

<sup>8</sup>R. H. Wade and J. Silcox, *Appl. Phys. Lett.* **8**, 7 (1966).

<sup>9</sup>G. T. Rado and J. R. Weertman, *J. Phys. Chem. Solids* **11**, 315 (1959).

<sup>10</sup>R. F. Soohoo, *J. Appl. Phys.* **32**, 1488 (1961).

<sup>11</sup>In the spectrum plot of Ref. 10, it is not clear what value of the damping constant was used.

<sup>12</sup>The surface impedance of only one side of the film is negative for some values of the applied field. Thus,

both terms in Eq. (7) must be used, or else the power absorbed by the film would have a physically meaningless negative value.

<sup>13</sup>In order to compare the theoretical and experimental intensities, it was necessary to consider that, for the same mode, the experimental and theoretical linewidths were different and that the linewidth changed with order number. Thus, all intensities were normalized to the main line and multiplied by  $\Delta H_n/\Delta H_0$ .

## $\text{Na}_3[\text{Ce}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 15\text{H}_2\text{O}$ : A New Material for Millikelvin Thermometry\*

J. C. Doran,<sup>†</sup> U. Erich,<sup>‡</sup> and W. P. Wolf

*Department of Physics and Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520*

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Magnetic specific heat and susceptibility measurements have shown that  $\text{Na}_3[\text{Ce}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 15\text{H}_2\text{O}$  has extremely weak effective spin-spin interactions, suggesting that this material may be a useful alternative to cerium magnesium nitrate for very low temperature thermometry.

Since the original work on cerium magnesium nitrate (CMN), more than eighteen years ago,<sup>1,2</sup> the method used almost exclusively for determining temperatures below 100 mK has been to measure the susceptibility of a CMN thermometer. To a good first approximation this obeys Curie's law and the magnetic temperature  $T^* = \lambda/\chi$  is close to the true temperature  $T$ , where  $\chi$  is the susceptibility and  $\lambda$  is the appropriate Curie constant.<sup>3</sup> However at the lowest temperatures deviations from Curie's law become increasingly important and there has been a considerable amount of controversy over the proper  $T$ - $T^*$  relation under different conditions. In particular, there has been much discussion of the effects of using powdered CMN and nonellipsoidal sample shapes, the most common being a right circular cylinder with length equal to diameter, and even for the case of a single-crystal sphere there are significant discrepancies in the  $T$ - $T^*$  relation for  $T < 3$  mK.<sup>4-7</sup> It is clear that another salt which closely follows Curie's law at very low temperatures would be quite valuable, either for establishing a more reliable scale for CMN or as a thermometric substance useful in itself. In this Letter we report the first results for a substance we refer to as CDP, a promising new material of this kind.

CDP denotes "cerium dipicolinate," which is our abbreviation for trisodium tris-(pyridine-2,6-dicarboxylato) cerate (III) pentadecahydrate,  $\text{Na}_3[\text{Ce}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 15\text{H}_2\text{O}$ , one of a large class of

complex organic rare earth salts whose structures have recently been studied by Albertsson.<sup>8,9</sup> Many of these are magnetically very dilute with atomic volumes  $V_a$  close to  $1000 \text{ \AA}^3/\text{rare earth ion}$ , so that one would generally expect quite weak interactions between the magnetic ions. We chose CDP specifically for three main reasons: (i) All cerium isotopes have zero nuclear spin, so that there is no complication from the hyperfine structure; (ii)  $\text{Ce}^{3+}$  ions, with only one  $4f$  electron, have relatively weak magnetic moments which should further reduce the magnetic interactions; and (iii) CDP is readily prepared and is reasonably stable. These are the same considerations which first led to the work on CMN<sup>1</sup> but in CDP we have the additional advantage that the average spacing between the  $\text{Ce}^{3+}$  ions is some 16% larger while the mean square moment turns out to be some 31% smaller, with the result that the effective spin-spin interaction is only about one half of that found for CMN.

