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Cerium compounds with very low magnetic heat capacities: The Casimir–du Pré method applied to polycrystalline samples[*]

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As part of a continuing search for materials useful as magnetic coolants and thermometers in the millikelvin region, the magnetic heat capacities of the cerium diglycollate compounds $Na_3[Ce(C_4H_4O_5)_3] \cdot 2NaClO_4 \cdot 6H_2O$ (CDG) and $Na_3[Ce(C_4H_4O_5)_3] \cdot 9H_2O$ (TCDG) have been investigated at helium temperatures. The Casimir–du Pré method involving adiabatic susceptibility measurements was used. As only polycrystalline samples of CDG could be prepared, the thermodynamic equations generally valid for the application of the method to such samples have been examined. The expressions obtained were checked by a comparison of the results from powder and single-crystal measurments on cerium magnesium nitrate (CMN), before the method was applied to CDG. Expressed as the coefficient b in the "high"-temperature expansion $C_M/R = b/T^2 + \cdots$, the resuls are 3.78(20) mK^2 from the powder measurmeents on CDG and 3.57(3) mK^2 from measurments on a single crystal of TCDG. Judged from their small magnetic heat capacities, both CDG and TCDG should be comparable to or better than CMN as refrigerants and thermometers.

I. INTRODUCTION

In some organic cerium compounds containing tris(diglycollato)- or tris(dipicolinato)-cerate(III) complexes the separation of the cerium ions is very large, 9–10 Å.[1,2] This results in extremely weak spin interactions and the materials should therefore follow Curie's law down to very low temperatures ($T < 10$ mK). As a consequence they may be useful as magnetic coolants and thermometers in the millikelvin region, supplementing the widely used cerium magnesium nitrate $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (CMN).

Studies of the magnetic properties of CDP, trisodium tris(dipicolinato)-cerate(III) 15-hydrate, have previously been made in this laboratory.[3-5] In the temperature range investigated, 0.05–4.2 K, the expected good magnetic behavior was indeed found, but a study at even lower temperatures subsequently made by Webb and Wheatley[6] showed that the magnetic ordering in CDP may occur at a somewhat higher temperature than in CMN, so that CDP is probably not as useful as CMN for low-temperature applications. We therefore decided to take up work on other similar compounds, with the hope of finding one which might in fact follow Curie's law to lower temperatures than CDP and CMN. The first material chosen was the trigonal trisodium tris(diglycollato)-cerate(III)di(sodium perchlorate)-hexahydrate (CDG).

It is very easy to prepare polycrystalline samples of CDG. The material is stable in air at room temperature and is unchanged after repeated cooling down to helium temperatures. It crystallizes in the space group $R32$,[7] with the cerium ions on the trigonal axes.[1] Its $\overleftrightarrow{g}$ tensor must therefore be axially symmetric, as is the case with the likewise trigonal CMN.[8] The volume per cerium ion in CDG is 790 $Å^3$, compared to 916 and 593 $Å^3$ in CDP and CMN, respectively, so that its "magnetic dilution" is greater than that of CMN, although not quite as great as that of CDP. However, the distance to the nearest neighbors is 9.81 Å, compared to 8.97 and 8.51 Å in CDP and CMN, respectively, which suggests that CDG could have weaker interactions than either of these two compounds. The next-nearest neighbors are at 11.03 Å. All this made CDG a very promising material at the outset of our study. However, even after serious efforts over more than a year, we have to report that it has not yet been possible to grow any crystals of trigonal CDG large enough for magnetic single-crystal work. In spite of this we decided to try to investigate the magnetic properties of CDG, using the polycrystalline samples at hand.

In one attempt to crystallize the trigonal CDG by slow evaporation at room temperature, large single crystals of a triclinic phase of trisodium tris(diglycollato)-cerate(III) nonahydrate were obtained. We denote this compound TCDG below. Its structure has been determined with x-ray single-crystal diffractometry by Elding.[9] The space group is $P\bar{1}$,[7] with a volume of 708 $Å^3$ per cerium ion. Each cerium ion has four nearest neighbors at a distance of 8.10–8.71 Å, two next-nearest neighbors at 10.36 Å, and six more cerium ions at 11.16–11.62 Å. The cerium ions are therefore somewhat more closely spaced in TCDG than in CDG, but since magnetic dipole-dipole interactions also depend on the actual $\overleftrightarrow{g}$ tensors, this fact does not immediately rule out a weaker interaction in TCDG than in CDG. To compare the two compounds we have therefore also investigated TCDG, using a single crystal.

The thermodynamic quantity best suited to describe the microscopic magnetic interactions in a material is C_M, the heat capacity at constant magnetization.[10] A determination of C_M is possible using an experimental technique originally proposed by Casimir and du Pré.[11] The usual application of the method requires that susceptibility measurements are made on a single crystal oriented with one of its principal axes along the measuring fields. Scalar quantities can then be used to describe its magnetic properties.[12] If instead measurements are made on a polycrystalline sample with arbitrarily oriented crystallites, a tensor description is necessary for each single grain. Measurable quantities are obtained from these tensors by averaging over all possible orientations of the crystallites.

