PHYSICAL REVIEW B VOLUME 7, NUMBER 11 1 JUNE 1973

Thermal and Magnetic Properties of $CeCl_3$[†]

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(Received 11 December 1972)

Thermal and magnetic properties of $CeCl_3$ have been measured between 0.050 and 4.2 K in magnetic fields up to 14 kOe. The magnetic contribution to the specific heat C_M was estimated from the total measured specific heat using additional measurements on diamagnetic $LaCl_3$ which indicated a Debye temperature $\Theta_D = 155 \pm 2$ K. From the variation of C_M between 3.5 and 4.2 K it was possible to estimate the energy of the first excited doublet to be 59 ± 3K. Between 1 and 4.2 K, C_M followed a law of the form $C_M T^2/R = (170 \pm 10) \times 10^{-4}$ ascribed to interactions between the Ce^{3+} ions. Between 2 and 4.2 K, the susceptibility could be described by a Curie–Weiss law of the form $\chi = C/(T - \Theta)$, where the value of Θ could be determined self-consistently from each of two possible sets of interaction parameters for the Hamiltonian of the system. These parameters were found from the present data in combination with earlier EPR results. At low temperature the specific heat exhibits a peak near 0.11 K, while the susceptibility appears to level off to a value near 3.0 emu/mole. An anaylsis of the data shows it to be impossible at present to distinguish which set of interaction parameters is correct, and a consideration of simplifying one-dimensional-model approximations shows them to be inadequate in describing the behavior of $CeCl_3$.

I. INTRODUCTION

A number of papers have attempted to explain the properties of the rare-earth trichlorides using optical methods,[1–4] electron-paramagnetic-resonance (EPR) techniques,[5–7] and by studying the bulk thermal and magnetic properties.[8–14] This work has shown a range of unusually interesting and complex behavior, but has also been complicated by a number of significant features.

It appears that many of the trichloride crystals previously studied have contained small amounts of phase impurities, the presence of which may give rise to large and so far unexplained anomalies in either or both the specific heat and susceptibility.

Another complication arises from the nature of the interactions between the rare-earth ions. Some are quite anisotropic, and while an Ising-model Hamiltonian may be used as a first approximation, there are significant non-Ising contributions which vitiate any quantitative comparison between experimental results and predictions based on such a simplification.

A third difficulty arises rather surprisingly from the unusually *simple* structure of the trichlorides[15–17] (Fig. 1). As a result of this, several different antiferromagnetic spin arrangements become degenerate in energy, and the nature of the actual ordered state cannot be readily predicted.

In order to facilitate the study of some of these features, it seemed desirable to obtain a fairly complete set of magnetothermal data on good single crystals of the one compound of the series which one might expect to be the simplest. This is $CeCl_3$, and in the present paper we shall report on specific-heat and susceptibility measurements from 4.2 to below 0.1 K. Complementary EPR experiments and a preliminary analysis of the interactions have been published elsewhere.[5,6,18]

The magnetothermal properties of $CeCl_3$ might be expected to be simple because the ground state of Ce^{3+} ions is an almost pure $|J_z = \pm\frac{5}{2}\rangle$ doublet belonging to the free-ion state $(4f^1)^2F_{5/2}$.[1,2,4,7,10] This doublet is well separated in energy from the first excited state, and previous optical,[1,2,4] relaxation,[19,20] and susceptibility[10,11] experiments gave values for the splitting ΔE between 53 and 68 K.

