

phase. It was found that the crystallographic transition occurs at a much slower rate than the phase separation, hence, it was possible to distinguish between the two processes. The measurements were taken at a rate such that the changes in P due to the crystallographic changes were small compared with those due to the phase separation.

Also several instances of crystallographic changes in the mixed or partially mixed samples have been observed. No attempt to locate these phase boundaries has been made since attaining equilibrium conditions would require waiting for very long times. For some concentrations, the phase separation has been observed at one pressure for which the mixed structure was bcc and at a higher pressure for which the mixed structure was hcp. This difference in crystal structure appears to have very little if any effect on the phase-separation temperature.

For a given concentration, the time constant for the phase separation always increased with increasing pressure. For example, in the $x = 0.485$ sample, τ increased from ~ 30 sec at 30.5 atm to ~ 500 sec at 38.5 atm. Although we do not have conclusive quantitative results concerning the dependence of τ on the temperature and concentration, some qualitative conclusions appear valid. For a fixed concentration the time constant is longer in the vicinity of the phase-separation temperature than at lower temperatures, and is longer on cooling than on warming. Also τ appears to be longer for the smaller He^4 or He^3

concentrations, particularly the latter. EMD find $\tau \sim 15$ sec at 35.8 atm, independent of x and T . Apparently the time constant is affected by the dimensions of the sample since that of EMD was contained in pores of $10\text{-}\mu$ diam while the smallest dimension of our sample was 0.8 mm.

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MAGNETIC THERMOMETRY WITH CERIUM MAGNESIUM NITRATE AND ITS RELATION TO THE PROPERTIES OF He^3 †

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Direct comparison of the magnetic temperature of one cerium-magnesium-nitrate powder thermometer with that of a single-crystal sphere shows that the former is less than the latter by $\Delta = +(0.46 \pm 0.05)$ mdeg K. Comparison of other powdered thermometers suggests that Δ may vary from thermometer to thermometer by 0.1 to 0.2 mdeg K. These values of Δ do not lead to serious difficulties when comparing experimental properties of He^3 with theories of the Fermi liquid.

We have made a direct comparison of the magnetic temperatures indicated by a powder (size less than 420μ) of cerium magnesium nitrate (CMN) in the form of a right circular cylinder with diameter equal to height and by a sphere of

CMN. The results, obtained over the range 10-38 mdeg K, are described by

$$T_S^* = T^* + \Delta, \quad (1)$$

where T^* is the magnetic temperature indicated by the powder and T_S^* is the magnetic temperature indicated by the sphere. In a recent Letter, Abraham and Eckstein¹ conclude that Δ in Eq. (1) is +1.7 mdeg K. It is commonly assumed furthermore that once T^* has been corrected by adding Δ , the same relation between $T^* + \Delta$ and T , the Kelvin temperature, may be used as was derived by Hudson and Kaeser² using the "thermodynamic" method. Neither of these conclusions is supported by the direct experimental evidence presented below.

In the present experiments the CMN thermometers were immersed in the saturated solution of He^3 in He^4 in a special epoxy mixing chamber for our dilution refrigerator.³ The mixing chamber was designed so that the assembly containing the thermometers could be cut out, inverted, and resealed into the apparatus without changing any of the immediate surroundings of the thermometers. Temperatures down to below 10 mdeg K were maintained constant to assure thermal equilibrium between the two thermometers, which were in contact by a column of helium 8.0 cm long and 0.95 cm in diameter located below any flowing helium. The powdered CMN, mass 0.824 g, occupied a volume of 0.762 cm³. The sphere was either two hemispheres, total mass 0.507 g, ground from the same optically clear crystal or an optically clear single-crystal sphere of mass 0.136 g. The measuring field was along a direction of maximum susceptibility of the spheres. Two essentially identical sets of measuring coils were used to make alternate measurements of magnetic temperature by means of a 17-Hz bridge.⁴ Care was taken in regard to small nonlinearities of this bridge.