To obtain a quantitative estimate of the interactions in CDP we have carried out two types of experiments: (i) a measurement of the magnetic specific heat  $C_M$  in the region of 1 K using the Casimir-du Pré relaxation method,<sup>10</sup> and (ii) a preliminary study of the susceptibility down to 50 mK using a  $\text{He}^3$ - $\text{He}^4$  dilution refrigerator and a CMN thermometer. Some additional adiabatic demagnetization experiments to very low temperatures were also carried out.

For relaxation specific heat measurements one

requires a single crystal and this was grown from aqueous solution as described in detail elsewhere.<sup>11</sup> The crystals grew in the form of small (~0.2 g) flat, yellow platelets which effloresced slowly on exposure to the atmosphere. Coated with a grease such as Apiezon *N* or an oil such as Apiezon *J* or liquid paraffin, they could be kept indefinitely. The usual care had to be taken to prevent dehydration by exposure to a vacuum at room temperature.

Since the crystal structure of CDP is quite complex,<sup>9,12</sup> it was impossible to predict the optimum orientation for the relaxation measurements, and an empirical study of the anisotropy had to be undertaken to find the maximum susceptibility axis. Conveniently, this turned out to be very nearly perpendicular to the (010) face of the room-temperature structure, i.e., the most prominent flat face of the crystals, and all single-crystal measurements were therefore made along this perpendicular direction.

The Casimir-du Pré method for determining magnetic specific heats<sup>10</sup> involves measuring the field dependence of the adiabatic susceptibility  $\chi_s$ , and for this we used a mutual inductance apparatus similar to that of McKim and Wolf.<sup>14</sup> In zero dc field  $\chi_s$  is equal to  $\chi_T$ , the isothermal susceptibility, and measurements of this in the helium range gave a law of the expected form

$$\chi_T = \lambda/T + \chi_{VV}, \quad (1)$$

with no significant higher order terms in  $1/T$ . The temperature-independent term  $\chi_{VV}$  was ~0.011 emu/mole, consistent with another estimate to be discussed below. The Curie constant  $\lambda$  was  $0.285 \pm 0.010$  emu K/mole which corresponds to an rms  $g$  value perpendicular to the crystal plate of  $1.74 \pm 0.04$ .<sup>15</sup> This was subsequently confirmed by ESR measurements<sup>13</sup> which gave  $\langle g_{\perp}^2 \rangle^{1/2} = 1.73 \pm 0.03$ .

In the presence of a dc field  $H$ , the adiabatic susceptibility of a material which follows Eq. (1) is given by<sup>16</sup>

$$\chi_s = \frac{\chi_T - \chi_{VV}}{1 + H^2/H_i^2} + \chi_{VV}, \quad (2)$$

where  $H_i^2 = C_M T^2/\lambda$ . For a system such as CDP the only contribution to  $C_M$  is expected to arise from the effective spin-spin coupling, and  $H_i$  thus gives a convenient measure of the strength of the interactions which will ultimately give rise to deviations from Curie's law at very low temperatures.

To measure  $\chi_s$  one must use a measuring fre-

quency  $\omega$  such that  $1/T_1 \ll \omega \ll 1/T_2$ , where  $T_1$  and  $T_2$  are the spin-lattice and spin-spin relaxation times, and it is also necessary for the measuring field  $h$  to be very much smaller than  $H_i$ .<sup>17</sup> These conditions were found to be well satisfied in our case by using  $\omega = 210$  Hz at  $T = 1.43$  K and  $h < 6$  Oe. Figure 1 shows the results for the variation of  $\chi_s$  with  $H$  under these conditions, for dc fields up to about 300 Oe. It can be seen that there is a rapid decrease at quite low fields, indicating quite clearly that the interactions are indeed very weak. The solid line shows the fit to Eq. (2) which gives  $H_i = 25.7 \pm 0.6$  Oe and  $\chi_{VV} = 0.011 \pm 0.004$  emu/mole.