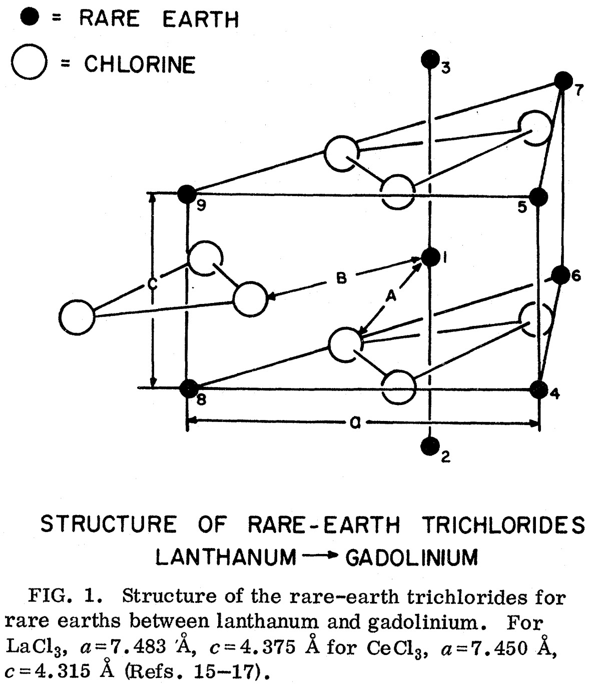

FIG. 1. Structure of the rare-earth trichlorides for rare earths between lanthanum and gadolinium. For $LaCl_3$, $a = 7.483$ Å, $c = 4.375$ Å for $CeCl_3$, $a = 7.450$ Å, $c = 4.315$ Å (Refs. 15–17).

At helium temperatures the ions are thus well represented by effective spins $S'=\frac{1}{2}$.

The g values for Ce^{3+} in $LaCl_3$ are found to be $g_\parallel = 4.037 \pm 0.002$ and $g_\perp = 0.20 \pm 0.10$,[6,7] and as will be seen, they are essentially the same in concentrated $CeCl_3$. Moreover, the relatively large difference between the J_z values of the ground-state components ($\Delta J_z = 5$) suggests that the interactions between neighboring spins should be highly anisotropic. Indeed, EPR experiments on Ce^{3+} pairs in $LaCl_3$[5,6] have shown such an anisotropy for the interaction between nearest neighbors. Quite surprisingly, the next-nearest-neighbor interactions were found to be almost *isotropic* and this can only be explained by invoking a significant contribution from a high-degree anisotropic-exchange interaction of the form $(J_i^+)^5(J_j^-)^5$.[6,21]

Another rather minor advantage of studying $CeCl_3$ is that cerium is the only rare earth all of whose isotopes have zero nuclear spin so that there are no hyperfine interactions to complicate the interpretation of the low-temperature measurements.

In this paper we shall combine the results of our zero-field specific-heat and susceptibility measurements with the earlier results of EPR experiments on Ce^{3+} pairs in $LaCl_3$ to derive values for the different effective spin-spin interactions, using a previously published analysis[18] which was based on preliminary measurements.[22] The final values for the experimental parameters are essentially unchanged; but as the low-temperature scale used in the earlier work was found to be in error, the low-temperature measurements were repeated and the range substantially extended. A consideration of these data shows that it is not yet possible to unambiguously choose between two alternative sets of solutions for the interactions, as has been attempted in the past.

The experimental methods used are described in Sec. II and the results of the measurements are given in Sec. III. The analysis in terms of various thermodynamic functions is discussed in Sec. IV, while in Sec. V consideration is given to the attempt to choose the proper spin-spin interactions. The conclusions are summarized in Sec. VI.

II. EXPERIMENTAL METHODS

A. Sample Preparation

Single-crystal samples used in all the experiments were grown by Mroczkowski of this laboratory using a version of the Bridgeman–Stockbarger method.[23]

The starting material was obtained in the form of polycrystalline nominally anhydrous $CeCl_3$ (purity 99.99%) from Nuclear Corp. of America. Since purity is of primary importance in the growth of high-quality crystals, this material was subjected to additional purification procedures. In order to prevent the formation of oxychlorides it was first exposed to a further dehydration process. This was achieved by a method similar to that used by Fong and Yocom.[24] The material was placed in the upper portion of a quartz tube which was divided into two sections by a quartz frit (pore size 40–90 μ) and heated in a stream of gaseous HCl. The HCl gas was purified and dried by first passing it through two traps containing concentrated H_2SO_4.

The temperature of the quartz tube was slowly raised to 120 °C where it was held for a period of 12 h. The temperature was then raised to 450 °C and held for a similar time and finally was increased to slightly above the melting point (802 °C) where it was maintained for four more hours. This slow heating and dehydration process, especially the first step, is essential if the oxychloride phase is to be suppressed.