The results of the measurements are shown in Fig. 1. Straight lines were fitted to the data using the method of least squares. In the first experiment (circles) the hemispheres were on top (nearest the source of refrigeration). The resultant Δ was $+0.38 \pm 0.05$ mdeg K. In a second experiment (squares) the thermometers were inverted, no other changes being made, so that the hemispheres were on the bottom. The resultant Δ was $+0.54 \pm 0.02$ mdeg K. This difference in Δ can be accounted for by a $\sim 10^{-2}$ erg/sec heat flux up the helium column; we have assumed this to be true in averaging the two results to obtain $\Delta_{\text{av}} = +0.46 \pm 0.05$ mdeg K for the powder thermometer. At the lowest temperatures the thermal diffusivity of the CMN hemispheres is very low. Thus any possible lack of equilibrium

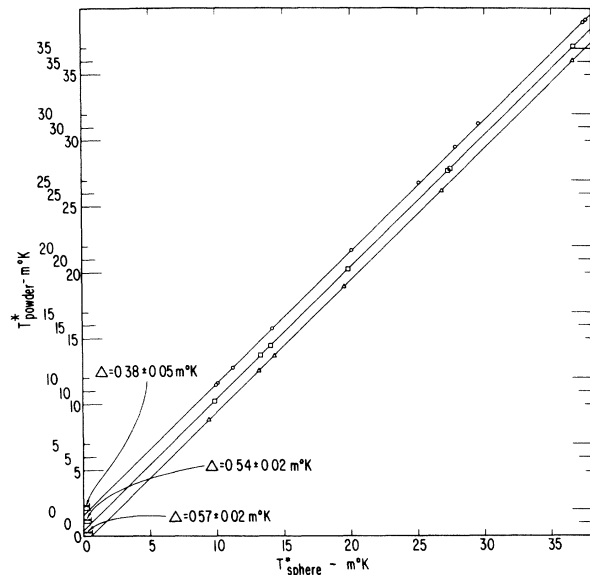


FIG. 1. Magnetic temperature of a CMN powder thermometer versus that for a CMN crystal sphere. Circles: sphere made from two hemispheres; sphere on top. Squares: sphere made from two hemispheres; sphere on bottom. Triangles: single-crystal sphere; sphere on bottom.

or extraneous heat input directly to the crystals will tend to make the hemispheres hotter than the powder and thus spuriously increase the value of Δ derived from the measurements. Therefore, the above value of Δ should be regarded as an upper limit. In a third experiment (triangles) we replaced the hemispheres with the sphere, making no other changes. The resultant Δ was $+0.57 \pm 0.02$ mdeg K, agreeing with the result given above for the two hemispheres and showing that no mysterious effects are present. The average susceptibility of the powder per unit mass was within 5% of $\frac{2}{3}$ of that for the single crystal, as expected for this salt.

The quantity Δ can be written $\Delta = (4\pi/3 - \eta)C$, where η is an effective demagnetizing factor, $4\pi/3$ for a sphere, and C is the Curie constant per unit volume, 0.3 mdeg K for the present powder thermometer. Owing to nonuniformity in packing and changes of average density from thermometer to thermometer, it cannot be expected that the value of Δ measured here precisely represents all powder thermometers, though one would expect $|\Delta| \approx C \approx 0.3$ mdeg K. Evidence for the sort of reproducibility in Δ from one thermometer to another may be obtained from measurements by Abel et al.⁵ in which two powder thermometers (grain size $< 37 \mu$), one of mass 0.230 g and 68% crystalline den-

sity (lower) and one of 11.76 g and 54% crystal-line density (upper), were in thermal contact by means of pure He³. A plot of T_{upper}^* vs T_{lower}^* is shown in Fig. 2. These data are fitted well by the expression $T_{\text{upper}}^* = T_{\text{lower}}^* + (\Delta_L - \Delta_U)$, where $\Delta_L - \Delta_U = 0.11$ mdeg K. It is thus reasonable to expect that Δ will vary by 0.1 to 0.2 mdeg K from one thermometer to another.

Although T^* for the powder thermometers is the same as T_S^* within a few tenths of a millidegree at higher temperatures, this is not true at the lowest temperatures. The lowest values of T^* observed for the powders show no systematic grain-size dependence and vary from 1.7 to 1.9 mdeg K.⁶⁻⁸ Minimum values for T_S^* for the single crystals are 3.68 mdeg K for Ref. 2, and 3.20 mdeg K for Daniels and Robinson⁹ and Frankel, Shirley, and Stone.¹⁰ The susceptibility of the powder near the ordering temperature in CMN is thus different from that for a single-crystal sphere. We therefore conclude that at the lowest temperatures any relation between T_S^* and T for single-crystal spheres is not the same as that between $T^* + \Delta$ and T for powders.