The result for  $H_i$  may immediately be related to the coefficient  $b$  in the usual "high"-temperature series expansion for  $C_M/R = b/T^2 + \dots$ , where  $R = Nk_B$  and  $N$  is the number of magnetic ions. For CDP this gives  $b = \lambda H_i^2/R = (2.31 \pm 0.20) \times 10^{-6}$ . This value may be compared with the corresponding coefficient for CMN, which has been determined by several investigators<sup>18</sup> to have a value near  $6.4 \times 10^{-6}$  close to that calculated on the basis of magnetic dipole-dipole coupling.<sup>19</sup> We thus see that the high-temperature magnetic specific heat of CDP is about one third

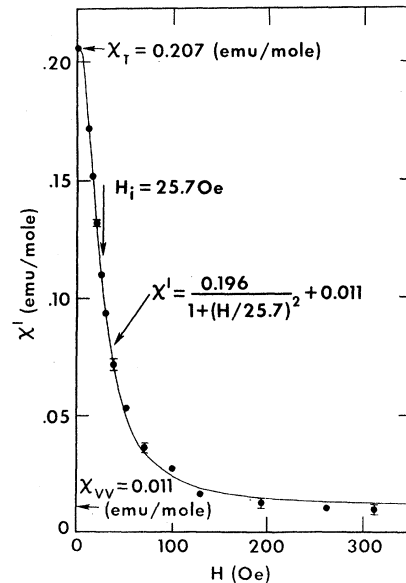


FIG. 1. Variation of differential susceptibility  $\chi'$  with applied dc field  $H$ , for CDP at 1.43 K and a measuring frequency of 210 Hz. Circles are measured values averaged for  $\pm H$  (to eliminate the effect of the Earth's field); the solid line is the calculated variation, Eq. (2), with  $\chi_T = 0.207$  emu/mole,  $\chi_{VV} = 0.011$  emu/mole, and  $H_i = 25.7 \pm 0.6$  Oe. This corresponds to a magnetic specific heat constant  $b = 2.31 \pm 0.06$  K<sup>2</sup>.

of that of CMN, and we can conclude that CDP is indeed a competitor with CMN for very low-temperature applications.

In comparing the two materials it is of interest also to consider the relative *volume* susceptibilities, since these enter into demagnetizing corrections and thus the whole problem of shape effects in nonellipsoidal powder samples. For this purpose we require the average Curie constant per unit volume,  $\langle\lambda_v\rangle$ , which can be calculated from the rms  $g$  value averaged over all directions,  $\langle g^2\rangle$ , and the atomic volume,  $V_a$ . The latter is known from x-ray structure<sup>9</sup> and  $\langle g^2\rangle$  can be calculated from the ESR results.<sup>13</sup> The corresponding values of  $\langle\lambda_v\rangle$  are shown in Table I which also contains a number of other useful parameters describing CMN and CDP, including the density  $\rho$  and the separation between nearest neighbors,  $r_{nn}$ . It can be seen that  $\langle\lambda_v\rangle$  for CDP is some 55% smaller than for CMN, indicating that demagnetizing corrections should also be less important by this factor.

To study the usefulness of CDP under actual low-temperature conditions, we compared the susceptibility of a powdered cylindrical sample (length = diam = 1.25 cm) with a similar sample of powdered CMN using copper wires and Apiezon  $J$  oil to establish thermal contact. In the first experiments we attempted to isolate the two samples and to achieve low temperatures by adiabatic demagnetization, but the extremely low heat capacity combined with the relatively large heat leak in our apparatus and the irreversible heating due to the anisotropy in the powders made it impossible to obtain reliable results. We there-

fore connected the two samples thermally to a somewhat larger sample of chromic methylammonium alum (CMAA) to provide a more stable heat sink.<sup>20</sup> With this arrangement we were able to establish equilibrium between the two samples down to 50 mK, and we were able to show that  $T_{\text{CMN}}^* = T_{\text{CDP}}^*$  to within 2% in this range. This sets an upper limit of 4 mK on any possible Curie-Weiss  $\theta$  for DCP, but on the basis of the specific heat measurements we might expect the actual value to be considerably less than this.<sup>21</sup>

We have so far been unable to establish thermal equilibrium below about 50 mK, but an indication of the very low-temperature behavior could be obtained from the values of  $T^*$  observed for the two salts immediately after demagnetization. Thus, for example, starting from an initial field of 10 kOe and a temperature of  $\sim 0.8$  K, we found magnetic temperatures  $T_{\text{CMN}}^* = 3.4$  mK and  $T_{\text{CDP}}^* = 3.15$  mK, and this again suggests that CDP has somewhat weaker spin-spin interactions than CMN.<sup>22</sup>