Abraham *et al.*[13] have recently worked out some equations necessary for an application of the Casimir-du Pré method to a polycrystalline sample of a magnetically very dilute material with an axially symmetric $\overleftrightarrow{g}$ tensor. Their final result is the same as ours [Eq. (14)] but, as we shall show, their derivation of the basic equations is correct only for a specially simple magnetic equation of state $M_\alpha = \lambda_\alpha H_\alpha / T$, where $\vec{M}$ is the magnetization, $\vec{H}$ the field, T the temperature, and α denotes x, y, or z. Such an equation of state is in fact a good first approximation for both CMN and CDG under the conditions of the experiments, but it is useful to consider more generally valid expressions. These are given in Sec. II, together with the equations necessary for the interpretations of our measurements.

A powdered sample of CMN was used by Abraham *et al.*[13] to check their equations experimentally. The results showed some fairly sizable discrepancies with the results obtained using a single crystal of CMN, and this disagreement was not resolved. We therefore decided to repeat their measurements both on a single crystal and on powdered samples of CMN before applying the method to powdered samples of CDG. We have found that the theoretical equations do in fact account for the experiments in our case, so that the earlier discrepancies were probably due to some undetected systematic errors in the experiments.

II. THEORY

We first consider a single crystallite in a powdered sample in a magnetic dc field, and derive the thermodynamic equations governing its differential susceptibilities in the general case. The application of the Casimir-du Pré theory is then discussed. Finally, we specialize the derived equations to the case of a powdered sample of CMN or CDG and calculate the averaged susceptibility for the case in which the measuring field is parallel to the applied field.

A. Thermodynamic equations

Our magnetic system is a crystal with a fixed but arbitrary orientation in a field. We describe its properties as functions of the temperature T and field $\vec{H}$. To derive our equations we use the same principles as in the single-crystal case[12] but, since we ultimately have to average over all orientations of the crystallites in the sample, a tensor instead of a scalar description of the magnetic properties of the crystal has to be used to take its magnetic anisotropy into account.

The first and second laws of thermodynamics and the magnetic equation of state $\vec{M} = \vec{M}(\vec{H}, T)$ give us

$$T\,dS = C_H\,dT + T\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}} \cdot d\vec{H}\ , \tag{1}$$

$$d\vec{M} = \left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}} dT + \left(\frac{\partial\vec{M}}{\partial\vec{H}}\right)_T \cdot d\vec{H}\ , \tag{2}$$

where C_H is the heat capacity at constant field and S the entropy. The adiabatic and isothermal susceptibility tensors are defined by $\overleftrightarrow{\chi}_S = (\partial\vec{M}/\partial\vec{H})_s$ and $\overleftrightarrow{\chi}_T = (\partial\vec{M}/\partial\vec{H})_T$, respectively. In the adiabatic case $T\,dS = 0$. Eliminating dT from Eqs. (1) and (2) then results in

$$\overleftrightarrow{\chi}_S = \overleftrightarrow{\chi}_T - \frac{T}{C_H}\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}}\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}}\ , \tag{3}$$

where $(\partial M/\partial T)_{\vec{H}}(\partial\vec{M}/\partial T)_{\vec{H}}$ is to be taken as a dyadic. We want to determine the heat capacity of constant magnetization C_M since that quantity is the one most directly related to the interactions. By using $\vec{M}$ and T as variables we obtain the $T\,dS$ relation

$$T\,dS = C_M\,dT - T\left(\frac{\partial\vec{H}}{\partial T}\right)_{\vec{M}} \cdot d\vec{M}\ . \tag{4}$$

We equate Eqs. (1) and (4) and insert Eq. (2) in the result. This gives (i) a relation between C_M and C_H,

$$C_H = C_M - T\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}} \cdot \left(\frac{\partial\vec{H}}{\partial T}\right)_{\vec{M}}\ , \tag{5}$$

and (ii) a relation expressing the fact that of the variables $\vec{H}$, $\vec{M}$, T only two are independent:

$$\left(\frac{\partial\vec{M}}{\partial\vec{H}}\right)_T \circ \left(\frac{\partial\vec{H}}{\partial T}\right)_{\vec{M}} = -\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}}\ . \tag{6}$$

Hence

$$C_H = C_M + T\left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}} \circ (\overleftrightarrow{\chi}_T)^{-1} \cdot \left(\frac{\partial\vec{M}}{\partial T}\right)_{\vec{H}}\ . \tag{7}$$

Equations (3) and (7) are the thermodynamic equations which connect the differential susceptibilities with the magnetic heat capacity for a single crystal, taking its magnetic anisotropy into account. If our sample consisted of a single crystal aligned with the field along one of its principal axes such a formulation would be unnecessarily complicated. We could then simplify Eqs. (3) and (7) to obtain the usual single-scalar relationship[12]

$$C_M = \frac{T(\partial M/\partial T)_H^2}{\chi_T}\,\frac{\chi_S}{\chi_T - \chi_S}\,, \tag{8}$$

where M and H are the magnitudes in the measuring direction of the magnetization and field, respectively.

