

Heat Capacity of Diluted Cerium Magnesium Nitrate and Its Potential for the Production of Very Low Temperatures*

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We present measurements of the magnetic heat capacity of pure cerium magnesium nitrate (CMN) and La-diluted CMN. From the measurements, we conclude that it may be possible to use the diluted salt as a refrigerant to 0.7 mK.

The lowest temperatures reached by the technique of adiabatic demagnetization of a paramagnetic salt have been obtained using $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, and are in the vicinity of 2 mK. This minimum temperature can be estimated from the coefficient of the leading term of the spin specific heat $C_M/R = b/T$.² The temperature dependence of the zero-field spin entropy (for a spin- $\frac{1}{2}$ system) would in this approximation be given by $S_M = R \ln 2 - (Rb/2T^2)$. We shall assume that the demagnetization is started at a low enough temperature that the lattice entropy ($S_L = \frac{1}{3}aT^3$) is negligible and at a high enough field that the spin entropy is reduced to zero. If the magnetic field is then reversibly removed, the final temperature reached will be $T_{\min} = [b/(2 \ln 2)]^{1/2}$. Using the value of $b \approx 6.4 \text{ mK}^2$ determined in this experiment, one arrives at $T_{\min} \approx 2.15 \text{ mK}$, in good agreement with the temperatures obtained in practice. Thus, to reach lower temperature using the adiabatic demagnetization technique, one must use a salt with a smaller b .

The magnitude of b is set by the strength of the interaction between the spins. In a magnetically dilute crystal such as cesium magnesium nitrate (CMN), the classical dipole-dipole interaction dominates, there being a negligible exchange interaction and no hyperfine interaction ($I = 0$). Van Vleck¹ has shown that for a regularly spaced array of dipoles the constant b is proportional to the fourth power of the magnetic moment and to the square of the number of spins per unit volume. Thus, one way to reduce b is to use a smaller magnetic moment, i. e., nuclear moments. Alternatively, one can replace most of the magnetic ions with chemically similar nonmagnetic ions in order to increase the average distance between the magnetic ions. If one dilutes the number of spins by a factor of ξ while keeping them regularly spaced, the specific heat will be reduced by a factor of ξ^2 and the minimum achievable temperature by a factor of ξ . In practice, the magnetic ions in the diluted salt will not crystallize in a regularly spaced array but rather the magnetic and nonmagnetic ions will be distributed randomly. This results in a higher

heat capacity for the random salt compared with that of an ordered array of the same dilution.

Lower temperatures have been achieved experimentally with diluted salts by De Klerk and Polder.² They diluted $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by replacing most of the Cr^{+++} atoms with Al^{+++} . In so doing, they were able to achieve a temperature of 5.4 mK. This is to be compared with the value of $\sim 15 \text{ mK}$ usually obtained with pure potassium chrome alum.

We have diluted CMN by replacing most of the Ce ions with La ions (which have the same valence but no net electron spin) such that $\xi = n_{\text{Ce}}/(n_{\text{Ce}} + n_{\text{La}}) = 0.089$. The approximate value of ξ for the diluted salt was set by the relative amounts of the constituents in the solution used to prepare the crystals. The actual value of ξ was determined by chemical analysis on the material used in the heat capacity experiments.

The heat capacity of pure CMN and La-diluted CMN was measured using the method of Casimir and du Pré.³ In this technique, one measures the magnetic field dependence of the ac susceptibility at frequencies such that $\omega T_1 \gg 1$ where T_1 is the spin-lattice relaxation time. This is the condition for measuring the adiabatic susceptibility χ_S . In order that the spin system be in equilibrium with itself one must also maintain the condition $\omega T_2 \ll 1$ where T_2 is the spin-spin relaxation time. The condition $\omega T_1 \gg 1$ is satisfied for frequencies greater than 10^3 Hz in the temperature range below 1.1 K for CMN.^{4,5} Measurements of the spin resonance linewidth⁴ show that $\omega T_2 \ll 1$ for the frequencies used in this experiment. Under these conditions the susceptibility for a single crystal is given (in the region $\mu H/kT \ll 1$) by

$$\chi_S(H) = \chi_S(0) [1 + (c/b)H^2]^{-1}, \quad (1)$$

where $c = (Ng\mu_B/2R)^2$ is the Curie constant per gram ion divided by the gas constant and $\chi_S(0)$ is the zero-field susceptibility. By plotting $\chi_S(0)/\chi_S(H)$ versus H^2 one can determine the constant b from the resulting straight line. The g factor in CMN is highly anisotropic having the form $g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$ with $g_{\parallel} = 0.25$ and $g_{\perp} = 1.84$,