It is clear from all this that a detailed study of the low-temperature properties of CDP is now called for. It is to be hoped that this will confirm in detail our present conclusions that CDP is at least as good as CMN for millikelvin thermometry, with the additional advantage of smaller demagnetizing corrections because of its weaker volume susceptibility. The unusually small magnetic specific heat which we have observed indicates that the effective spin-spin interactions are smaller by almost a factor of 2 and it is therefore reasonable to expect that CDP will obey Curie's law down to about 3 or 4 mK.

TABLE I. Magnetic and structural parameters of CDP and CMN.

	$V_a$ [ $\text{\AA}^3/(\text{Ce}^{3+}$ ion)]	$r_{nn}$ ( $\text{\AA}$ )	$\rho$ (g/cm <sup>3</sup> )	$\lambda$ (emu/mole)	$\langle g^2\rangle$	$\langle\lambda_v\rangle$ (emu/cm <sup>3</sup> )	$H_i$ (Oe)	$b$ ( $10^{-6}$ K <sup>2</sup> )
CDP	916 <sup>a</sup>	9.00 <sup>a</sup>	1.75 <sup>a</sup>	0.285 <sup>c</sup>	1.57 <sup>e</sup>	$2.67 \times 10^{-4}$ g	25.7 <sup>h</sup>	2.31 <sup>h</sup>
CMN	593 <sup>b</sup>	8.51 <sup>b</sup>	2.14 <sup>b</sup>	0.315 <sup>d</sup>	2.26 <sup>f</sup>	$5.95 \times 10^{-4}$ g	41.1 <sup>i</sup>	6.4 <sup>j</sup>

<sup>a</sup> Calculated from room-temperature x-ray structure (Ref. 9).

<sup>b</sup> Calculated from room-temperature x-ray structure (Ref. 1).

<sup>c</sup> Measured perpendicular to crystal plate, i.e., perpendicular to the (010) face of the room-temperature structure (this work).

<sup>d</sup> Measured perpendicular to  $c$  axis (Ref. 1).

<sup>e</sup> Mean square  $g$  value averaged over four inequivalent sites and all directions (after Ref. 15).

<sup>f</sup> Mean square  $g$  value averaged over all directions (after Ref. 1).

<sup>g</sup> Curie constant per unit volume for powder, calculated from  $\langle\lambda_v\rangle = \langle g^2\rangle \mu_B^2 / 4k_B V_a$ .

<sup>h</sup> This work.

<sup>i</sup> Calculated from  $b = \lambda H_i^2 / R$  (after Ref. 6).

<sup>j</sup> Best estimate from several determinations (after Ref. 6).

We wish to express our thanks to Dr. J. Albertsson for a number of very helpful discussions, for providing us with the results of his work prior to publication, and for sending us a sample of CDP on which some of the preliminary measurements were made. The samples used for the measurements reported here were prepared by S. Mroczkowski and we would like to thank him for his enthusiastic and able help. We would also like to acknowledge the generous advice of T. Oversluisen and the skillful assistance of C. Sneider in the design and construction of the He<sup>3</sup>-He<sup>4</sup> refrigerator, and to thank Dr. C. Y. Wu for permission to quote his ESR results prior to publication.

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†Present address: Department of Physics, University of Utah, Salt Lake City, Utah 84112.

‡Postdoctoral Research Fellow supported by the Deutsche Forschungsgemeinschaft. Present address: Dornier System, D-799 Friedrichshafen, W. Germany.

<sup>1</sup>A. H. Cooke, H. J. Duffus, and W. P. Wolf, *Phil. Mag.* **44**, 623 (1953).

<sup>2</sup>J. M. Daniels and F. N. H. Robinson, *Phil. Mag.* **44**, 630 (1953).

<sup>3</sup>The magnetic temperature  $T^*$  is strictly defined as  $\lambda/(\chi - \chi_{VV})$ , where  $\chi_{VV}$  is the temperature-independent susceptibility. In most experimental determinations of the low-temperature susceptibility,  $\chi_{VV}$  is eliminated by including its contribution with the instrumental zero-point correction.