In a similar calculation for a crystallite in a powdered sample Abraham *et al.*[13] derived the equation

$$\overleftrightarrow{\chi}_S = \left[\underline{1} - \frac{1}{C_M}\left(\frac{\partial \vec{M}}{\partial T}\right)_{\vec{H}} \vec{H}\right]^{-1} \cdot \overleftrightarrow{\chi}_T \tag{9}$$

by using Eq. (2) and a relation

$$T\,dS = C_M\,dT - \vec{H}\cdot d\vec{M}\ . \tag{10}$$

A comparison of Eq. (10) with the exact relationship (4) shows that Eq. (9) can be used only when the magnetization obeys the condition

$$\left(\frac{\partial \vec{M}}{\partial T}\right)_{\vec{H}} = -\frac{1}{T}\,\overleftrightarrow{\chi}_T \cdot \vec{H}\ . \tag{11}$$

This is the case for the simple equation of state $M_\alpha = \lambda_\alpha H_\alpha / T$, which describes CMN and CDG adequately under the actual experimental conditions, but already when the magnetization has to be expressed as $M_\alpha = \lambda_\alpha H_\alpha/(T-\Theta)$ Eq. (11) is invalid, so that Eq. (9) will give an incorrect result.

B. Casimir-du Pré condition

With an oscillating measuring field of frequency $\omega/2\pi$, the magnetic susceptibility of a paramagnetic system is in general composed of a real part and an imaginary (phase-lagging) part which are both functions of the temperature, the applied dc field, and the frequency:

$$\overleftrightarrow{\chi}(T,\vec{H},\omega) = \overleftrightarrow{\chi}'(T,\vec{H},\omega) - i\,\overleftrightarrow{\chi}''(T,\vec{H},\omega)\ . \tag{12}$$

The basic concept of the Casimir-du Pré theory is that of a spin temperature, which requires the spins to reach an internal equilibrium in a short time compared to the spin-lattice relaxation time τ_{SL}. This is usually the case at low temperatures, since τ_{SL} becomes quite long while the spin-spin relaxation times τ_{SS} remain essentially independent of temperature and quite short.[14] The value of the spin-lattice relaxation time will in general be dependent on the orientation of the crystal in the dc field and for a powdered sample we then have a range of relaxation times $\tau_{\min} \le \tau \le \tau_{\max}$. If we can choose our measuring frequency such that $1/\tau_{\mathrm{SL},\,\min} \ll \omega \ll 1/\tau_{\mathrm{SS},\,\max}$, the measuring field recognizes the spin system of each grain as being thermally isolated from the lattice. That is to say, for each grain $\overleftrightarrow{\chi}' = \overleftrightarrow{\chi}_S(\vec{H}, T)$ and $\overleftrightarrow{\chi}'' \equiv \underline{0}$. Likewise, if $\omega \ll 1/\tau_{\mathrm{SL},\,\max}$ the measuring field recognizes each spin system as being in thermal equilibrium with the lattice. Hence $\overleftrightarrow{\chi}' = \overleftrightarrow{\chi}_T$ and $\overleftrightarrow{\chi}'' \equiv \underline{0}$. Measurements of χ' on a powder sample under these conditions will therefore give the proper average of $\overleftrightarrow{\chi}_S$ and $\overleftrightarrow{\chi}_T$ corresponding to the thermodynamic theory. $\overleftrightarrow{\chi}_T$ can also be estimated by measuring $\overleftrightarrow{\chi}_S(H=0)$, this is, in fact, what is usually done.[10]

C. Application to powdered CMN and CDG

The trivalent cerium ion has a single $4f$ electron. Spin-orbit coupling results in a multiplet ${}^2F_{5/2}$ which splits in the crystal field. At helium temperatures only the ground-state doublet is expected to be populated. The ions can then be described in terms of a fictitious spin, $S' = \frac{1}{2}$. For materials like CMN, CDG, and TCDG with very large separations between the magnetic ions, the interaction energy between spins at different sites is predominantly of the dipole-dipole type and very weak. The actual experimental conditions $[1.3 \le T(\mathrm{K}) \le 4.2,\ 0 \le H(\mathrm{Oe}) \le 600]$ then permit us to write the magnetization as

$$\vec{M} = (N\mu_B^2/4k_B T)\,(g_x^2 H_x,\ g_y^2 H_y,\ g_z^2 H_z)\ , \tag{13}$$

where N is the number of magnetic ions, μ_B is the Bohr magneton, and k_B is the Boltzmann constant. We assume here all cerium ions in the material to be magnetically equivalent, and use the directions of the principal axes of the $\overleftrightarrow{g}$ tensor as the directions of the crystallite coordinate axes. From the magnetic equation of state (13) and Eqs. (3) and (7) we then calculate $\overleftrightarrow{\chi}_S$:

$$\overleftrightarrow{\chi}_s = \frac{N\mu_B^2/k_B T}{1+4q(g_x^2H_x^2+g_y^2H_y^2+g_z^2H_z^2)}\begin{pmatrix} g_x^2[\frac{1}{4}+q(g_y^2H_y^2+g_z^2H_z^2)] & -qg_x^2g_y^2H_xH_y & -qg_x^2g_z^2H_xH_z \\ -qg_x^2g_y^2H_xH_y & g_y^2[\frac{1}{4}+q(g_x^2H_x^2+g_z^2H_z^2)] & -qg_y^2g_z^2H_yH_z \\ -qg_x^2g_z^2H_xH_z & -qg_y^2g_z^2H_yH_z & g_z^2[\frac{1}{4}+q(g_x^2H_x^2+g_y^2H_y^2)] \end{pmatrix}, \tag{14}$$

where we have put $q = N\mu_B^2/16k_B C_M T^2$. Since $\vec{M}$ of Eq. (13) obeys the condition in Eq. (11) this is the same equation as the one derived by Abraham *et al.*[13] from the generally inapplicable equation (9).

