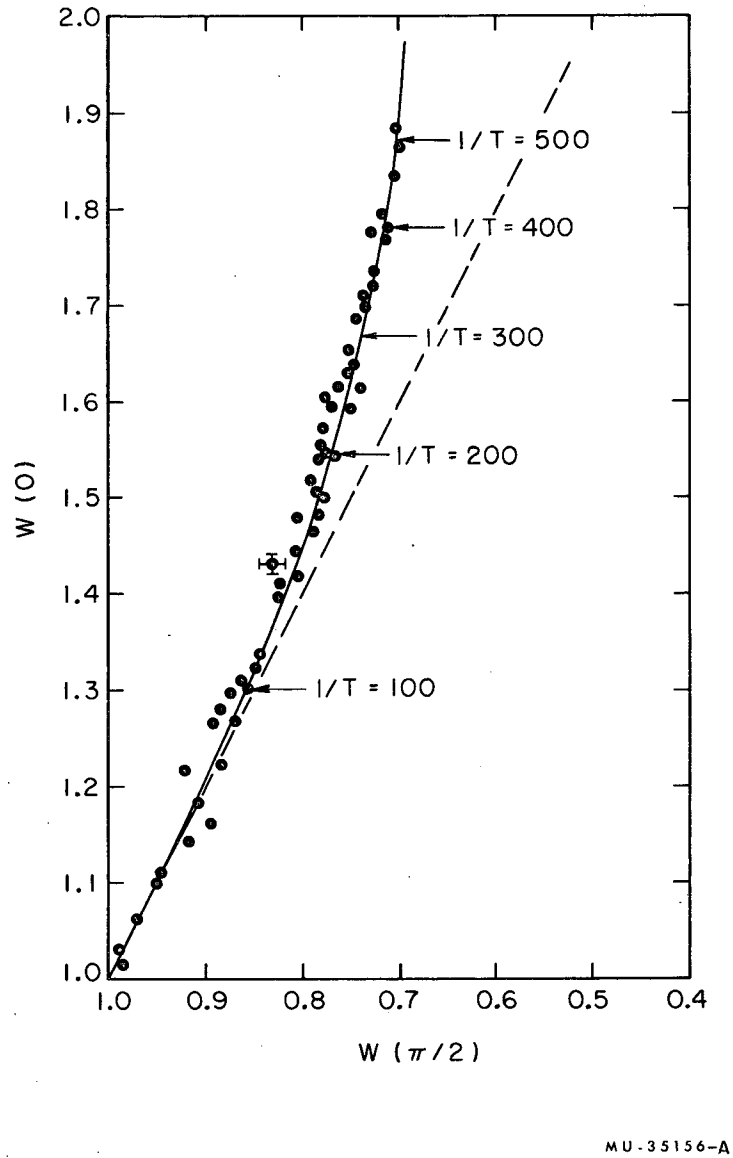
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
W (0)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
W (π/2)
1/T = 500
1/T = 400
1/T = 300
1/T = 200
1/T = 100
MU-35156-A

Fig. 4

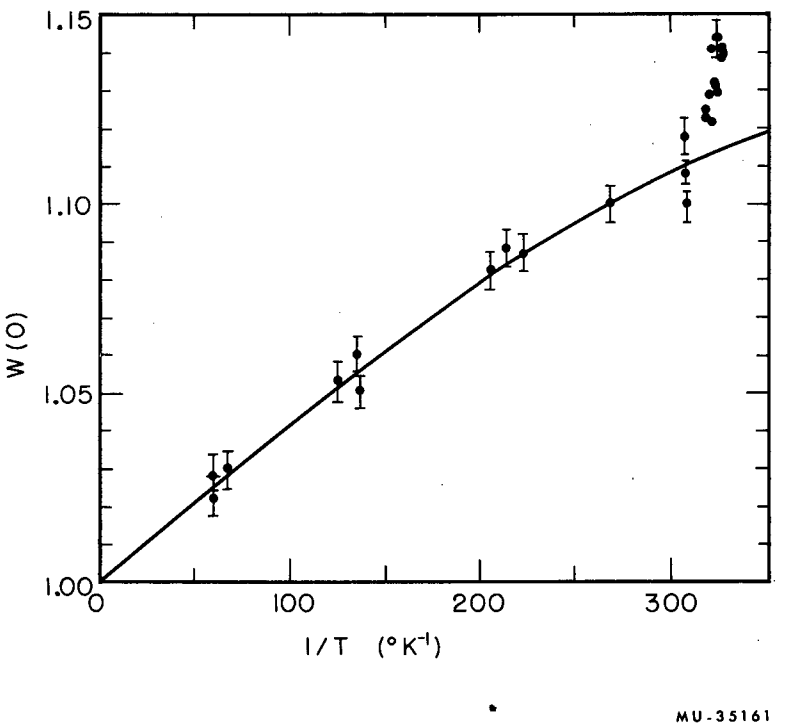

Fig. 5

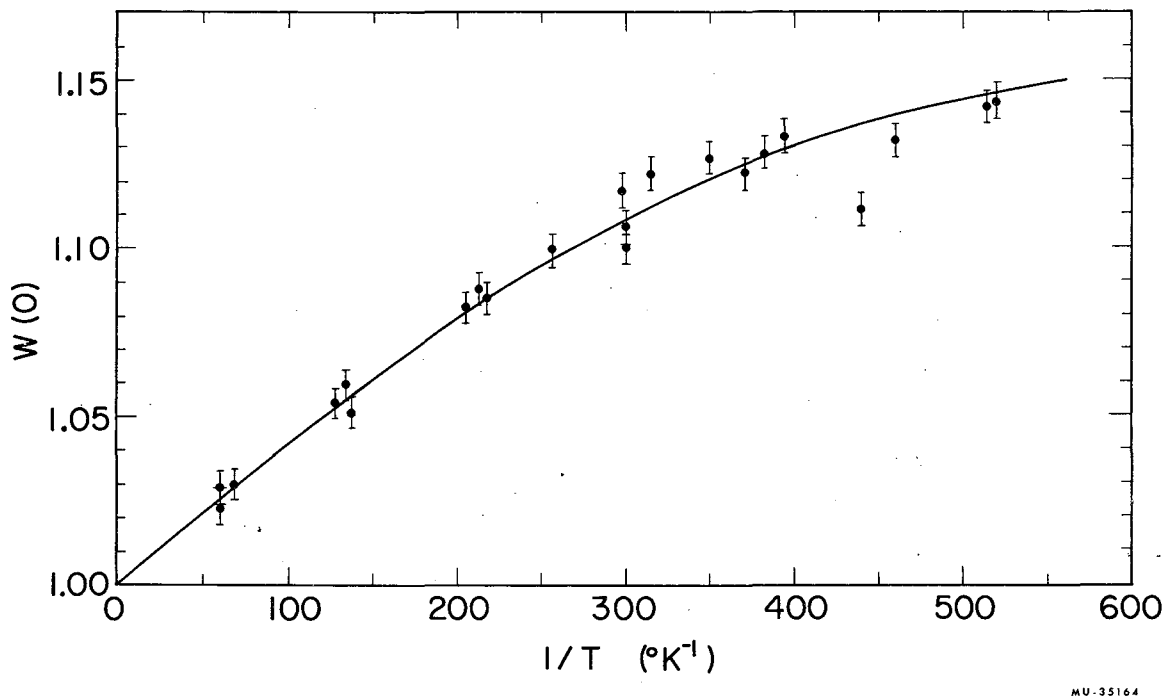

Fig. 6

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