<sup>4</sup>R. P. Hudson, *Cryogenics* **9**, 76 (1969).

<sup>5</sup>*Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews Univ. Press, St. Andrews, Scotland, 1969), Vol. I, pp. 489-512.

<sup>6</sup>B. H. Abraham and Y. Eckstein, *Phys. Rev. Lett.* **24**, 666 (1970).

<sup>7</sup>A review of the earlier work and a comprehensive list of references may be found in Refs. 4-6.

<sup>8</sup>J. Albertsson, *Acta Chem. Scand.* **22**, 1563, 1700 (1968), and **24**, 1213, 3527 (1970).

<sup>9</sup>J. Albertsson, to be published.

<sup>10</sup>H. B. G. Casimir and F. K. du Pré, *Physica (Utrecht)* **5**, 507 (1938).

<sup>11</sup>S. Mroczkowski, J. Albertsson, and J. C. Doran, to be published.

<sup>12</sup>While the room-temperature x-ray structure contains two equivalent Ce<sup>3+</sup> ions per unit cell (see Ref. 9), ESR measurements have indicated (C. Y. Wu, to be published) that there are in fact four inequivalent ions at

low temperatures, suggesting either a crystallographic transition below room temperature or a subtle crystal modification which cannot be detected readily by x rays. The  $g$  tensors of the four types of ions are all quite similar, consistent with relatively small changes from a structure with only two ions per unit cell.

<sup>13</sup>F. R. McKim and W. P. Wolf, *J. Sci. Instrum.* **34**, 64 (1957).

<sup>14</sup>Assuming an effective spin  $S' = \frac{1}{2}$  for each Ce<sup>3+</sup> ion.

<sup>15</sup>Wu, Ref. 12.

<sup>16</sup>In the original Casimir-du Pré theory (Ref. 10), the temperature-independent term,  $\chi_{VV}$ , was neglected. Since its contribution to  $\chi$  is strictly additive and independent of  $H$ , this has no effect if only *changes* in  $\chi$  are measured, but in the method (Ref. 13) which was used in the present work, the total susceptibility was determined for each field and temperature, and the effect of  $\chi_{VV}$  then had to be taken into account.

<sup>17</sup>M. J. M. Leask, thesis, Oxford University, 1960 (unpublished).

<sup>18</sup>There is a surprisingly large spread in the values of  $b$  for CMN reported in the literature (Refs. 4-7). Many of the discrepancies may be due to the neglect of higher order terms in the expansion of  $C_M$  in the analysis of very low-temperature data, but the spread probably also reflects the great difficulty in measuring such a small specific heat. This problem will be even worse for CDP.

<sup>19</sup>Because of the complicated crystal structure (Refs. 9 and 12) it is not possible at this time to compare the value of  $b$  for CDP with that calculated on the basis of magnetic dipole-dipole coupling, as was done in the case of CMN (Ref. 1); but it would seem clear that this must again be the dominant mechanism, and the result for  $b$  does in fact correspond to the order of magnitude one might expect.

<sup>20</sup>Details of the final arrangement used are given by J. C. Doran, thesis, Yale University, 1971 (unpublished), which also includes a description of the mutual inductance coil system used to measure the susceptibilities of the two samples.

<sup>21</sup>This can only be a qualitative statement based on the single fact that  $b$  is proportional to the sum of squares of the individual interaction parameters, while  $\theta$  is proportional to the sum of (positive and negative) interactions. A more quantitative theoretical analysis would require knowledge of detailed crystal structure (but see Ref. 12) and also the relation of the different  $g$ -tensor axes to the crystal axes.

<sup>22</sup>This qualitative conclusion ignores the difference in anisotropy of the two materials. For CMN the  $g$  values range from 1.84 to <0.2, while for CDP they range from 1.78 to 0.67 (Ref. 15). It is not immediately clear how this will affect the relative values of  $T^*$  immediately after demagnetization from a given initial field, but the effect of this difference should not be very large under the conditions of the present experiments.