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Proposed Absolute Temperature Scale for Cerium Magnesium Nitrate below 0.003 K*

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The absolute temperature scale for single-crystal cerium magnesium nitrate (CMN) has been extended to entropies as low as $S/R=0.002$ by adiabatic demagnetization from values of H/T up to 68 kOe/K. The temperature dependence of the highly anisotropic angular distribution of the 255-keV γ ray from oriented ^{137m}Ce in the CMN provided the thermometric parameter. The nuclear-orientation results were interpreted with the spin Hamiltonian $\mathcal{H}=g_\perp \beta H_x S_x + B(S_x I_x + S_y I_y)$, where H_x is a calculated dipolar field. The hyperfine-structure constant B was determined by normalizing the higher-temperature nuclear-orientation results to the calorimetric results of Hudson and Kaeser and of Mess *et al.* at high entropies. A provisional temperature scale, based on both our nuclear-orientation results and the calorimetric work, is proposed. This scale is compared in detail with the results from earlier studies of CMN. The ^{137m}Ce γ-ray thermometer was also used to investigate the thermal behavior of cerium zinc nitrate (CZN). The preliminary nuclear-orientation results indicate a high degree of similarity between CZN and CMN.

I. INTRODUCTION

Cerium magnesium nitrate, $Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$ (CMN), has long been recognized as a substance capable of being cooled by adiabatic demagnetization to extremely low temperatures. The pioneer investigation of the temperature scale for single-crystal CMN was reported by Daniels and Robinson[1] in 1953. Using calorimetric methods, they found that the minimum temperature reached was 3.08 mK (millidegrees K) and was constant for all values of the magnetic entropy in the range $S/R \leq 0.45$. Above 6 mK Curie's law was found to be obeyed, with T and S related by $\ln 2 - S/R = 3.2\times 10^{-6} T^{-2}$. In a subsequent reanalysis of their data, de Klerk[2] asserted that the temperature did not become constant at $S/R=0.45$ but continued to decrease to 2.25 mK at $S/R=0.150$.

In 1965 Frankel, Shirley, and Stone[3] demonstrated that nuclear orientation could be used to determine the temperature scale of CMN. They found that both of the above T-S relations were unable to explain the nuclear-orientation results for ^{137m}Ce in CMN below 3 mK. Using their data and the Daniels-Robinson results above 6 mK, Frankel *et al.* derived a new T-S relation. They found that the temperature did not become constant at any value of entropy in the range available to them and at $S/R=0.303$ (the lowest entropy which they reached), they reported $T=1.94$ mK.

In a recently reported investigation of single-crystal CMN, Hudson and Kaeser[4] studied both spherical and ellipsoidal samples using the calorimetric γ-ray heating method. They found no shape dependence in the T-S correlation, and they confirmed that Curie's law was obeyed down to 6 mK. However, they found that for the Curie-law region $\ln 2-S/R=2.88\times10^{-6}T^{-2}$, in significant disagreement with the value given by Daniels and Robinson. At temperatures greater than 15 mK they observed a departure from the T^{-2} dependence. At the low-temperature end of the scale their results differed somewhat from those of Frankel *et al.*, and below $S/R=0.296$ they found the temperature to be essentially constant and equal to 1.53 ± 0.3 mK.

Shortly after the present experimental work was completed, a calorimetric study of CMN was reported by the Leiden group (Mess *et al.*[5]). This work differed from the earlier calorimetric studies in two respects. First, the energy input was accomplished by Joule heating rather than by γ-ray heating. Secondly, lower entropies were obtained through a two-stage adiabatic demagnetization process. The results of this work can be summarized as follows: In the temperature range $8\leq T\leq 20$ mK, $\ln 2-S/R=(2.4\pm0.1)\times10^{-6}T^{-2}$ while for $20\leq T\leq 150$ mK the T^{-2} dependence is not obeyed. Above 150 mK, $\ln 2-S/R=3.1\times10^{-6}T^{-2}$. The lowest temperature measured was 1.0 ± 0.3 mK at $S/R=0.02$. Finally, magnetic susceptibility measurements indicated that at $T=1.9\pm0.1$ mK CMN undergoes a transition to a ferromagnetic state. This last point has been disputed by Abeshouse *et al.*,[6] who interpret their susceptibility results as indicative of an antiferromagnetic transition.

The thermal properties of powdered CMN in the shape of a right circular cylinder have been investigated by Wheatley and colleagues[7,8] and by Abraham and Eckstein.[9] Although the experimental data were in agreement, a sharp controversy arose concerning the magnitude of the shape-dependent correction Δ to be applied to T^*. Abraham and Eckstein found Δ to be about 1.7 mK, whereas Anderson,[10] Black,[11] and Abel and Wheatley[12] found a much smaller value of Δ. Hudson[13] reviewed these results and showed that the consequence of a small Δ is that the heat capacity of CMN is not simply proportional to T^{-2}, but contains higher-order terms. Abraham *et al.*[14] have investigated the heat capacity of CMN using an ac susceptibility method, and they obtained results similar to those of Abraham and Eckstein. Finally, Abraham and Eckstein[15] have recently studied the heat capacity of three powdered CMN specimens, two spheres and one right circular cylinder with diameter equal to height. They found the following:

At all T,

$$T^*\ (\text{cylinder of powder})+0.8\ \text{mK}=T^*\ (\text{sphere of powder});$$

for $T\geq 6.5$ mK,

$$T^*\ (\text{sphere of powder})+0.3\ \text{mK}=T\ (\text{thermodynamic});$$

and for $T<6.5$ mK,

$$T^*\ (\text{sphere of powder})+0.6\ \text{mK}=T^*\ (\text{single-crystal sphere}).$$

Using these values of Δ, they fitted their heat-capacity data to an expression involving terms in T^{-2} and T^{-3}. Unfortunately, however, when the results of all these investigations are considered together, the picture is still not clear. Thus since we were interested only in the thermodynamic properties of single crystals of CMN, we have chosen not to consider these results in our work.

The work reported in this paper was undertaken to extend the entropy-temperature relation over a wide range via the nuclear-orientation method. The theory of this method is given in Sec. II. Section III concerns experimental details, and results are given in Sec. IV. The results are discussed and compared with other work in Sec. V. Section VI deals with a preliminary nuclear-orientation study of cerium zinc nitrate.

II. THEORY OF THE NUCLEAR-ORIENTATION METHOD

In nuclear-orientation studies employing CMN, it is important to know the absolute temperature of the cooled crystal. The original objective of this research was simply to establish a relation between T_f, the final temperature attained on adiabatic demagnetization, and the initial conditions before demagnetizing, i.e., the magnetizing field H and the bath temperature T_i. But H and T_i determine the initial entropy, $S(H,T_i)$. Thus, provided that the demagnetization is adiabatic ($S_i=S_f$), a knowledge of $T_f(H,T_i)$ is equivalent to a knowledge of $T_f(S_f)$, i.e., the low-temperature zero-field T-S relation. The usual method for determining this relation employs an external heat input (calorimetric method). At the lowest temperatures the calorimetric method loses accuracy, however, while the accuracy of the nuclear-orientation method improves. The reason for this is that the magnetic susceptibility, which is the thermometric parameter for the calorimetric method, becomes only very weakly temperature dependent while the γ-ray anisotropy, which is the thermometric parameter in the nuclear-orientation method, retains considerable temperature sensitivity at the lowest temperatures attained. The nuclear-orientation method is also subject to some uncertainties which will be discussed in detail in Sec. V. Despite these uncertainties it seemed worthwhile to use nuclear orientation to shed what light it can on the T-S relation for CMN at the lowest temperatures. We feel that the nuclear-orientation method may be the best of a rather poor set of choices for determining the T-S relation of CMN at the lowest temperatures.