The quantity Δ can be determined indirectly in a variety of ways: (1) If one accepts the result of Ref. 2 that the heat capacity of CMN, C_{CMN} , obeys the T^{-2} law between 6 and 15 mdeg K then one can plot $(C_{\text{CMN}}/R)^{-1/2}$ vs T^* to find Δ as intercept. (2) If one assumes that at sufficiently

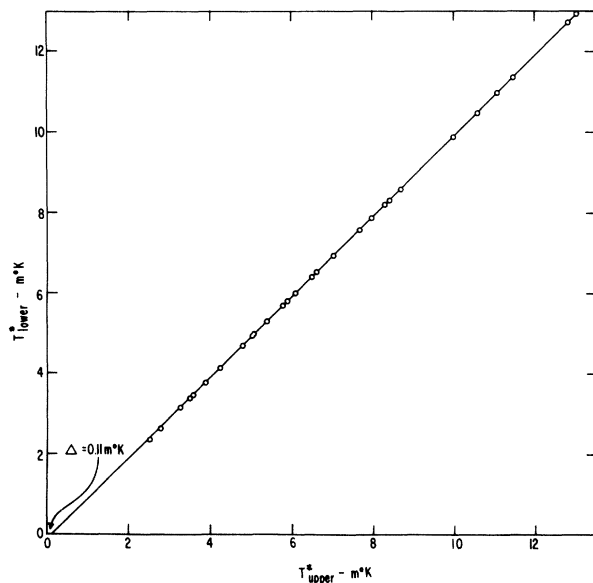


FIG. 2. Magnetic temperatures of two CMN powder thermometers in thermal equilibrium as found in Ref. 5. The designations "upper" and "lower" refer to the physical location of these thermometers in the cell.

low temperatures the specific heat of a Fermi liquid depends linearly on T then one can plot C_3^* vs T^* to obtain Δ as intercept. This can be done both for pure He³ at 0.28 and 27.0 atm¹¹ and for dilute solutions of He³ in He⁴.¹² In the case of pure He³, C_3^*/T^* does continue to increase as T^* decreases so that for the numerical analysis, data should be used only to a high enough temperature to obtain reasonable precision. Use of higher-temperature data will increase the derived value of Δ . It is important to recognize that the He³ heat-capacity data and our CMN heat-capacity data¹¹ were obtained simultaneously in the same cell and the same experiment. For the temperature ranges used, the He³ data generally have higher precision. Data for the dilute-solution heat capacity were derived from raw data using the CMN heat capacity obtained in Ref. 11. (3) If one assumes that the spin-diffusion coefficient for a Fermi liquid varies as T^{-2} then one can plot $D^{-1/2}$ vs T^* to obtain Δ as intercept. Again it is desirable to use data for the lowest possible temperatures since according to Rice¹³ $(DT^2)^{-1}$ decreases as T increases. (4) Some semiquantitative information can be obtained from Osgood and Goodkind's¹⁴ He³ heat-capacity data obtained using an NMR temperature scale. We assumed C_3 to be linear in T_{NMR} since C_3^* is linear in T^* . The intercept gives the amount T^* would have to be translated to make the CMN scale and the NMR scale have the same zero and hence estimates Δ .

The results of the above analysis are given in Table I. The value of Δ from CMN heat capacity is very substantially greater than that determined by our direct measurements. The NMR data of Ref. 14 favor a negative Δ when one weights all points equally as in our analysis. Osgood,¹⁵ using a somewhat different weighting and allowing curvature in C_3 vs T , finds that Δ is moved toward positive values. Taken together, the He³ heat-capacity data using CMN thermometry favor a Δ of from 0 to +0.3 mdeg K, not unreasonable on the basis of our direct measurements, Figs. 1 and 2, but very different from Δ as derived from the CMN heat capacity. The spin-diffusion results of reasonable precision for Δ give both positive and negative values for Δ . In the case of spin diffusion at the lowest temperatures we had some difficulty in measuring the very large values of D for the 5.0% solution. The spin-diffusion Δ 's may also be different from those for heat capacity since the thermometer was immersed in an approximately 20-G field in the diffusion measurements. Finally,

Table I. Experimental determinations of Δ .