The HCl stream was then stopped and the lower section of the quartz tube partially evacuated through a small side arm. This drew the molten salt through the porous frit, which eliminated the possibility of contaminating the melt by oxychloride or transition-metal impurities since these would be present as precipitates in the molten salt. A small amount of residue was generally observed to remain in the upper portion of the tube, but its nature was not investigated. It might be speculated that it is related to the anomalous behavior found in earlier experiments.[8,12] In any case some aspect of our purification procedure must be significant since our *untreated* starting material did in fact show the anomalous peak in the specific heat but was absent in the purified samples.[25]

The quartz tube was once again exposed to the gaseous HCl and cooled. It was then evacuated and sealed off. To produce a single crystal from the fused sample obtained in this way, the sealed sample tube was lowered through a temperature gradient in a Bridgeman furnace over a period of seven days.[26] The crystal was then cooled slowly for two days to prevent cracking. Generally clear crystals 25 mm long and 15 mm in diameter (~20 g) could be obtained in this way. (One large single crystal of $LaCl_3$ was also grown using the same technique.)

Analysis of one of the $CeCl_3$ samples showed 0.01-at.% Ca and 0.01-at.% Er as the only impurities in greater abundance than 0.001 at.%, though the analysis would not have been sensitive to the most likely harmful impurities involving oxygen or hydrogen. However, our results on the physical properties suggest that the crystals were in fact quite free from such contaminants.

B. Specific-Heat Measurements

Specific-heat measurements were obtained in either a He^3 cryostat or dilution refrigerator, both of which are described elsewhere.[27,28] The sample was suspended by threads below the He^3 pot or mixing chamber, and in both apparatuses a mechanical heat switch could be used to cool the sample in a magnetic field. A typical starting temperature for a demagnetization was ~0.5 K, and was generally limited by the deteriorating thermal contact between switches and samples as the temperatures of the cryostats were reduced. When the magnetic field (12–15 kOe) was removed, the samples would cool to ~0.080 K from which point the measurements began.

Specific heats were measured by the standard heat-pulse method. The sample was usually heated for 50–100 sec and drift rates were measured until thermal equilibrium was reestablished. The necessary times ranged from 200 to 1400 sec after each heating interval. The total heat input to the specimen was measured with a Dymec 2401C integrating digital voltmeter.

The thermometers for all the specific-heat measurements were type-1002 $\frac{1}{2}$ W, 470- or 220-Ω Speer carbon resistors; the detection circuit was an ac Wheatstone bridge run at 33 Hz with an PAR Hr-8 lock-in amplifier serving as both the oscillator and null detector. The power dissipated in the resistor ranged from about 10^{-8} W above 1 K to less than 10^{-11} W at 0.080 K.

Between 0.4 and 4.2 K, the resistors were calibrated against He^3 and He^4 vapor-pressure measurements. Below 0.4 K the resistor used in the He^3 cryostat was calibrated against the susceptibility of chromic methylamine alum, while the resistor used in the dilution refrigerator was calibrated against the susceptibility of cerous magnesium nitrate. The former calibration was subject to a larger error due to uncertainties in the T-T^* relation for chrome alum, but an accuracy of 5% or better was expected.[29–32]

We were able to measure the specific heat of $CeCl_3$ in zero field from 0.080 to 4.2 K. (The results are given in Sec. III A.) We have also measured the specific heat of $CeCl_3$ with magnetic fields up to 12 kOe applied along the c axis. The lowest temperatures achieved in the presence of a magnetic field were of course higher than that for the zero-field case, e.g., 0.31 K for 4.55 kOe and 0.62 K for 12.1 kOe. The fields in all cases were produced by a Pacific Electric Motor Co. electromagnet and were measured with either a Rawson rotating-coil gaussmeter or a Bell Hall probe. Both devices were calibrated to an accuracy of 0.1% using NMR.

The heat capacity of the sample holder including the resistance thermometer and heater was measured separately and subtracted from the results which included both the sample holder and sample. In order to estimate the lattice contribution to the specific heat of $CeCl_3$ the specific heat of a single crystal of $LaCl_3$ was measured in another separate experiment. Below 1.5 K the corrections to the heat capacity of $CeCl_3$ for both the addenda and the lattice were negligible, but at 4.2 K the respective contributions were as large as 17 and 66% of the total heat capacity.

The estimated accuracy of the specific-heat measurements was 1% between 4.2 and 0.45 K. Below this the accuracy became worse, falling to 5% at 0.2 K. Below 0.2 K, the specific-heat data are characterized by a large amount of scatter and the accuracy fell still further to 15–20%. The reason for this scatter is not entirely clear, but probably reflects a combination of effects arising from the long thermal equilibrium times encountered in this region and a relatively large heat leak to the sample. The uncertainties encountered in this temperature range did not seriously affect the conclusions to be drawn from the data, however.