Our procedure is described in detail below. Briefly it is to calculate S from the measured values of H and T_i prior to demagnetization and to obtain T from the γ-ray anisotropy of the radioactive isotope ^{137m}Ce. Since the magnetic susceptibility χ is irrelevant in this work (and relatively temperature insensitive at the lowest temperatures anyway), we have not measured $\chi(T)$. Accordingly, our measurements provide the T-S relation for CMN, and they also yield data that allow the use of ^{137m}Ce in CMN as a nuclear thermometer. Of course, the γ-ray distribution, rather than $\chi(T)$, is the thermometric parameter.

The evaluation of S and T for ^{137m}Ce in CMN is described below.

Entropy

The nuclear entropy of the ^{137m}Ce present (about 10^{10} atoms) is negligible as is the CMN lattice entropy at $T_i < 1$ K. We therefore need only consider the electronic-magnetic entropy of the Ce^{3+} ions. The entropy removed during the isothermal magnetization of a paramagnetic salt may be calculated from a knowledge of the partition function:

$$Q = [\sum \exp(-\epsilon_j/kT)]^N, \tag{2.1}$$

$$S = k \ln Q + kT(\partial \ln Q/\partial T)_H, \tag{2.2}$$

where ϵ_j are the energies of the electronic energy levels and N is the number of ions. Ce^{3+} has a single $4f$ electron outside a closed shell, and in the double nitrate crystal the three lowest states are Kramers doublets split by the crystal field from the lowest (mainly $^2F_{5/2}$) free-ion level. The lowest doublet lies approximately $36K$[16] below the next doublet, and consequently only this state is significantly populated at temperatures in the liquid-helium range. High field magnetization and electron-spin resonance measurements by Williamson *et al.*[17,18] indicate that the ionic crystal-field model adequately explains their data and that the energies of the lowest Kramers doublet states are given by

$$E_1 = -\tfrac{1}{2} g_\perp \beta H - B'(\beta^2 H^2/k) + C(\beta^3 H^3/k^2), \tag{2.3}$$

$$E_2 = \tfrac{1}{2} g_\perp \beta H - B'(\beta^2 H^2/k) - C(\beta^3 H^3/k^2), \tag{2.4}$$

where $g_\perp = 1.840$,[18–20] β is the Bohr magneton, and B' and C are constants evaluated by second- and third-order perturbation theory. It can be shown that the second-order term gives no contribution to the entropy. The contribution of the third-order term to the entropy is negligible under our experimental conditions, its maximum value in our experiments being $|\Delta S_3| < 0.001R$ at $H = 20$ kOe and $T = 0.31$ K. Thus S can be regarded as a function of H/T only and can be read from the tabulation of Hull and Hull[21] for a spin-$\frac{1}{2}$ paramagnet.

Absolute Temperature

The entropy of a system having energy levels ϵ_j is given by

$$S = -k \sum_j P(\epsilon_j) \ln P(\epsilon_j), \tag{2.5}$$

where $P(\epsilon_j)$ is the occupation probability of the level of energy ϵ_j,

$$P(\epsilon_j) = \frac{\exp(-\epsilon_j/kT)}{\sum_j \exp(-\epsilon_j/kT)}. \tag{2.6}$$

Thus any measurement that determines occupation probabilities also determines the absolute temperatures—provided that all the relevant ϵ_j are known. Nuclear orientation is such a technique. It is useful only for measuring temperatures much less than 1 K, because the ϵ_j are separated by only $\sim 10^{-2}$ cm^{-1}. The angular distribution of radiation from oriented nuclei is expressed as

$$W(\theta, T) = 1 + \sum B_k(T) U_k F_k g_k P_k(\cos\theta). \tag{2.7}$$

The summation runs from 2 to the lesser of $2L$ or $2I$, where L is the transition multipolarity and I is the nuclear spin. U_k is an angular momentum factor concerned with preceding unobserved transitions (if any), and F_k is an angular correlation coefficient for the observed transition. The coefficient g_k corrects for the finite solid angle subtended by the detector, and $P_k(\cos\theta)$ is a Legendre polynomial.

All the temperature information is contained in the statistical tensors $B_k(T)$, which can be written as

$$B_k = (2I+1)^{1/2}(2k+1)^{1/2} \times \sum_m (-1)^{I-m} \begin{pmatrix} I & I & k \\ m & -m & 0 \end{pmatrix} \rho_{mm}, \tag{2.8}$$

where ρ_{mm} is a diagonal element of the density matrix in the nuclear manifold. For a radioisotope to be useful as a thermometer, the following three conditions must be met: The nuclear temperature and the ionic temperature must be equal; $W(\theta, T)$ must be sensitive to T over the whole temperature range of interest; and the form of the spin Hamiltonian must be known. For CMN the first condition should be met if the radioisotope is a Ce atom because the nuclear and electronic systems are coupled through the hyperfine interaction. No evidence of slow relaxation effects was found in this work. Previous experiments[3,22,23] in this laboratory have shown that the second condition is satisfied by the isotope ^{137m}Ce. The spin Hamiltonian is discussed below.

The decay scheme of ^{137m}Ce is shown in Fig. 1. The transition of interest is the 255-keV γ ray from the $\frac{11}{2}$-state in ^{137m}Ce. Frankel *et al.*[23] have concluded that this transition should be very pure M4. The maximum value of k in Eq. (2.7) is therefore 8, and the values of F_k may be obtained from the tabulations of Ferentz and Rosenzweig.[24] Since there are no preceding transitions, $U_k \equiv 1$ for all k. In all the experiments reported herein the sample was 10 cm from the face of a 3×3-in. NaI(Tl) scintillation detector. The values of g_2 and g_4 were obtained by graphical interpolation from the tabulation of Yates.[25] g_6 and g_8 were calculated from Rose's[26] formula for unit efficiency:

$$g_k = \frac{P_{k-1}(\cos\theta) - \cos\theta P_k(\cos\theta)}{(k+1)(1-\cos\theta)}. \qquad (2.9)$$

An "effective" $\cos\theta$ was chosen so as to reproduce the photopeak values of g_2 and g_4 given by Yates and was found to be 0.9464.[27] The coefficients g_6 and g_8 were then calculated from this value of $\cos\theta$, and the values of the various g_k and F_k are tabulated in Table I. The angular distribution can then be written

$$W(\theta, T) = 1 - 0.8191 B_2(T) P_2(\cos\theta) + 0.3346 B_4(T) P_4(\cos\theta) + 0.0169 B_6(T) P_6(\cos\theta) - 0.0774 B_8(T) P_8(\cos\theta). \qquad (2.10)$$