where θ is measured from the trigonal axis.⁴ Since the measurements reported here were performed on powdered material it is necessary to average the above expression over all angles. If we neglect g_{\parallel} (in comparison with g_{\perp}) the result is

$$\chi_S(H) = \chi_S(0) \left[-\frac{3b^2}{2c^2H^4} (1 + b/cH^2)^{-1/2} \right. \\ \left. \times \tanh^{-1} (1 + b/cH^2)^{-1/2} + 3b/2cH^2 \right], \quad (2a)$$

$$\chi_S(H) = \chi_S(0) \left(1 - \frac{4}{5}cH^2/b + \frac{31}{35}c^2H^4/b^2 + \dots \right). \quad (2b)$$

If the magnetic heat capacity does not go as T^{-2} , then the effective b determined by the above technique will be temperature-dependent. It is natural to inquire whether one would expect the magnetic heat capacity of CMN to go as T^{-2} in the temperature range used in this experiment (0.8–1.1 K). The next highest spin state ($S = \frac{3}{2}$) for the Ce ion is in the vicinity of 35 K, which results in a Schottky anomaly in the specific heat.⁶ If we evaluate the specific heat at 1.1 K from the low-temperature side of the Schottky peak, we find that the contribution of the state $S = \frac{3}{2}$ to be less than 0.1%.

Figure 1(a) illustrates the temperature dependence of the adiabatic susceptibility of CMN at 1.7 kHz for three magnetic fields. Observe that the susceptibility goes as T^{-1} as expected. If we couple this T^{-1} dependence together with the fact that there is a strong magnetic field dependence we would conclude that we are in the adiabatic region.

(There is no field dependence in the isothermal region, and a strong temperature dependence of T_1 precludes a T^{-1} dependence of the susceptibility in the intermediate region.) Figure 1(b) shows a similar plot for a La (91.1%)-Ce(8.9%) salt. We again observe a T^{-1} dependence at the field extremes. In order to evaluate the constant b , we must plot the field dependence of the susceptibility at fixed temperature. Figure 2 shows the measured values of $[\chi_S(0)/\chi_S(H) - 1]$ versus cH^2/b for the pure and diluted salt. For a single crystal we would expect a straight-line dependence with a slope of unity and an intercept of zero. From the expansion given in Eq. (2b) we would expect a limiting slope of $\frac{4}{3}$ (at fields such that $cH^2/b \ll 1$) in a powdered specimen. The solid line shows a plot of the universal function $[\chi_S(0)/\chi_S(H) - 1]$ versus cH^2/b obtained using Eq. (2a). The values of c/b used in plotting the experimental points for the pure and diluted CMN were adjusted to give a best fit to this function. Using $g_{\perp} = 1.84$, which gives $c = 3.82 \times 10^{-9}$, we find $b = 6.4 \text{ (mK)}^2$ for pure CMN and $b = 0.68 \text{ (mK)}^2$ for the diluted salt. With the same technique but using a single crystal of pure CMN, Cook, Duffus, and Wolf⁴ found $b = 7.5 \text{ (mK)}^2$. Our value for pure CMN can also be compared with calorimetric measurements. Some caution must be exercised since at temperatures low enough that a calorimetric determination is possible, uncer-