The measurements of specific heat in a magnetic field had an additional small uncertainty due to possible errors in the corrections for the magnetoresistance of the thermometer. Nevertheless, for $T > 0.5$ K, the specific heat should be accurate to 3% or better.

C. Entropy Measurements

Entropy measurements were made using several different techniques. The first involved numerical integration of C'_H/T, where C'_H is the specific heat in a constant applied field corrected for the lattice contribution and the small Schottky tail due to the first excited state. This yields entropy changes ΔS relative to the entropy at the highest measured temperatures (~4.2 K). Since these temperatures are far above the ordering temperature, the absolute entropy in zero field may readily be estimated using the high-temperature approximation

$$S/R \approx \ln 2 - b/2T^2, \tag{1}$$

where b is the leading coefficient in the zero-field specific-heat expansion (see Sec. IV B).

To obtain the absolute entropies for the curves in nonzero fields, one must either fit the different curves to high-temperature approximations in a similar manner, which can introduce quite large errors, or one may relate them all to the zero-field entropy by finding S as a function of H at a single temperature (~1.25 K in our case). This may be done either by a calculation using the tables of Hull and Hull[33] or by a direct measurement of the isothermal heat of magnetization.

In the former case, one neglects spin-spin interactions. This is a good approximation for $CeCl_3$ since the interactions are relatively weak compared with the effect of typical applied fields. The error incurred in this approach may be checked theoretically by calculating the first-order correction term from the expression for the free energy given in Sec. IV B.

To measure the entropy of magnetization experimentally one must make the very reasonable assumption that magnetization processes are reversible, at least at high temperatures. The entropy of magnetization may then be measured readily from the amount of electrical heat $\Delta Q(H)$ required to maintain a fixed temperature while the field is reduced to zero: $S(0)-S(H)=\Delta Q(H)/T$, where $S(0)$ is given by Eq. (1). In practice, $\Delta Q(H)$ was found from the output voltage of a lock-in detector (PAR HR-8) monitoring the temperature of the sample and controlling it by means of feedback to a heater located on the sample. The accuracy of these direct determinations of entropy was quite good (~ ± 4%) and it was confirmed by the good agreement with the calculated values.

D. Magnetic-Susceptibility Measurements

The magnetic susceptibility was measured using a standard ac mutual-inductance method. For temperatures greater than 0.5 K, the He^3 cryostat was used. The sample was cooled to some initial temperature in a magnetic field by the use of an change gas, the exchange gas was pumped away, and the field then reduced to zero. The susceptibility was then measured as the sample was warmed by a heater, and the temperature was measured with a resistance thermometer. Since the He^3 cryostat employed a vertical measuring field while the electromagnet provided a horizontal field, it was necessary to mount the sample with the c axis (i.e., axis of large g value) at a 45° angle to the vertical. This allowed the sample to be demagnetized to a reasonably low temperature, while the fact that $g_{\parallel} \gg g_{\perp}$ ensured that essentially only the component of the susceptibility parallel to the c axis would contribute to the measured inductance. A second arrangement was also tried in which the large $CeCl_3$ sample was aligned with its c axis parallel to the magnet's axis, while a smaller ellipsoidal sample was suspended by a bundle of copper wires below the large crystal. The smaller crystal had its c axis aligned parallel to the axis of the mutual-inductance coil. By demagnetizing the large sample we were able to cool the small ellipsoidal sample to ~ 0.090 K.

For $T<0.5$ K, susceptibility measurements were obtained using the dilution refrigerator. For most of these measurements, a small (~ 8-mm diameter) single-crystal sphere of $CeCl_3$ was coated with Apiezon N grease and wrapped in a cylinder of coil foil.[34] The foil was then wrapped in approximately 1000 No. 42 AWG copper wires and fastened with GE 7031 varnish. One end of the wire bundle was hard soldered to four copper posts which in turn were hard soldered to a copper ring. The latter was coated with Apiezon N grease and screwed tightly to the bottom of the copper mixing chamber. The other end of the bundle of wire was thermally anchored to a 100-Ω $\frac{1}{2}$-W Speer resistor which was calibrated against the susceptibility of cerous magnesium nitrate. A small mutual-inductance coil placed around the sample but thermally isolated from it, allowed the susceptibility to be measured.