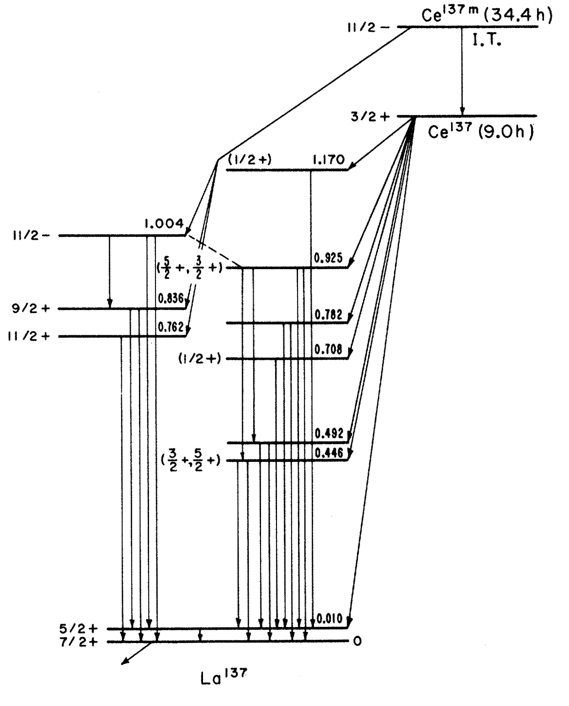

FIG. 1. $^{137m+g}$Ce decay scheme. This figure was taken from Ref. 22.

To calculate the $B_k(T)$ the spin Hamiltonian must be known. The form of the Hamiltonian may be deduced from the electron-spin resonance work of Kedzie *et al.*[28] for ^{141}Ce ($I=\frac{7}{2}$) in the isomorphous, diamagnetic crystal $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$. They found

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y), \quad \text{with } B \gg A. \qquad (2.11)$$

In the concentrated salt both dipolar and exchange interactions between the Ce^{3+} ions may be present and should be included in the Hamiltonian. If the dipolar interaction is regarded as an effective magnetic field acting on the Ce^{3+} ions, classical calculations by Felsteiner[29] yield a value of 60.67 Oe for this field. Culvahouse *et al.*[30] have performed a quantum-mechanical calculation using the density-matrix formalism and find that the dipolar effects can be approximated by a weighted superposition of local fields at the Ce site for the high-temperature region (i.e., above 6 mK). This reduces to a local field of 58 Oe at the lower temperatures. The effective field is perpendicular to the

TABLE I. F coefficients and solid-angle factors for ^{137m}Ce.

k	F_k	g_k
2	−0.88902	0.9214±0.0029
4	+0.44341	0.7545±0.0080
6	+0.03197	0.5297±0.0152
8	−0.26243	0.2948±0.0066

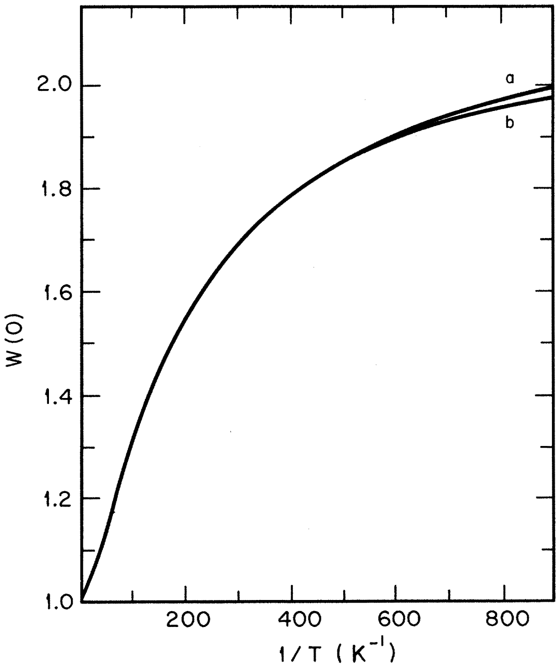

FIG. 2. $W(0)$ versus $1/T$. Curve a represents the case $H_x=0$ while curve b corresponds to $H_x=60.67$ Oe. The appropriate solid-angle corrections are included in these curves.

trigonal axis of CMN for a given Ce^{3+} site, but in the ensemble it is distributed equally along the three trigonal directions. Thus the effective field does not, *in the ensemble,* destroy the axial symmetry and create new components of B_k; it just changes the magnitude of B_k. Because of the large distance (8.56 Å)[31] between the Ce ions, the exchange interaction is expected to be very small, and we shall neglect it. We have used the following zero-external-field Hamiltonian for the purpose of analysis:

$$\mathcal{H}=B(S_xI_x+S_yI_y)+g_\perp\beta H_xS_x, \qquad (2.12)$$

where we have set $A=0$ (this is discussed in Sec. IV) and represented the dipolar interaction by an effective magnetic field $H_x=60.67$ Oe. The effect of the dipolar field on the temperature dependence of $W(0)$ is shown in Fig. 2.

III. EXPERIMENTAL

Cryogenics

All the experiments reported in this paper were performed in a ^{3}He refrigerator manufactured by Cryonetics Corp. (Model 302, Burlington, Mass.) and substantially modified in this laboratory. The apparatus is a continuously operating refrigerator of the type described by Ambler and Dove[32] and is capable of maintaining temperatures as low as 0.3 K. A detailed description of the apparatus is given in Ref. 37; however, it is worth pointing out several important features. The ^{3}He bath chamber was machined from high-purity copper in the shape of a right circular cylinder (diameter 2.5 cm) closed at the bottom. Ten high-purity copper rods of approximately 1 mm diam and 10 mm length protruded upwards from the bottom of the chamber. The ^{3}He chamber was hard soldered to a thin-walled stainless-steel tube which passed through the 1.2-K ^{4}He bath to the ^{3}He circulation pump. The experimental chamber, a stainless-steel cylinder approximately 20 cm long, was soft soldered to a copper sleeve extending downward from the ^{3}He bath. The 1.2-K ^{4}He bath, the ^{3}He pumping tube, the ^{3}He bath, and the experimental chamber were surrounded by a common vacuum jacket. The experimental chamber could be evacuated through a stainless-steel tube concentric with and running through the ^{3}He pumping tube and bath. The depth of liquid ^{3}He ranged between 4 and 7 mm. Calculations indicated that the temperature difference between the Cu chamber and ^{3}He resulting from the Kapitza resistance and the heat leak was small. Moreover, temperature gradients resulting from the hydrostatic head of the liquid ^{3}He were minimized through the use of the Cu chamber and rods.

Thermal contact between the ^{3}He bath and the sample was achieved by a small pressure (0.02 Torr) of ^{3}He heat-exchange gas which could be removed prior to demagnetization. Most of the demagnetizations were from initial temperatures of 0.5 K, where the vapor pressure of ^{3}He is about 0.16 Torr; only the lowest-entropy runs originated from 0.3 K. The initial temperature of the sample was determined by measuring the vapor pressure of the ^{3}He bath with a McLeod gauge (Consolidated Vacuum Corp. GM-100A) and correcting for thermomolecular pressure differences with the results of Roberts and Sydoriak.[33] The vapor-pressure measurement was made only when thermal equilibrium was attained (i.e., when the heat of magnetization had been completely dissipated into the ^{3}He bath). This point could be determined by monitoring the exchange gas pressure and the ^{3}He bath pressure with thermocouple gauges. The major uncertainties in the temperature determination arise from hydrostatic pressure effects in the liquid ^{3}He, uncertainties associated with the McLeod gauge, and small pressure fluctuations in the ^{3}He system. For the maximum liquid ^{3}He depth of 7 mm the maximum effect of the hydrostatic head in a perfectly nonconducting chamber would be to increase the temperature of the bottom of the ^{3}He chamber by 17 mK at 0.5 K, the temperature from which the most important demagnetizations were made, and by 123 mK at 0.3 K. In our system, however, such a temperature gradient was not possible because of the high thermal conductivity of the copper ^{3}He chamber and the copper rods protruding through the liquid. Thus this correction was taken to be zero. Uncertainties associated with the other two effects were estimated to be ±0.0015 K at 0.5 K and ±0.003 K at 0.3 K.