We now consider a powdered specimen in a cylindrical container located in the measuring apparatus in such a way that the specimen has a macroscopic rotational symmetry about the magnetic field axis. The over-all susceptibility is then described by a diagonal tensor with two equal components perpendicular to the field and one parallel component. The calculation of these components from Eq. (14) is described in detail by Abraham *et al.*[13] In our setup we can only measure the averaged adiabatic susceptibility parallel to the field, $\chi_{\parallel}$. The expression for this is

$$\chi_{\parallel}=\frac{N\mu_B^2R}{32\pi^2k_BT}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{(g_x^2\cos^2\phi+g_y^2\sin^2\phi)\sin^2\theta+g_z^2\cos^2\theta}{R+(N\mu_B^2H^2/4k_Bb)[(g_x^2\cos^2\phi+g_y^2\sin^2\phi)\sin^2\theta+g_z^2\cos^2\theta]}\sin\theta\,d\theta\,d\phi\,d\psi\ , \tag{15}$$

where H is the magnitude of the applied field, ϕ, θ, and ψ are Euler angles describing the orientation of an individual crystallite in the sample, and $R=Nk_B$. We have introduced $b=C_MT^2/R$ in Eq. (15) and thus neglected all but the first term in the "high"-temperature expansion $C_M/R=b/T^2+b'/T^3+\ldots$, which is consistent with the approximation used to obtain Eq. (13).

The integral (15) cannot be evaluated analytically unless the $\overleftrightarrow{g}$ tensor is axially symmetric, i.e., $g_x=g_y=g_\perp$ and $g_z=g_\parallel$. CMN does in fact have an axially symmetric $\overleftrightarrow{g}$ tensor and, as discussed in the Introduction, the same should be true for CDG. To evaluate Eq. (15) under these conditions we have to consider three cases: (i) $g_\perp=g_\parallel$; (ii) $g_\perp<g_\parallel$; (iii) $g_\perp>g_\parallel$. To simplify the notation we define $\alpha(0\le\alpha\le\frac{3}{2})$ to describe the anisotropy of the g factor: $g_\perp^2=\alpha g^2$, $g_\parallel^2=(3-2\alpha)g^2$, where g is the rms value, i.e., $g^2=\frac{1}{3}(2g_\perp^2+g_\parallel^2)$. The averaged Curie constant for the powder is then $\lambda=N\mu_B^2g^2/4k_BT$. Since b is proportional to the mean-square interaction energy we define an internal field of magnitude H_i by $H_i^2=bR/\lambda$ to describe this interaction. Note that H_i defined in this way is a macroscopic property of the sample since it depends upon the averaged Curie constant.

Our three cases are now as follows:

$$\text{(i)}\ \ \chi_{\parallel}=\frac{\lambda/T}{1+(H/H_i)^2}\quad(\alpha=1)\ . \tag{16}$$

This is the same relation as obtained from Eq. (8) for a single crystal with magnetization $M=\lambda H/T$.

$$\text{(ii)}\ \ \chi_{\parallel}=\frac{\lambda}{T}\left(\frac{H_i}{H}\right)^2\left(1-\left\{3(1-\alpha)\left(\frac{H}{H_i}\right)^2\left[1+\alpha\left(\frac{H}{H_i}\right)^2\right]\right\}^{-1/2}\times\tan^{-1}\left(\frac{3(1-\alpha)(H/H_i)^2}{1+\alpha(H/H_i)^2}\right)^{1/2}\right)\quad(0\le\alpha<1)\ ; \tag{17}$$

$$\text{(iii)}\ \ \chi_{\parallel}=\frac{\lambda}{T}\left(\frac{H_i}{H}\right)^2\left(1-\left\{3(\alpha-1)\left(\frac{H}{H_i}\right)^2\left[1+\alpha\left(\frac{H}{H_i}\right)^2\right]\right\}^{-1/2}\times\tanh^{-1}\left(\frac{3(\alpha-1)(H/H_i)^2}{1+\alpha(H/H_i)^2}\right)^{1/2}\right)\quad(1<\alpha\le\tfrac{3}{2})\ . \tag{18}$$

In spite of their rather different analytical form, the three expressions for $\chi_{\parallel}$ in Eqs. (16)–(18) have identical series expansions in powers of H^2:

$$\chi_{\parallel}=\frac{\lambda}{T}-\frac{\lambda}{T}\left(\frac{34\alpha^2-38\alpha+9}{5H_i^2}H^2+\frac{16\alpha^3-132\alpha^2+216\alpha-135}{35H_i^4}H^4+\ldots\right), \tag{19}$$

as we would expect.