For some of the susceptibility points at the lowest temperatures ($T \lesssim 0.1$ K), the sphere was isolated from the mixing chamber, cooled with a heat switch in the presence of a magnetic field, and then cooled further by adiabatic demagnetization. A small mutual-inductance coil again surrounded the sample and the c axis of the crystal and the axes of the coil and of the electromagnet were all parallel. A carbon thermometer was also attached to the sample in this configuration.

III. EXPERIMENTAL RESULTS

A. Specific Heat of $LaCl_3$

Above 1 K an increasingly important contribution to the specific heat of $CeCl_3$ comes from the lattice. In order to estimate this contribution we have measured the specific heat of the isomorphic diamagnetic salt $LaCl_3$. The results can then be scaled to give a good estimate for $CeCl_3$ (see Sec. IV A).

The heat capacity of the sample holder plus 22.5 g of $LaCl_3$ was measured, as well as the heat capacity of the sample holder alone. Comparison of the two gives an indication of the magnitude and uncertainty of the holder correction (see Fig. 2). For the $CeCl_3$ measurements, the relative correction was even smaller.

For $LaCl_3$ we would expect a heat-capacity variation close to a law of the form $a_{LaCl_3}T^3$ while for the holder we would expect a variation of the form $a'T^3+\beta T$, where the linear term is due to the electronic specific heat of the metal parts. In Fig. 2 we have therefore plotted C/T as a function of T^2, and, as can be seen, both sets of data lie on straight lines within the experimental uncertainty. Taking the difference between the two sets we find $a_{LaCl_3}=(6.26\pm0.15)\times10^{-5}$ J/mole corresponding to a Debye temperature $\Theta_D=155.2\pm1.3$ K[35] for one formula unit of $LaCl_3$.

B. Specific Heat of $CeCl_3$

Preliminary measurements were made on a fused and not carefully purified polycrystalline sample. Since the sample was composed of many small randomly oriented crystallites with $g_{\perp}\approx 0$, we were unable to reach temperatures below 0.29 K (starting from a field of 15 kOe at 1.15 K). For this reason we were not able to reach the ordering temperature. Moreover, the results of this measurement showed a small peak near 1 K, presum-

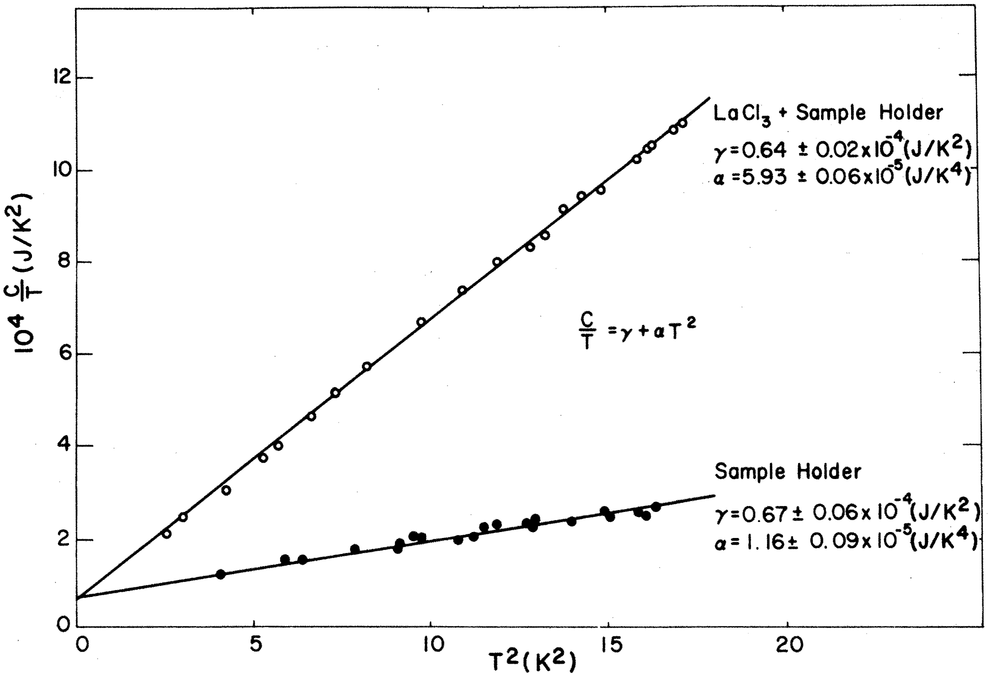

FIG. 2. Heat capacity of sample holder plus 22.5 g of $LaCl_3$ (top line) and of the sample holder alone (lower line).