Magnetic Field

Magnetic fields up to 21 kOe were produced across a $2\frac{5}{8}$-in. gap by a water-cooled iron-core solenoid. The magnet power supply was capable of producing currents up to 300 A with a current regulation of better than one part in 10^5 over the whole range. The field was measured with a Rawson rotating-coil gauss meter[34] (Rawson Electrical Instrument Co., Cambridge, Mass.) during each magnetization. At the end of each series of runs the Rawson meter was calibrated against a model 203 George Associates rotating coil gauss meter (George Associates, Berkeley, Calif.). The estimated uncertainty in the field measurements is no larger than 1% for all values of the field used in this experiment.

Sample Preparation

^{137m}Ce was produced in the Berkeley 88-in. Cyclotron by a $(p, 3n)$ reaction on ^{139}La in high-purity La_2O_3. The Ce was separated from the La by a solvent extraction method described by Glendenin *et al.*[35] The Ce^{3+} was purified on a Dowex-50 cation-exchange column and was then stripped off the column with 6*M* HCl. The solution was boiled to dryness, and the residue was dissolved in saturated CMN solution at 5°C. Clear, visibly faultless, natural single crystals of CMN between 10 and 15 mm diam and about 2 mm thick were placed in the solution. This solution was refrigerated at 5°C, and the radioactivity was allowed to grow into the crystals for 16–20 h. The crystals were then removed from the solution, dried, and placed into a nonradioactive CMN solution at 5°C. An inactive layer was allowed to grow for 16–24 h. The CMN solution and crystals had been prepared in the usual way, i.e., by mixing stoichiometric amounts of high-purity $Ce(NO_3)_3$ and $Mg(NO_3)_2$ as hydrates to form a saturated solution, repeated recrystallization until the resulting crystals and solutions were clear, and subsequent growth of the crystals from the saturated solution at 5°C. A spectrochemical analysis[36] of the CMN crystals revealed no significant impurities. The results of this analysis are given in the Appendix.

IV. RESULTS

The CMN crystals were demagnetized from various values of H/T. When zero field was reached, a timer was started, the magnet was rolled away, the counters were rolled into position, and the counting was begun. Several "cold" counts of 15- or 30-sec duration ("live" time) were taken, and after approximately 5 min the crystals were warmed to the ambient bath temperature by admitting ^{3}He gas into the experimental chamber. A single "warm" count of 5- or 10-min duration was taken for normalization. All the data were accumulated in a PDP-7 computer (Digital Equipment Corp., Maynard, Mass.). For most of the 48 demagnetizations the counting rate did not change until several of the cold counting periods (between two and eight) had elapsed. The total cold count was taken as a summation over the period where the counting rates were essentially constant. The maximum warmup rate for an initial temperature of 2 mK was about 0.07 mK/min. For four of the demagnetizations into the high-temperature region, however, the counting rate changed more rapidly as a function of time and had to be extrapolated back to the time of demagnetization. This was done empirically with a linear least-squares method. For the worst case the warmup rate was 2 mK/min. Values of $W(\theta=0)$ are plotted against $\ln 2-S/R$ in Fig. 3. The data have been corrected for background under the 255-keV γ ray; details of this correction are given in Ref. 37. Corrections have also been made for source decay. The statistical uncertainty in the isothermal cold counts typically ranged between approximately 0.5 and 1% whereas for the nonisothermal cold counts statistical uncertainties as high as 1.5% were encountered. The uncertainty in the warm count was typically 0.5% or less. The error bars on $W(0)$ represent 1 standard deviation and are calculated in the usual way from the statistical errors in the cold and warm counts and an estimated 6% uncertainty in the background correction. The error limits on the entropy are about the size of the points in Fig. 3. These entropies

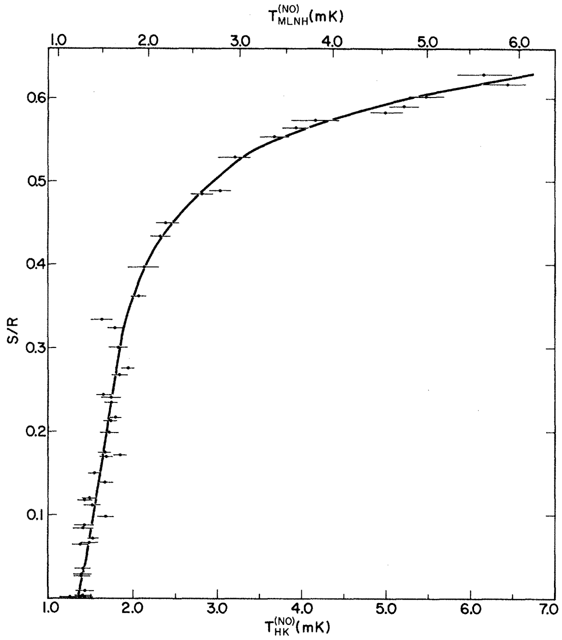

FIG. 4. S/R versus T. The solid curve represents our smoothed results. Note the two temperature scales, obtained by normalization of the nuclear-orientation results to the two sets of high-temperature calorimetric data. The scales are not linearly interrelated.

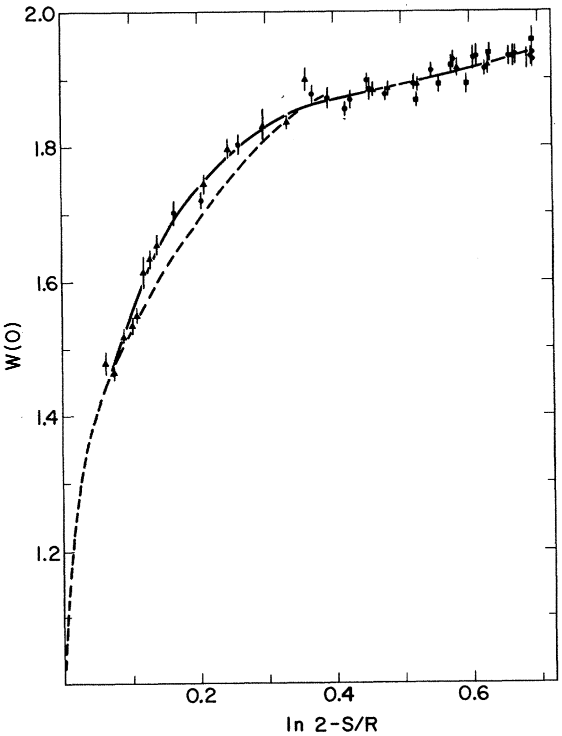

FIG. 3. $W(0)$ as a function of $\ln 2-S/R$. The solid curve through the data represents our smoothed results and the broken curve the smoothed results of Frankel, Shirley, and Stone (Ref. 3).

TABLE II. Entropy-temperature relations for CMN, including proposed T_A scale.