D. Van Vleck paramegnetism

So far we have treated powdered CMN and CDG as an ensemble of spin systems, where each spin can occupy one of two energy levels. Using this simple picture we have calculated the adiabatic susceptibility and averaged it over all grains in the sample. Thus the terms "adiabatic" and "isothermal" used above only refer to our spin systems and do not include other intra-atomic interactions. For each cerium ion in CMN, CDG, and TCDG there is, however, an additional nondiagonal matrix element of the magnetic moment connecting the ground state with excited states in the crystal field. The result of this is a small field- and temperature-independent contribution of Van Vleck paramagnetism,[15] χ_{VV}, which has to be added to the right-hand sides of Eqs. (16)–(18) to describe the actual measurements. The Van Vleck term can be obtained experimentally, either as the asymptotic value of $\chi_{\parallel}$ at large fields, since Eqs. (16)–(18) show that the field-dependent part then goes to zero, or as the high-temperature intercept of the zero-field Curie law $\chi_{\parallel}(0)=\lambda/T+\chi_{VV}$.

III. EXPERIMENTAL

The susceptibility measurements were made in a mutual-inductance apparatus similar to the one described by McKim and Wolf.[16] Alternating current, 5–50 mA, at audio frequencies 80–400 Hz, was used in the primary coil to produce a measuring field with rms magnitude of about 2–20 Oe. The secondary coil consisted of two similar halves connected in opposition, and in a measurement the sample was moved from the lower to the upper half. In each position the voltage induced across the coil was compensated by mutual inductances and resistances in a Hartshorn bridge. A tuned amplifier (General Radio 1232-A) was used as a null detector. The difference in mutual inductance between the two positions of the sample is proportional to the real part of the parallel component of the averaged susceptibility tensor, while the imaginary part is proportional to $\Delta R/\omega$, where ΔR is the difference in resistance setting for the bridge and $\omega/2\pi$ is the frequency used. The coil system was immersed in liquid helium, which was pumped in order to vary the temperature of the sample in the range 1.3–4.2 K. A dc field was provided by a solenoid surrounding the cryostat. The maximum field which could be applied was about 600 Oe. This solenoid and the measuring coil system had a common axis along which the sample was moved. To eliminate the influence from the veritical component of the earth's field on our low-field data ($H < 100$ Oe) measurements were taken with the current flowing through the solenoid in both directions. The mean result for each current was used.

The variable mutual inductance in the Hartshorn bridge was calibrated against the susceptibility of ammonium manganese (II) sulphate, as described by McKim and Wolf.[16] The factor obtained at 210 Hz was $1.494(1)\times10^{-6}$ emu/Oe μH. The smallest detectable change in inductance was 0.015 μH.

CMN, TCDG, and CDG were prepared as described in Refs. 8, 9, and 17, respectively. Cerium carbonate, 99.99% pure with respect to other lanthanoids, was used as starting material so that all detectable magnetic effects in the compounds were due to the cerium ions. X-ray powder photographs were used to check that the correct compounds had been obtained.

For the powder measurements on CMN and CDG a freshly powdered sample weighing about 0.2 g was transferred together with silicone oil (Dow Corning 704) to a cylindrical container about 5 mm wide and 20 mm long. These containers were made of Teflon and cleaned in aqua regia before every use. The chemically very inert silicone oil was used for thermal contact between the powder grains and to keep them in a fixed position when a field was applied at helium temperatures. Checks both with and without applied fields showed no discernible magnetic effects from the sample holders or the oil. The single crystals of CMN and TCDG, weighing 0.1705 and 0.2515 g, respectively, were also mounted in Teflon cylinders: CMN with the trigonal axis perpendicular within 2° to the field axis, and TCDG with the b axis along the field axis.

IV. RESULTS

A. Method of analysis

With χ_{VV} added to the right-hand side of Eq. (19), it is apparent that a convenient function to use in the determination of α and H_i is

$$f(H^2)=[\chi_{\parallel}(0)-\chi_{\parallel}(H^2)]/[\chi_{\parallel}(0)-\chi_{VV}]\;. \qquad (20)$$

This function is independent of temperature and of the amount of the material used, so that data taken with different samples at different temperatures can be treated simultaneously. As can be seen in Eqs. (16)–(19), the parameter H_i has the effect of a normalizing factor; i.e., f can be taken as a function of $(H/H_i)^2$ instead of H^2, leaving α as the only parameter. Normalized curves for several values of α are shown in Fig. 1. The family of curves is bounded upwards by the curve $\alpha=0$ and downwards by the curve with $\alpha=1$. For fixed values of H/H_i, f is approximately symmetric about $\alpha=1$ in the interval $0.5<\alpha<1.5$; i.e., if $0<x<0.5$, only a minor change in H_i is required to make $\chi_{\parallel}$ [calculated from Eq. (17) with $\alpha=1-x$] equal to $\chi_{\parallel}$ [calculated from Eq. (18) with $\alpha=1+x$]. Hence, in the interval $0.5<\alpha<1.5$ it is not possible to determine α and H_i uniquely (except for the case $\alpha=1$) using susceptibility data only. Figure 1 also indicates that the relatively small differences between the curves when $\alpha\gtrsim0.5$ makes a simultaneous determination of good values of H_i and α quite difficult. However, we can still try to estimate values of both H_i and α with a nonlinear least-squares method. The one we chose to use has been proposed by Powell.[18]

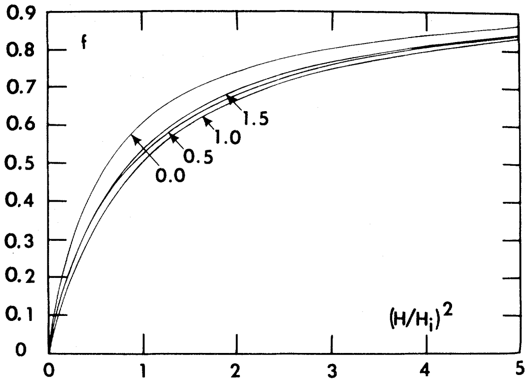

FIG. 1. Normalized curves f as a function of $(H/H_i)^2$ [Eq. (20)] for several values of α.