ably due to impurities.[25] The approximate entropy associated with the anomaly was 0.01*R*ln2. It was soon obvious that higher-purity single crystals were needed to reach lower temperatures as well as to avoid spurious effects due to impurities, and all further specific-heat experiments were carried out on two such crystals.

Figure 3 shows the specific heat of $CeCl_3$ in zero field and in fields up to 14 kOe for temperatures between 0.076 and 4.2 K. (The specific heat of the composite sample described above was also measured in zero field below 0.5 K. The results for this specimen agreed well at all temperatures with the values obtained for the first single crystal but

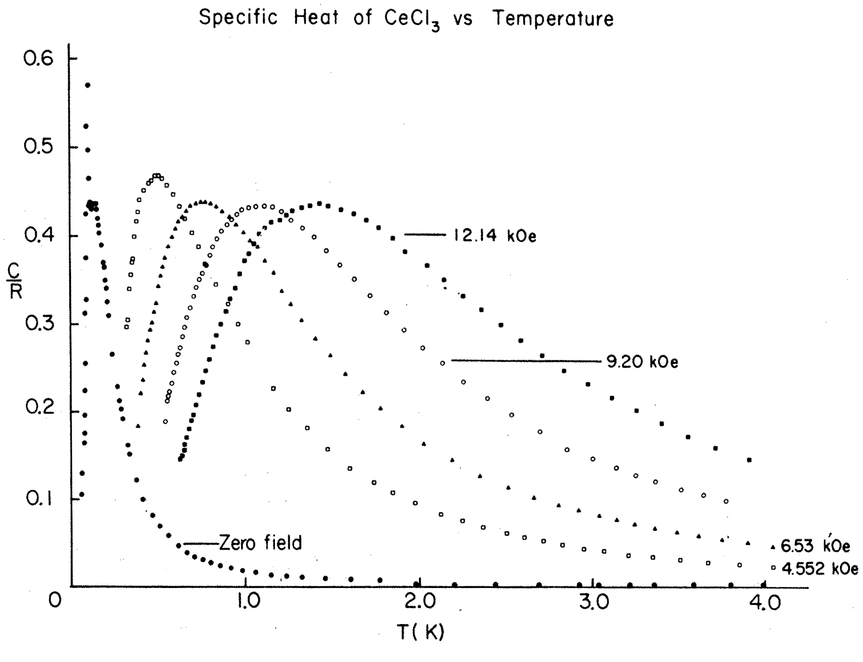

FIG. 3. Specific heat of $CeCl_3$ in zero field and with applied fields along the *c* axis: ●—zero field; □—4.552 kOe; ▲—6.35 kOe; ○—9.20 kOe; ■—12.14 kOe.