S/R	T_{MLNH}, mK	T_{HK}, mK	T_A, mK
0.002			1.29(9)[b]
0.010			1.30(9)
0.020	1.0[a]		1.32(9)
0.040			1.36(9)
0.050	1.2		1.38(9)
0.070			1.41(9)
0.100	1.42		1.46(9)
0.130			1.51(9)
0.150	1.60		1.54(9)
0.170			1.57(9)
0.200	1.75	(1.53)[a]	1.62(9)
0.230	1.82	(1.53)	1.66(10)
0.250	1.86	(1.53)	1.69(10)
0.270	1.88	(1.53)	1.72(10)
0.300	1.92	1.53	1.77(10)
0.330	1.93	1.54	1.83(11)
0.350	1.94	1.56	1.88(12)
0.370	1.95	1.64	1.95(13)
0.400	1.97	1.81	2.07(13)
0.420	2.00	1.94	2.18(14)
0.450	2.07	2.24	2.37(15)
0.480	2.16	2.57	2.62(15)
0.500	2.25	2.84	2.81(17)
0.510	2.34	2.98	2.92(17)
0.520	2.45	3.06	3.04(18)
0.530	2.58	3.32	3.18(18)
0.540	2.75	3.50	3.35(19)
0.550	2.94	3.69	3.55(20)
0.560	3.20	3.92	3.79(22)
0.570	3.58	4.20	4.05(23)
0.580	3.75	4.48	4.34(25)
0.590	4.07	4.87	4.68(27)
0.600	4.40	5.30	5.06(29)[c]
0.610	4.80	5.75	5.47(30)
0.620	5.30	6.26	5.93(32)
0.630	6.00	6.76	6.46(35)

[a] We have made graphical interpolations, where necessary, using the values of T given in Table I of Ref. 4 and in Table 1 of Ref. 5. The precision of the interpolation is $2\text{–}3\times10^{-5}$ K.

[b] Errors in last place are given parenthetically for the T_A scale. Errors in the other two scales are not indicated here. See Refs. 4 and 5.

[c] For $S/R>0.590$, T_A depends on the other two scales through the normalization procedure discussed in text. For $S/R<0.590$, T is derived directly from the (normalized) nuclear-orientation data. Only in the entropy range $0.655\leq S/R\leq0.687$ is T_A equal to $\frac{1}{2}(T_{\mathrm{MLNH}}+T_{\mathrm{HK}})$.

have not been corrected for radioactive heating effects during the isolation period of the magnetization because a calculation[37] showed that this correction was negligible.

To convert the values of $W(0)$ into temperatures, the value of the hyperfine-structure constant B in Eq. (2.12) must be determined. Because a magnetic resonance value of B (^{137m}Ce) was unavailable, it was necessary to determine B by normalizing our high-temperature results to the calorimetric results of Hudson and Kaeser[4] and/or to those of Mess *et al.*[5] For the former there was no problem in doing this, and the entropy range $0.529\leq S/R\leq 0.660$ was used for the normalization. In this region both methods (calorimetric and nuclear orientation) should be sensitive and reliable. The value of B was varied until the best least-squares fit to the Hudson and Kaeser data was obtained. This gave $B/k=0.00820\pm0.00042$ K. An independent check of this procedure is that the normalization of the Frankel *et al.* data to the Hudson and Kaeser results in the same entropy range yields $B/k=0.00826$ K, in close agreement with the value obtained from our results. It was, however, not possible to normalize our data directly to the results of Mess *et al.* because the two sets of data (ours and those of Mess *et al.*) diverged considerably over the whole common entropy range. Fortunately, an alternative procedure could be used because our data and the nuclear-orientation data of Frankel *et al.*[3] converge below $\ln2-S/R=0.070$. Thus the Frankel *et al.* data, which extend to higher temperatures and entropies, were combined with ours and the combined set of nuclear-orientation data was compared to the data of Mess *et al.* to obtain another value of B. The most favorable region for such a normalization is the one in which both sets of data obey a Curie law (i.e., $S/R=\ln2-bT^{-2}$), namely, $0.655\leq S/R\leq 0.687$. This normalization yields $B/k=0.00749$ K.

Thus two separate temperature scales, differing by 9%, were obtained. These correspond to the two values of B/k obtained by high-temperature normalization of our data to the two sets of calorimetric data. With these values of B/k the $W(0)$ data throughout the whole entropy range were converted to temperature points with the aid of Eqs. (2.8) and (2.10). The results are plotted in Fig. 4. Note that the upper horizontal scale corresponds to the Mess *et al.* normalization ($T_{\mathrm{MLNH}}{}^{(\mathrm{NO})}$) and the lower to the Hudson and

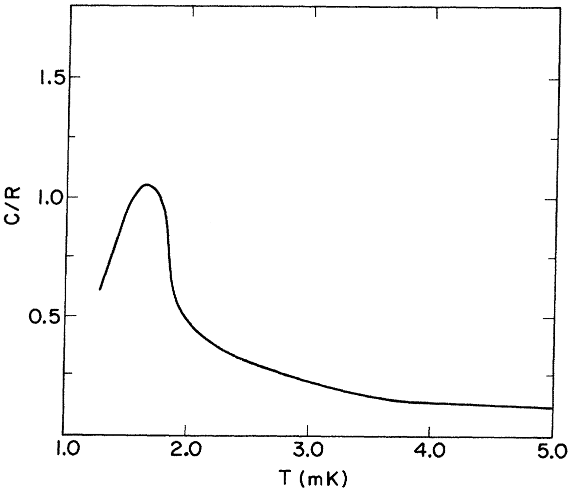

FIG. 5. Heat capacity versus T, obtained by differentiating T-S curve.

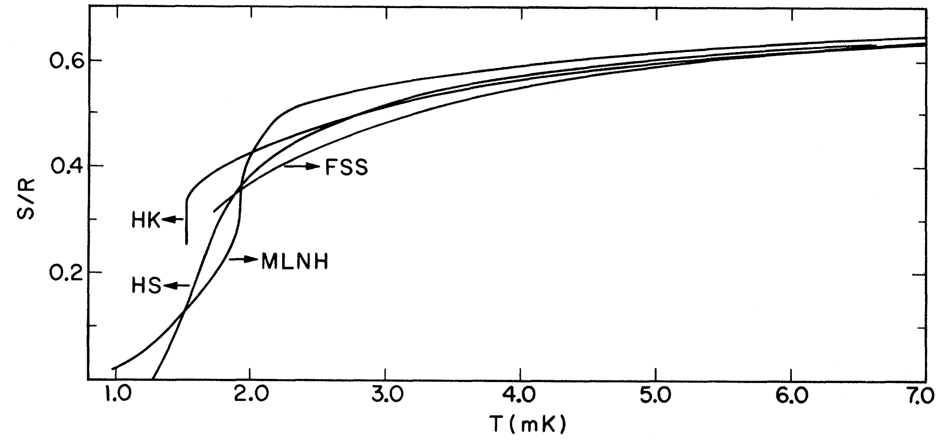

FIG. 6. S/R versus T. Hudson and Kaeser (HK) (Ref. 4); Mess *et al.* (MLNH) (Ref. 5); Frankel *et al.* (FSS) (Ref. 3); this work (HS).

Kaeser normalization ($T_{\mathrm{HK}}^{(\mathrm{NO})}$). The solid curve through the data represents a least-squares computer fit to the data except in the entropy region $0.340 \leq S/R \leq 0.540$, where the data were fitted by hand.