Experiment	Temperature Range ^a	Δ
	m ^o K	m ^o K
CMN heat Capacity ^b	6.0 - 14.9	+ (1.48 ± .24)
CMN Heat Capacity ^c	5.4 - 16.6	+ (2.5 ± 0.5) ⁱ
Heat Capacity - pure He ³ , 0.4 atm ^d	4.7 - 11.7	- (0.7 ± 0.7)
Heat Capacity - pure He ³ , 0.28 atm ^b	6.1 - 12.4	- (0.02 ± .24)
Heat Capacity - pure He ³ , 27.0 atm ^b	4.1 - 11.2	+ (0.20 ± .09)
Heat Capacity - 5.0% Solution He ³ in He ^{4 e}	3.1 - 13.5	+ (0.13 ± .15)
Spin Diffusion - pure He ³ , 0.2-0.3 atm ^f	3.6 - 9.0	- (0.32 ± .06)
Spin Diffusion - 5.0% Solution of He ³ in He ^{4 e}	3.0 - 9.9	+ (0.75 ± .28)
Spin Diffusion - 1.3% Solution of He ³ in He ^{4 e}	3.0 - 10.0	+ (0.12 ± .06)
CMN powder - CMN sphere ^g	10 - 38	+ (0.46 ± .05)
CMN powder - CMN powder ^h	2.5 - 13.0	$\Delta_L - \Delta_U = 0.11$

^aThese are directly observed empirical temperatures.

^bSee Ref. 6.

^cSee Ref. 1.

^dSee Ref. 14, NMR scale.

^eSee Ref. 12.

^fSee W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, *Physics* **1**, 337 (1965).

^gPresent experiment.

^hSee Ref. 6.

ⁱThis figure is different from 1.7 mdeg K since, following Ref. 2, the measurements given in Ref. 1 are fitted over a restricted temperature range.

our results can be distorted at the lowest temperatures by ignorance of the $T-(T^*+\Delta)$ relation. Any Δ intrinsic to a CMN sphere is included when Δ is found from He³ properties. The present measurements determine the shape Δ only. Assuming the intrinsic Δ small we conclude that a positive Δ of a few tenths of a millidegree allows most of the He³ experiments to be explained by Fermi-liquid concepts and gives reasonable agreement with the present measurements.

We can use the above estimate of Δ to re-evaluate our thermal conductivity data⁵ for pure He³ in the light of Rice's¹³ theory. The best fit between 3 and 30 mdeg K to the formula $[\kappa(T^*+\Delta)]^{-1} = a - b(T^*+\Delta)$ is obtained for $\Delta = +0.3$ mdeg K though is not particularly sensitive to the assumed Δ . We find $a = (2.87 \pm 0.1) \times 10^{-2}$ sec cm/

erg and $b = (18 \pm 3) \times 10^{-2}$ sec cm/erg K^o.

Since direct measurements of Δ appear to rule out those determined from CMN heat capacity we conclude that the T^{-2} law is not precisely valid for CMN (at least in our powders) between 6 and 15 mdeg K. On the other hand, Hudson and Kaiser² find CT^2/R for single crystals of CMN to be constant between 6 and 15 mdeg K. The discrepancy may be caused by differences between the heat capacities of powders and single crystals, although this seems unlikely on basis of the grain size independence of the heat capacity indicated in Ref. 6; by differences due to impurities, whose presence is suspected by Hudson and Kaiser²; or by differences due to some unknown difficulties in the experimental measurements or their interpretation. In view of the discrepancy

the quantitative correctness of the thermodynamic temperature scale derived in Ref. 2 for single crystals should be questioned.

Central to the discussion of the properties of CMN is the assumption that CT^2/R at high temperatures is constant for the actual salts measured. Although the case of CMN is different from those of other salts we have sought experimental precedent for this assumption in other salts at higher temperatures where, in our opinion, thermometry is not a problem. Quantitative results of Rayl, Vilches, and Wheatley¹⁶ are available for $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, like CMN an effective spin- $\frac{1}{2}$ salt. It has a λ -type heat-capacity anomaly at 30 mdeg K, approximately a factor 10 higher than the temperature range² in which the entropy decreases substantially in CMN. The magnetic-interaction contribution to CT^2/R for this salt increases by about 20% between 60 and 150 mdeg K. In the range from 6 to 15 mdeg K the value of $C(T^* + 0.3 \text{ mdeg K})^2/R$ for CMN from Ref. 11 increases by 25%. Whether or not CT^2/R is constant is a matter to be decided quantitatively.

Finally, in regard to the question raised above concerning the thermodynamic temperature scale, there is little precedent for the quantitative validity at very low temperatures of temperatures based on $T = \Delta Q / \Delta S$, where ΔQ is a measured heat flow and ΔS a calculated entropy change. Serious discrepancies exist for ferric ammonium alum,¹⁷ chromium potassium alum,¹⁷ manganous ammonium Tutton salt,¹⁷ potassium ferricyanide,¹⁶ and copper potassium Tutton salt.¹⁶

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