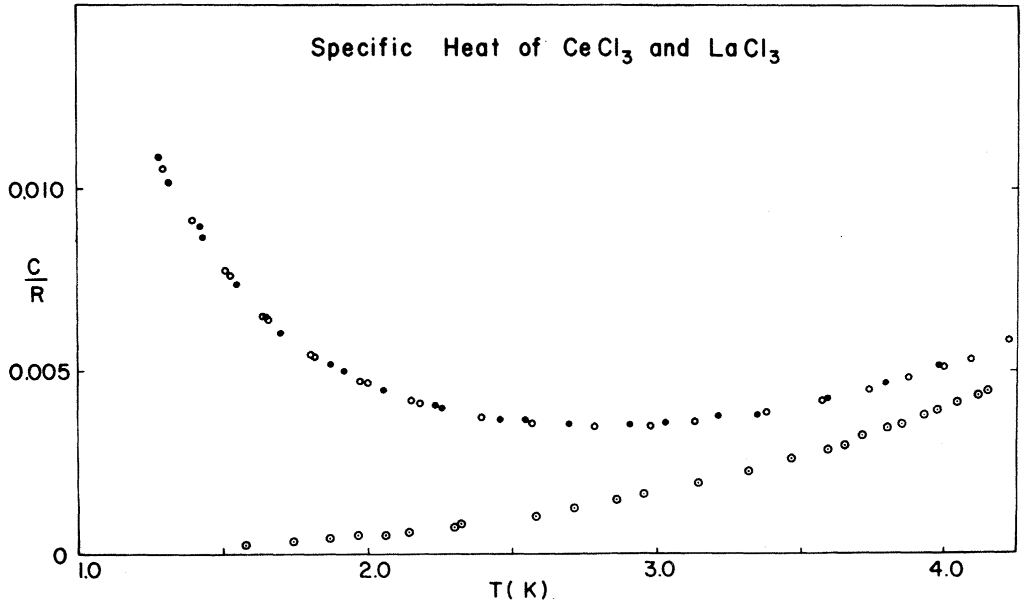

FIG. 4. Specific heat of $LaCl_3$ and $CeCl_3$ vs temperature from 1.2 to 4.2 K: $CeCl_3$: •, ○; $LaCl_3$: ⊙.

were used primarily as a check on the consistency of our temperature calibrations from run to run.) In zero field the specific heat showed a rounded peak at about 0.115 K.[36] The absence of peaks at 0.345 K, as in the susceptibility reported by other authors, or at 1 K as in the fused sample results (and other specific-heat measurements[8,12]), leads us to comment again on the necessity of using highly purified single crystals for these kinds of measurements.

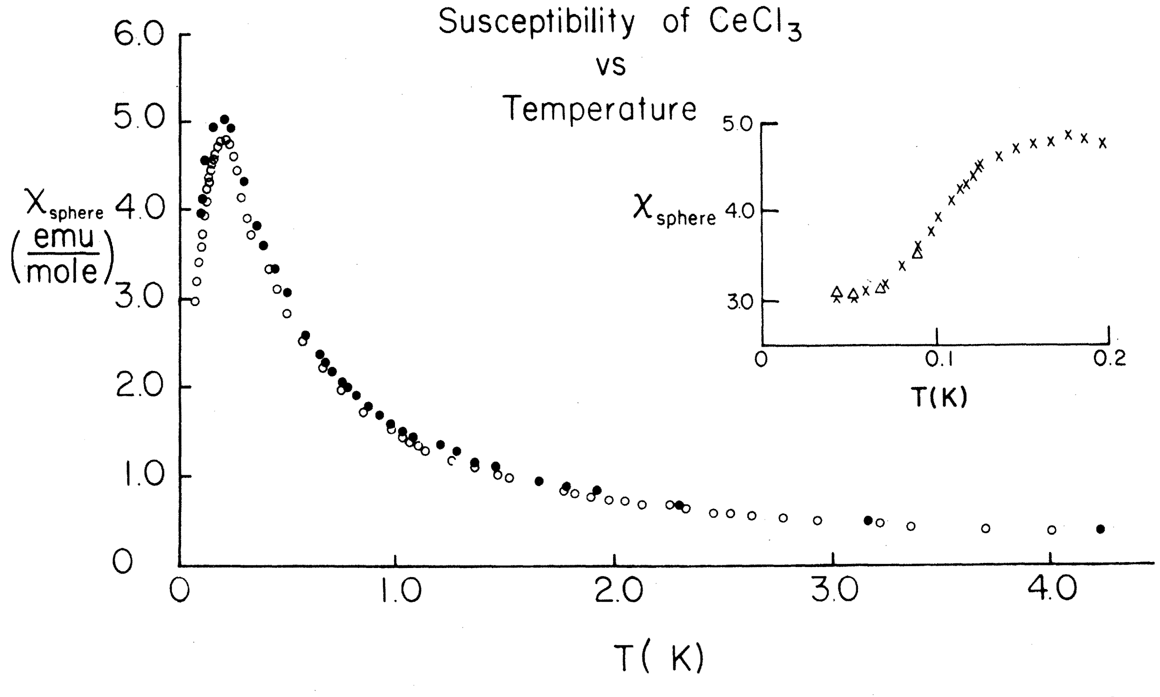

FIG. 5. Susceptibility of $CeCl_3$. Measurements were made on a large cylindrically shaped single crystal with $N = 3.2 \pm 0.2$ (●) and a small ellipsoidally shaped single crystal with $N = 0.63 \pm 0.03$ (○). The results have been corrected to a spherical sample using Eq. (2). The insert shows the susceptibility obtained on the small spherical sample below 0.2 K: continuous cooling data (×), data obtained after adiabatic demagnetization (Δ).