Of course two temperature scales are undesirable. No definitive choice can be made, however, until B/k is known both precisely and independently of the calorimetric results. To temporarily ameliorate this problem, however, we propose an "average" temperature scale (T_A) based on our nuclear-orientation results. Thus for a given entropy value

$$T_A = \tfrac{1}{2}[T_{\mathrm{MLNH}}^{(\mathrm{NO})} + T_{\mathrm{HK}}^{(\mathrm{NO})}],$$

where $T_{\mathrm{HK}}^{(\mathrm{NO})}$ and $T_{\mathrm{MLNH}}^{(\mathrm{NO})}$ represent our nuclear-orientation scales based on high-temperature normalization to the HK and MLNH scales. Selected values of S/R and T_A are tabulated in Table II. The uncertainties in the various values of T_A are indicated in parentheses. These uncertainties correspond to the square root of the sum of the squares of the uncertainties arising from the hyperfine-structure constant and from the curve-fitting procedure. As such they are a good measure of the *precision* of the T_A scale; its *accuracy* still depends on the accuracies of the calorimetric $T(S)$ relations in the high-temperature normalization range.

It is easily shown that setting $A=0$ has negligible effect on the interpretation of our data. The value of A can be approximated by the following relation: $A/B \approx g_{\|}/g_{\perp}$. Using $g_{\|}=0.03$ and $B/k=0.00820$ K, we find $A/k \approx 1.375 \times 10^{-4}$ K. From Eqs. (2.8) and (2.10) we calculated $W(0)$ with respect to T for $A/k=0$ and $A/k=1.375 \times 10^{-4}$ K and found that for a given value of $W(0)$ the largest temperature difference between the two cases is only 0.02 mK. Thus setting $A=0$ is justified.

The heat capacity $[C=T(dS/dT)]$ can be obtained by differentiation of the S-T curve. The results are depicted in Fig. 5. The maximum in the heat capacity falls at about 1.66 mK, which can be compared with the heat-capacity peak at 1.9 mK in the work of Mess *et al.* The maximum slope in the Hudson and Kaeser curve occurs at 1.53 mK. Only qualitative significance should be placed on our heat-capacity curve since it results from a differentiation of our experimental curve and is thus quite sensitive to the curve-fitting procedure. Of course in the calorimetric studies[1,4,5] the temperature scale itself is obtained by differentiation, and a heat capacity such as that reported by Mess *et al.* is obtained by *double* differentiation, of a curve through the data.

V. DISCUSSION

The four most recent T-S scales are shown in Fig. 6. The two nuclear-orientation scales (Frankel *et al.* and the present work) are in reasonable agreement although the Frankel *et al.* results yield systematically higher temperatures for a given entropy than do the present results. The results of Frankel *et al.* have been renormalized to the average of the Mess *et al.* and Hudson and Kaeser results at high temperatures in a manner similar to that described in Sec. IV. In Fig. 3 the γ-ray anisotropy data are compared for the two studies. The smooth line through the present results corresponds to the smooth line in Fig. 4, but with the values of T converted to $W(0)$. The broken line represents the results of Frankel *et al.* As in the T-S plot there is a systematic discrepancy between the two. The explanation for this difference probably lies in the method of correction for the background under the γ-ray peak. This is a difficult correction to make, and the present work represents a somewhat more sophisticated approach to the problem than used by Frankel *et al.* Moreover, inspection of the data of Frankel *et al.* reveals that their experimental scatter is somewhat greater than in our work. We believe, therefore, that the present results are definitely to be preferred over those of Frankel *et al.*

The disagreement between our results and the calorimetric results appears to be more serious—especially for temperatures below 2 mK. Furthermore

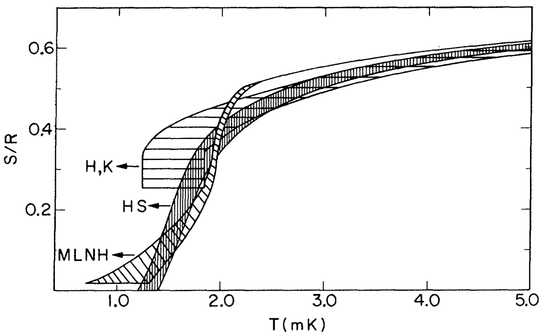

FIG. 7. Comparison of quoted experimental errors. Shaded area—this work; horizontal lines—Hudson and Kaeser (Ref. 4); slanting lines—Mass *et al.* (Ref. 5).

there is a complete lack of agreement between the two calorimetric scales themselves. In Fig. 7 the quoted errors are depicted for our work and for the two calorimetric scales. This figure illustrates one of the most important advantages of the nuclear-orientation method, namely, that it retains considerable sensitivity even to the lowest temperatures (see also Fig. 2), where the calorimetric methods deteriorate. Note that the error limits on our scale can be reduced by 50–70% when an accurate value of the hyperfine-structure parameter B is available.

Since the publication of the Frankel *et al.* results, which also originated from this laboratory, a number of comments have been made (in the comparison of different experimentally determined temperature scales for CMN) which indicate that a critical comparison of the different methods for obtaining T would be useful. The basic principle of the calorimetric procedure is to demagnetize from a known entropy and to measure the heat (Q) required to warm the sample to some known reference temperature. When this is done for a number of initial entropies, an S-Q curve is obtained. Differentiation of this curve yields the temperature ($T=dQ/dS$). In the nuclear-orientation technique one also demagnetizes from various initial entropies but measures γ-ray anisotropies instead of heat input, and therefore does not have to differentiate the data. The γ-ray anisotropies are converted to temperatures as described in Secs. II and IV.

An obvious requirement for all three methods is that the entropy of the sample be known immediately after demagnetization; that is, the demagnetization must be adiabatic. In general this condition is probably well satisfied. In the measurement of heat content, however, one must be concerned with three problems: the calibration of the heater, extraneous heat leaks, and the constancy (or lack thereof) of the rate of heat absorption by the CMN over the whole temperature range. The solution to the first is usually straightforward although quite critical since the temperature can be determined only as accurately as the rate of heating. Of course one can determine this rate by high-temperature normalization of the derived temperature. The problem of extraneous heat leak can be minimized by using a large rate of heating relative to the leak. In addition corrections for the heat leak must be estimated. The third condition (i.e., constancy of heat absorption) is usually assumed to be valid although not always verified experimentally. In the nuclear-orientation method the measurement of the γ-ray anisotropy must be made while the entropy of the sample is still known. Experimentally this is equivalent to making an essentially isothermal measurement as determined by the time rate of change of $W(0)$. If the measurement is not isothermal, then the results must be extrapolated back to the time of demagnetization. Such a situation generally occurs only in the relatively high-temperature, low-heat-capacity region. For all but four of the demagnetizations in this work, the isothermal condition was met for lengths of time sufficient to acquire reasonable counting statistics in $W(0)$.