Starting values of α and H_i^2 for the refinements were obtained by computing the sum of squares $S=\sum[f_{\text{obs}}(H^2)-f_{\text{calc}}(H^2)]^2$ as a function of α and H_i^2. Since $f_{\text{calc}}(H^2)$ depends only upon two parameters, approximate values for these are easily obtained by finding the region of the absolute minimum of $S(\alpha, H_i^2)$. It follows from the symmetry of f about $\alpha=1$ that the local minima of $S(\alpha, H_i^2)$ along lines of constant α form an approximately hyperbolic trough, roughly symmetric about $\alpha=1$.

As described in the Introduction, we decided to test our theoretical equations experimentally by a determination of the magnetic heat capacity of CMN from measurements on powdered samples before applying the method to an unknown material. Doing this, we learned that the particular way in which α and H_i enter our equations makes it quite difficult to detect even large systematic errors in a data set. Such a set could always be fitted to a pair of parameters (α, H_i^2) which, of course, then had wrong values, even though the agreement between observed and calculated values seemed to be as good as when data without systematic errors were fitted to the correct parameters. We conclude that when the Casimir-du Pré method is used on polycrystalline samples, great care has to be taken to avoid systematic errors in the experimental data.

B. CMN

We measured the field-dependent susceptibility for two powdered samples of CMN at 1.35 and 1.38 K, respectively; the frequency was 210 Hz and the measuring field had a rms value of 4 Oe. In this way the Casimir-du Pré condition, $\omega \gg 1/\tau_{\mathrm{SL,\,min}}$, was met and the measured susceptibilities were independent of the measuring field.[19] The data were fitted to the parameters α and H_i^2 as described in Sec. IV A. It is well known that $g_\parallel$ is very close to zero for CMN, so the value of α has to be very near 1.50 for powdered CMN. We therefore calculated the sum of squares $S(\alpha, H_i^2)$ for all pairs of (α, H_i^2) obtained by changing α in steps of 0.01 and H_i^2 in steps of 10 Oe^2 in the range $1.30 \le \alpha \le 1.50$, $2300 \le H_i^2(\mathrm{Oe}^2) \le 2500$. The absolute minimum of S in this region, 2.6×10^{-4}, is at $\alpha = 1.50$, $H_i^2 = 2420$ Oe^2 but, as could be expected from the similarity of the curves in Fig. 1 when $\alpha \gtrsim 0.5$, the value of S increases very slowly along the bottom of the trough described in Sec. IV A. At $\alpha = 1.41$, $H_i^2 = 2300$ Oe^2, S is only 3.0×10^{-4}. The nonlinear least-squares fit resulted in $\alpha = 1.50(11)$, $H_i^2 = 2420(160)$ Oe^2. The large estimates of the standard deviations should at least partly be ascribed to the flat minimum in S. The experimental data $[H^2, f_{\mathrm{obs}}(H^2)]$ are compared with the calculated curve in Fig. 2. The agreement is good. As noted above, this in itself does not, however, prove that the Casimir-du Pré theory works for powdered samples; since data with relatively large systematic errors might also be fitted to some pair of parameters α and H_i^2, we therefore have to check that the fundamental constants b, $g_\perp$, and $g_\parallel$ calculated from the powder data do in fact have the same values as those found from single-crystal measurements.

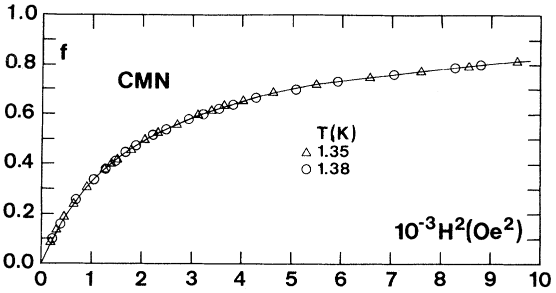

FIG. 2. Plot of f as a function of H^2 [Eq. (20)] for two powdered samples of CMN. Curve drawn is calculated using $\alpha = 1.50$ and $H_i^2 = 2420$ Oe^2.

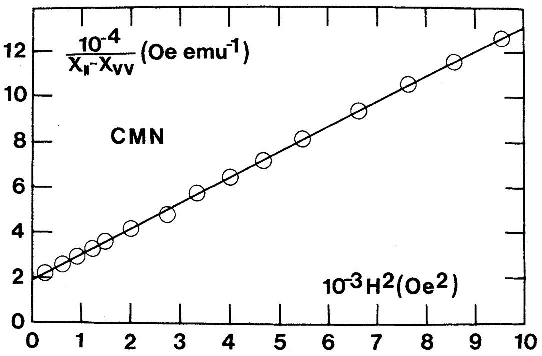

FIG. 3. Field dependence of $1/(\chi_\parallel - \chi_{VV})$ at 1.37 K for a single crystal of CMN. Line drawn is calculated using Eq. (21) with $\lambda = 0.317$ emu K/Oe mole and $H_i^2 = 1643$ Oe^2.