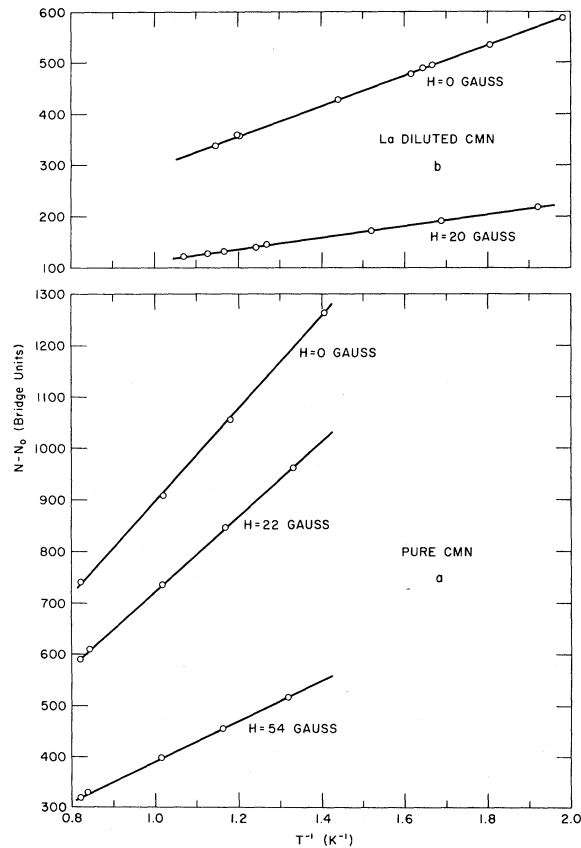


FIG. 1. (a) Temperature dependence of the magnetic susceptibility of pure $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$. (b) Temperature dependence of the magnetic susceptibility of $\text{La}_{1.82}\text{Ce}_{0.18}\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$.

tainties in the temperature scale may exist, and furthermore, the b/T^2 approximation to the heat capacity may be inadequate. It thus appears that

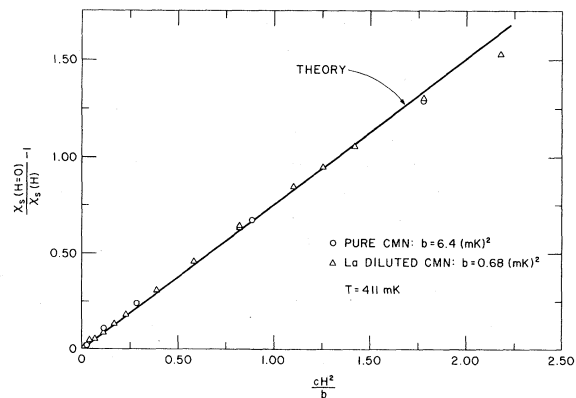


FIG. 2. The smooth curve is the universal function $\chi_S(0)/\chi_S(H) - 1$ versus cH^2/b . The Δ are CMN [$b = 6.4 \text{ (mK)}^2$] and the \circ are diluted CMN [$b = 0.68 \text{ (mK)}^2$].

the best method of determining b is with the technique of Casimir and du Pré. The calorimetric determinations of b may be found in Ref. 7.

We now examine the significance of the present results in relation to the production of very low temperatures. From the discussion given earlier one would expect a minimum temperature $T_{\min} \approx 0.70$ mK for this diluted salt. It should even prove possible to cool ^3He significantly. Using a one-shot dilution refrigerator⁸ the demagnetization could begin at 4.5 mK. If one assumes the volume of ^3He to be 5% of that of the salt, and furthermore, that one has an irreversible demagne-

tization, a short calculation shows a final temperature of 0.8 K should be possible. Such salts may be useful in resolving possible discrepancies in the magnetic temperature scale of pure CMN.⁷ Because of the fact that average interaction between the spins is smaller, these diluted salts may obey Curie's law to a lower temperature. As of the present the validity of Curie's law has been proven only down to 6 mK for pure CMN.⁹ Certainly the shape-dependent demagnetization correction is smaller by a factor of ξ in the diluted salt. Thus, such diluted salts are also promising as low-temperature thermometers.

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Identities for Total Momentum Fluctuations*

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Identities involving the total momentum of an interacting particle system are combined with inequalities to obtain lower bounds for the center of mass kinetic energy and the total kinetic energy. The results depend on the use of box boundary conditions rather than periodic boundary conditions; that is illustrated by analysis of the one-dimensional ideal Bose gas.

We present a discussion of the invariance of the canonical partition function for N interacting particles under gauge transformations. The invariance yields two identities for canonical averages of the total momentum. The first identity is that the average of the total momentum is zero; this is valid for a system confined to a stationary box and has been discussed previously.¹ The second identity is for the Kubo scalar product of the total momentum. Application of an inequality for this scalar product yields a lower bound for the c.m. kinetic energy. This in turn is a lower bound for the total kinetic energy, although not a restrictive one since in it an order-one, $O(1)$,

quantity is then used as a lower bound for an order- N , $O(N)$, quantity.

The derivation of the identities depends on the boundary conditions through the use of gauge transformations with a continuous parameter. The results are valid for a system confined to a box. The method of derivation is not valid for a system with periodic boundary conditions, and counter examples to the formal results can be constructed under these conditions. An Appendix is attached which contains an analysis of the total kinetic energy for the ideal one-dimensional Bose gas, to illustrate this point.

The canonical partition function is defined to be