The most serious problem encountered in the calorimetric technique is that the temperature is obtained by a *differentiation* of the experimental S-Q curve. Thus the derived temperature is very sensitive to the curve fitting of the S-Q data. Moreover, any experimental scatter at the lowest entropies can cause large uncertainties in the slope (T) since there is no fixed point other than absolute zero to anchor the T-S curve. It should be noted that the heat function Q is determined in the calorimetric experiments by heating the specimen from various low temperatures to a given high temperature T_0. It takes a given length of time $\Delta t'$ to heat the specimen from a given low-temperature point $T'(S')$ to T_0. Thus one must extract a heat function Q' from a time interval $\Delta t'$, making appropriate corrections for heat leak, etc. While certain checks can be made on the various assumptions that go into determining Q' from $\Delta t'$, we feel that these checks are not totally convincing. Even if one accepts the Q-S curve as being free of systematic error, the data that have been presented by the two groups doing calorimetric work (Fig. 5 in Ref. 4 and Fig. 7 in Ref. 6) do not seem to us to be a quality that can be differentiated with confidence to give $T=dQ/dS$ with very high accuracy below 2 mK.

The question of error estimates is also important. In the nuclear-orientation work the estimation of errors is rather straightforward, although quite involved,[37] and we believe that our error estimates give a realistic account of both random and systematic errors. From experience in this laboratory, however, we appreciate the difficulty associated with estimating errors in the calorimetric experiments, especially at the lowest temperatures. We note that the error estimates in the HK and MLNH studies are grossly different. At $S/R=0.50$, for example, the HK estimate is ±0.3 mK. Mess *et al.* give no error explicitly for this entropy, but their discussion implies that the error is much smaller than ±0.10 mK. This difference is not supported by the apparent relative quality of the two sets of Q-S data (Ref. 4, Fig. 5, and Ref. 5, Fig. 7). We note, on closer study, that the Q values for a given entropy are in very bad disagreement in these two figures, differing by about a factor of 1.5 at the highest entropies. This plight is illustrated in Fig. 8, where we have reproduced the two sets of Q-S data. Apparently *systematic* errors in the calorimetric work should receive further study before firm conclusions about magnetic transitions can be drawn, especially since the Q-S curves must be differentiated to yield the absolute temperature.

In the nuclear-orientation technique the temperatures are derived directly from the γ-ray anisotropies; no differentiation is required. However, the spin Hamiltonian must be known, and in particular the hyperfine-structure parameter B must be determined by normalization to the high-temperature calorimetric results. If a magnetic resonance value of B should become available, however, our T-S scale would then be independent of the calorimetric work. We feel that the weakest point in our work is the requirement that the *form* of the spin Hamiltonian be known. There is always a possibility that the Hamiltonian might change at the lowest temperature in some unexpected way and thus alter the γ-ray angular distribution.

Actually the spin Hamiltonian *must* change at the lowest temperatures because the magnetic entropy decreases rapidly, suggesting the onset of a collective transition. However, the resultant ~60-Oe magnetic field H_x perpendicular to the c axis has little effect on $W(0)$, and this small effect is calculable, as discussed above and illustrated in Fig. 2. In fact $W(0)$ is remarkably insensitive to H_x; Frankel[22] calculated $W(0)$ for $0<H_x<10^4$ Oe and found less than a 10% change. Thus we do not regard the existence of dipole-dipole interactions as a criticism to be taken seriously; the effect on $W(0)$ is small.

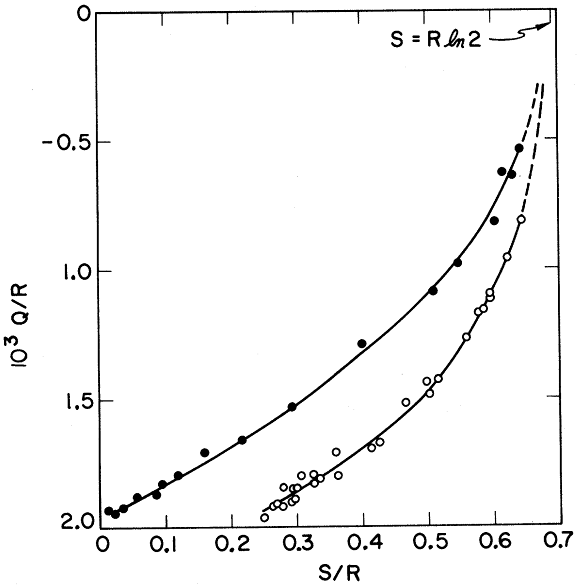

FIG. 8. Heat-content–entropy data from Fig. 5 of Ref. 4 (open circles) and Fig. 7 of Ref. 5 (filled circles). Curves through these two sets of data had to be differentiated to give the calorimetric temperature scales, $T=dQ/dS$.

Quadrupole coupling can also be shown to have a negligible effect for any reasonable value of the coupling constant.

It is just possible that some Ce-Ce exchange is present at the lowest temperatures, although with an interionic spacing of 8.56 Å the interaction would be very small. The major effect of exchange could be described phenomenologically by altering the value of H_x in the spin Hamiltonian. Even a fairly large variation in H_x will not affect $W(0)$ very much, and H_x cannot in fact be grossly different from 60 Oe if $gH_x \sim kT_c$. Still the possibility is always present that the nuclear-orientation results are affected at the lowest temperatures by exchange interactions.

As we have already pointed out, the two nuclear-orientation scales are reasonably consistent while the two calorimetric scales are quite different. Moreover it should also be pointed out that although the two nuclear-orientation scales originated from the same laboratory, the apparatus, the samples, and the methods of data analysis were different for the two scales. Thus any systematic errors peculiar to a particular apparatus can be ruled out. For this reason and those cited above, we feel that the low-temperature ($T<3$ mK) results of the present work represent the thermal behavior of CMN more closely than the calorimetric scales.

VI. NUCLEAR ORIENTATION OF ^{137m}Ce IN CERIUM ZINC NITRATE

In this section the preliminary results of a nuclear-orientation experiment for ^{137m}Ce in cerium zinc nitrate (CZN) are presented. This salt has also been used in low-temperature experiments, but its thermodynamic properties have never been investigated. It therefore seemed worthwhile to use the ^{137m}Ce thermometer to study the low-temperature behavior of CZN.

CZN has been used primarily by Culvahouse, Sapp, and colleagues at the University of Kansas. They measured the electronic g factors of Ce^{3+} in a CZN crystal with a small amount of Co substituted for the Zn and found $g_\perp = 1.823 \pm 0.007$ [38] and $g_{\parallel} = 0.125$.[39] Thornley[16] has measured the far-infrared spectrum of CZN and has determined the splitting between the two lowest Kramers doublets to be $\Delta/k = 30.2 \pm 0.4$ K. These values are quite similar to the values found for CMN and seem to indicate that CMN and CZN have similar crystal-field properties.

Culvahouse *et al.*[39] have investigated the crystal structure of CZN by the x-ray powder diffraction technique and find unit cell dimensions similar to those of

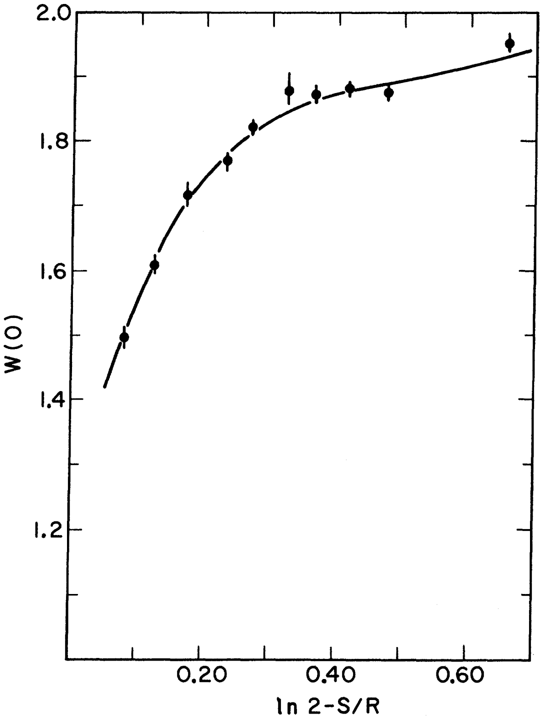

FIG. 9. ^{137m}Ce in CZN: $W(0)$ versus $\ln 2 - S/R$. The solid curve corresponds to the $[W(0),\ \ln 2 - S/R]$ correlation derived from the smoothed T, S/R curve for CMN.