From the value $\alpha = 1.50(11)$ we immediately deduce that $g_\parallel$ is very close to zero, in agreement with the known anisotropy. To estimate $g_\perp$ we use the value of the Curie constant $\lambda = 0.211$ emu K/Oe mole[20] determined from the zero-field susceptibility measurements together with the value of α. This gives 1.83 in excellent agreement with the single-crystal value 1.838.[21]

To estimate b we use $b = \lambda H_i^2/R$, and substituting the above values we find $b = 6.14(40)$ mK^2. This value should now be compared to the single-crystal value, but there is some uncertainty in this since a number of independent determinations have given[22] values ranging from 4.2 to 7.5 mK^2. We therefore found it desirable to make our own single-crystal determination of b for CMN, so that a consistent comparison with the results of the powder measurements could be made.

Measurements of the field dependence of the susceptibility were made on a single crystal of CMN at 1.37 K. A value of $H_i^2 = 1643(12)$ Oe^2 was determined using Eq. (16) by a least-squares fit of the data to the function

$$1/(\chi_\parallel - \chi_{VV}) = t + (t/H_i^2)H^2 , \qquad (21)$$

where $t = T/\lambda$. The good agreement between the experimental data and the calculated line is shown in Fig. 3. The value of H_i^2 found corresponds to $b = 6.26(1)$ mK^2, which is compatible with other values obtained by adiabatic susceptibility measurements on single CMN crystals: Hudson *et al.*[23]

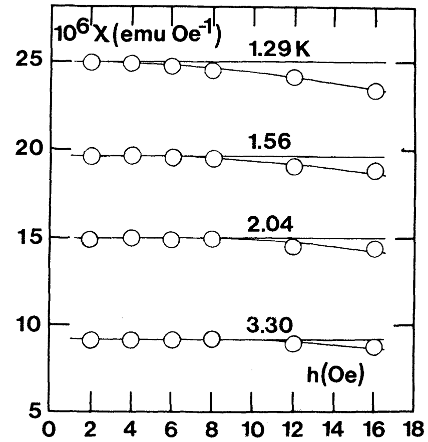

FIG. 4. Susceptibility at zero applied field as a function of temperature and rms measuring field (h) for a powdered sample of CDG.

found $b = 6.3$ mK^2, Mess *et al.*[22] $b = 6.2$ mK^2, and Abraham *et al.*[13] $b = 6.16(10)$ mK^2. We thus seem to have a very reliable b to compare with the b calculated from the powder measurements.

Such a comparison shows that, contrary to the earlier results of Abraham *et al.*,[13] the value of b obtained from the powder measurements is quite acceptable even if a relatively large error has to be assigned to it. We may therefore assume that the results from the polycrystalline samples of CDG should provide a reasonable estimate of b (and also of $g_\perp$ and $g_\parallel$) for that compound.

C. CDG

To find the maximum measuring field which could be used for CDG without influencing the observed susceptibilities, we measured a powdered sample at zero applied field for various amplitudes of the measuring field over a range of temperatures. The results are shown in Fig. 4. It can be seen that in order to obtain susceptibilities independent of the field over the entire temperature range, measurements should be made with rms amplitudes not exceeding 4 Oe.

The average Curie constant λ for the material was determined using zero-field data (T, $\chi_\parallel$) from two powdered samples. Fourteen and 20 different temperatures in the range 1.3–4.2 K were used. The frequency was 210 Hz. A least-squares fit of the data to the linear function $\chi_\parallel T = \lambda + \chi_{VV} T$ resulted in $\lambda = 0.1536(9)$ emu K/Oe mole and $\chi_{VV} = 0.0036(7)$ emu/Oe mole.

The range in which the Casimir-du Pré condition $\omega \gg 1/\tau_{\mathrm{SL,\,min}}$ is obeyed was found by measuring the in-phase and out-of-phase susceptibilities, $\chi'_\parallel$ and $\chi''_\parallel$, as functions of ω at an applied field of 55 Oe over a range of temperatures. An applied field of this magnitude was sufficient to reduce $\chi'_\parallel$ significantly from its isothermal value in zero field, as one might expect from previous experiments on similar materials.[3] For temperatures below 2.1 K, $\chi''_\parallel$ was found to be essentially zero and no variation could be detected in $\chi'_\parallel$ over the frequency interval 80–400 Hz. We conclude, therefore, that frequencies in this range are in fact high enough to ensure that the measured $\chi'_\parallel$ for $T \leq 2.1$ K is equal to the adiabatic susceptibility, as required for the Casimir-du Pré method.