Zalkin *et al.*[31] A Laue photograph of single-crystal CZN with the x-ray beam along the trigonal axis indicated C_{3v} symmetry in contradiction with the C_{3i} symmetry found by Zalkin *et al.* for CMN. Furthermore, investigation of the divalent sites in CZN by paramagnetic resonance[39] gave results which are in disagreement with the findings of Zalkin *et al.* for CMN. It seems unlikely that the structure of CMN and CZN are significantly different, but only a thorough crystallographic study will decide this question.

CZN has previously been used in nuclear-orientation experiments, but the absence of a temperature scale for this salt has hampered the interpretation of the data. Levi *et al.*[38] have studied the nuclear orientation of ^{60}Co in CZN and found a considerably larger anisotropy than found for ^{60}Co in CMN.[40,41] They interpreted the CZN results in terms of a temperature-dependent local magnetic field set up at the Co X sites and zero magnetic field at the Co Y sites with the ratio

$$(\text{Co in } X)/(\text{Co in } Y) = 1.6.$$

(There are two types of divalent sites; cf. Ref. 31.) The limiting field was found to be 165 Oe in contrast with the 66.71-Oe field calculated at a Mg site in CMN by Daniels and Felsteiner.[42] Carboni and Sapp,[43] however, have pointed out that the paramagnetic Co^{2+} ion will perturb the Ce long-range order and that the spatial reversal of one nearest-neighbor Ce dipole would more than compensate for the difference. Carboni and Sapp also suggested that the ^{60}Co in CMN results could be explained by a local field of 165 Oe,

$$(\text{Co in } X)/(\text{Co in } Y) = 2,$$

and a lowest temperature of 1.05 mK.

The temperature invoked by Carboni and Sapp for CMN is inconsistent with the results presented in Sec. IV, and the temperatures in the CZN experiments were not well known. The data which are given below suggest a high degree of similarity in the thermal properties of the two salts. Some qualitative conclusions may be drawn from these results. We present them here because of this and because we do not plan to do further work in the CZN problem.

The experimental technique and method of data reduction were identical to those described in Secs. III and IV of this paper. A spectrochemical analysis of the CZN crystal indicated a 1% Mg impurity—presumably as a substitutional impurity for Zn. Analysis of the solution from which the CZN crystals were grown, however, showed only 0.07% Mg. The apparent conclusion is that the double-nitrate lattice exhibits a strong preference for the smaller Mg^{2+} ion.

In Fig. 9, $W(0)$ is plotted against $\ln 2 - S/R$; the scarcity of data for $\ln 2 - S/R > 0.50$ is due to a failure in the apparatus. Entropy values have been calculated from H/T using $g_\perp = 1.823$ with the aid of the tabulation by Hull and Hull.[21] The values of $W(0)$ are corrected for radioactive decay between the cold and warm counts and for background but not for solid-angle effects. The background correction in the calculation of $W(0)$ amounted to about 11% of the warm count. The solid curve through the data represents the $W(0)$ versus $(\ln 2 - S/R)$ correlation derived from the smoothed T_A, S/R curve for CMN. The solid-angle corrections, which were identical for the two experiments, are incorporated into the curve.

Despite the small number of data points it is evident that the thermal behavior of CZN and CMN are quite similar. No reliable data were obtained in the entropy range $0.50 \le \ln 2 - S/R \le 0.60$, and so "anomalous" properties in this region cannot be ruled out. The point at $\ln 2 - S/R = 0.65$, however, was confirmed several times. The additional points at $\ln 2 - S/R = 0.65$ are not included in Fig. 9. The lack of any calorimetric work on CZN precludes the determination of the hyperfine-structure constant B for ^{137m}Ce in CZN, and therefore actual temperatures for CZN cannot be derived from these data. However, from the similarity in the nuclear-orientation data for ^{137m}Ce in CZN and CMN, it can be concluded that the hyperfine-structure constants for the two cases must be very nearly the same. If this is the case, then the minimum temperature obtainable with CZN is about 1.3 mK.

In light of the results presented here, the early nuclear-orientation work on CZN should probably be reinterpreted. For example, as was mentioned earlier, Levi *et al.*[38] derived a dipolar field of 165 Oe acting on a $^{60}Co^{2+}$ ion in a CZN X site from their nuclear-orientation data. They based their interpretation on a minimum $T^* \approx 3.3$ mK after demagnetization from $H/T \approx 26.8$ kOe/K. If the CZN and CMN T-S relations are identical, then the actual temperature for this value of H/T is 1.60 mK. With this temperature, however, the results of Levi *et al.* are reasonably well explained by the calculations of Daniels and Felsteiner,[42] who derived a dipolar field of 66.71 Oe at the Co site. Furthermore, the disagreement between the ^{60}Co in CMN results and the ^{60}Co in CZN results is difficult to understand since the thermal properties of the two salts seem similar. If the dipolar fields acting on the Co^{2+} ions are equal for the two salts, then the only remaining variable is the ratio (Co in X)/(Co in Y). Since the X and Y sites have quite different hyperfine-structure constants,[43] a large difference in the X/Y ratio between the two salts would have a significant effect on the nuclear-orientation results and could account for the disagreement.

APPENDIX: SPECTROCHEMICAL ANALYSIS OF CMN

The CMN was prepared from 99.9% $Mg(NO_3)_2 \cdot 6H_2O$ (J. T. Baker Chemical Co., Phillipsburg, N. J.) and "purified" $Ce(NO_3)_3 \cdot 6H_2O$ (Allied Chemical Co., Morristown, N. J.). Separate analyses of the $Ce(NO_3)_3 \cdot 6H_2O$ and of the La_2O_3 target material are given in Ref. 37.

The sample size of CMN was chosen to yield about 50 μg of Ce as the metal. Cu, Al, and Ca were observed at the limits of detection, all of which were 0.01 μg. Approximately 0.03 μg of Na were detected. The following impurity elements were searched for but were not detected. The limits of detection are indicated in parentheses.

Bi (0.05), Co (0.05), Cr (0.01), Dy (0.1), Er (0.05), Eu (0.01), Fe (0.05), Gd (0.05), Ho (0.05), La (0.05), Li (0.01), Lu (0.05), Mn (0.01), Nb (0.01), Nd (0.1), Ni (0.01), Pb (0.1), Pr (0.1), Sc (0.05), Si (0.01), Sm (0.05), Sn (0.1), Tb (0.5), Th (0.5), Ti (0.01), Tl (0.5), Tm (0.05), V (0.01), Zn (0.1), Zr (0.01).

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