Adiabatic-susceptibility data were obtained from three different samples at the temperatures 1.36 K (sample No. 1), 1.39 K (sample No. 2), 1.53 K (sample No. 1), and 1.69 K (sample No. 3) using a frequency of 210 Hz and a rms measuring field of 4 Oe. In view of our experience with CMN we are satisfied that no significant systematic errors should enter our data under these experimental conditions. The sum of square $S(\alpha, H_i^2)$ was computed in the entire range for α ($0 \leq \alpha \leq 1.50$) and in the range $1400 \leq H_i^2(\mathrm{Oe}^2) \leq 2100$. The absolute minimum was found near $\alpha = 0.1$. Since $\alpha < 0.5$ only one set of g values fits the measured susceptibilities. $S(\alpha, H_i^2)$ was minimized as for CMN. The result is $\alpha = 0.08(6)$, $H_i^2 = 2040(110)$ Oe^2. With $\lambda = 0.154(1)$ emu K/Oe mole these values give

$$b = 3.78(20)\ \mathrm{mK}^2, \quad g_\perp = 0.36(11), \quad g_\parallel = 2.16(3)$$

as the final set of fundamental constants for CDG. The experimental data are compared with the calculated curve in Fig. 5. The agreement is good.

D. TCDG

In an experiment on TCDG similar to the one depicted in Fig. 4 we found that rms values not bigger than 4 Oe should be used for the measuring field for this material. The Curie constant along the b direction of a single crystal of TCDG was determined from 33 different temperatures to be $\lambda = 0.1736(5)$ emu K/Oe mole. The Van Vleck term is $\chi_{VV} = 0.0019(4)$ emu/Oe mole. As with CDG, we

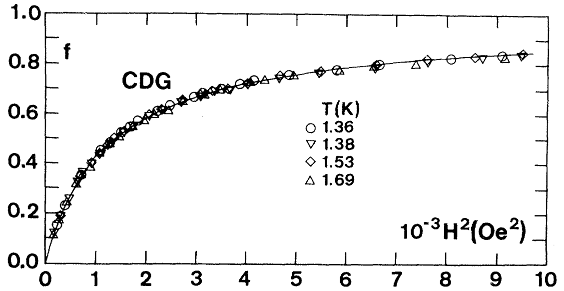

FIG. 5. Plot of f as a function of H^2 [Eq. (20)] for the powdered samples of CDG. Curve drawn is calculated using $\alpha = 0.08$ and $H_i^2 = 2040$ Oe^2.

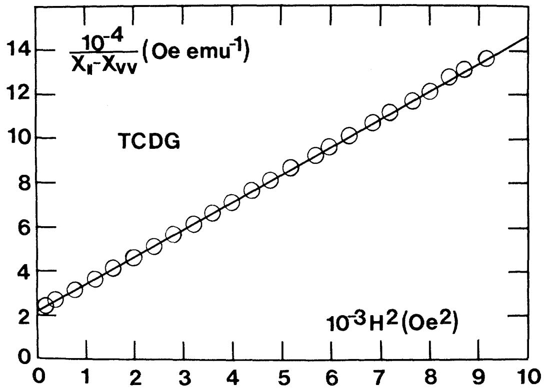

FIG. 6. Field dependence of $1/(\chi_{\parallel}-\chi_{VV})$ at 1.30 K for a single crystal of TCDG. Line drawn is calculated using Eq. (21) with $\lambda = 0.174$ emu K/Oe mole and $H_i^2 = 1710$ Oe^2.

found the Casimir-du Pré condition obeyed for frequencies in the range 90–390 Hz at temperatures below 2.1 K.

The field-dependent susceptibility was measured at 1.30 K. The frequency was 210 Hz and the measuring field had an rms value of 4 Oe. The value of H_i^2 was determined by a least-squares fit of the data to Eq. (21). The good agreement between the experimental points and the calculated line is shown in Fig. 6. With $\lambda = 0.1736(5)$ emu K/Oe mole, the fitted value $H_i^2 = 1710(11)$ Oe^2 corresponds to $b = 3.57(3)$ mK^2.

V. DISCUSSION

The experimental result $b = 3.78(20)$ mK^2 for CDG may be compared with the value calculated from magnetic dipole-dipole coupling. Using the expression appropriate for a system with anisotropic g values,[24] together with our estimates for $g_{\parallel}$ and $g_{\perp}$ and the available structural information,[1] we calculate $b_{\text{dipole}} = 3.48(31)$ mK^2, in excellent agreement with the experimental value. Since b depends on g^4, this agreement lends reassuring support to the g-value determination and indirectly to the whole analysis.

A similar comparison for TCDG is unfortunately not possible at this time, since this material has much lower symmetry and there is no information on the g values or the orientation of the g-tensor axes. However the experimental value $b = 3.57(3)$ mK^2 is not at all unreasonable for purely magnetic-dipole interactions.

The magnetic specific heats of CDG and TCDG in the region of 1 K are both about 0.6 of that of CMN, and one may therefore speculate that they might have lower values also in the millikelvin region. Such a conclusion must be treated with caution, since b only measures the mean-square interaction energy while the low-temperature behavior also involves other correlation energies. Thus, in the case of CDP which has $b = 2.26$ mK^2,[25] it turned out that the ordering temperature was actually higher than that of CMN.[6] However, in the case of CDG one may hope that the unusually long Ce-Ce nearest-neighbor distance (9.81 Å) could favor more ideal behavior at very low temperatures. Certainly the ease with which polycrystalline samples of CDG can be prepared and handled would make this material a useful substitute for CMN or CDP, as well as for the solid cerium complex with triphanyl phosphine oxide and thiocyanate which has been proposed as a possible coolant and thermometer by Abraham and co-workers.[26,27] Further evaluation of CDG and TCDG at lower temperatures would seem to be worthwhile.

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