The specific heats of $CeCl_3$ and $LaCl_3$ from 1.2 to 4.2 K after subtraction of the sample holder contribution, are shown in Fig. 4. From this figure it becomes clear that the magnetic contribution is quite small above 3 K. In fact, the magnetic specific heat is only 48% of the total at 3 K, and drops to 14% at 4.2 K.

The specific-heat curves with fields applied along the *c* axis closely resembled Schottky curves as may be seen in Fig. 3. We shall discuss all the specific-heat results more fully in Secs. IV and V.

C. Susceptibility of $CeCl_3$

The measured susceptibility of $CeCl_3$ for the large cylindrical specimen and the smaller spherical sample is shown in Fig. 5. The large crystal used for these measurements was in the shape of a cylinder with rounded edges. The cylinder was 2.1 cm long and 1.65 cm in diameter and its weight was 22.8 g; the effective demagnetizing constant was estimated to be $N = 3.2 \pm 0.2$.[37] For the small ellipsoidal sample, $N = 0.63 \pm 0.05$. For the nonspherical samples the susceptibility values have been corrected to those expected for a sphere, using the relation

$$\chi^{-1}_{\text{sphere}} = \chi^{-1}_{\text{sample}} + \left(\tfrac{4}{3}\pi - N\right), \qquad (2)$$

where N is the demagnetizing factor for the sample.

To find the susceptibility, the measured mutual inductance between 1 and 4 K was fitted to an equation of the form

$$M(T) = A/(T - \Theta) + M_0', \qquad (3)$$

where M_0' includes temperature-independent contributions from diamagnetic and Van Vleck paramagnetic effects. The constant A is proportional to the Curie constant C, where $C = N g_{\parallel}^2 \mu_B^2 / 4k = 1.53 \pm 0.01$ emu K/mole. The ratio A/C could then be used to relate inductance changes for $T < 1$ K to absolute susceptibility changes.

The two sets of results match well near 0.5 K. The susceptibility shows a rounded peak of about 4.8 emu/mole near 0.2 K, after which it falls smoothly, and then appears to level off to a value near 3.0 emu/mole at the lowest measured temperatures.

It was originally feared that the leveling off of the susceptibility might actually be an indication that the thermal contact between sample and thermometer was being lost. In that case, the thermometer might have been cooled by the mixing chamber to a temperature below that of the $CeCl_3$ sample. To check this possibility, the spherical sample was subsequently isolated from the mixing chamber and cooled by means of a mechanical heat switch in a magnetic field, the switch was opened, and the sample was then demagnetized. After demagnetization, the thermometer attached to the sample indicated a temperature *lower* than that of the mixing chamber, and hence could only have been cooled by the sample.

As can be seen in Fig. 5, the values of susceptibility obtained when the sample was demagnetized agree excellently with those obtained when the sample was continuously cooled by the mixing chamber. Hence, the leveling off of the susceptibility at low temperatures appear to be a real effect. The susceptibility measurements are discussed further in Sec. IV F.

IV. DETERMINATION OF THERMODYNAMIC BULK PROPERTIES

A. Specific Heat In Zero Field

The measured specific heat of $CeCl_3$ includes contributions from the lattice, from the first excited state, and from the interactions between the spins, and to a good approximation these contributions are independent. The dominant and most interesting term at low temperatures is of course the interaction or magnetic specific heat C_M, but in order to isolate this term we must first obtain estimates of the other two. Fortunately, a very accurate estimate of the lattice specific heat may be obtained from measurements on $LaCl_3$ which is very similar to $CeCl_3$, while the contribution from the first excited state becomes quite negligible below 3 K.

The lattice specific heat should be well represented by a term of the form aT^3, where a is very close to the value found for $LaCl_3$. To estimate the difference one might expect in going from $LaCl_3$ to $CeCl_3$ we can use the Debye approximation and assume a change given by $a_{CeCl_3} = a_{LaCl_3}[M(CeCl_3)/M(LaCl_3)]^{3/2}$, where $M(CeCl_3)$ and $M(LaCl_3)$ are the molecular weights of the two crystals. This predicts a change of only 0.7%. One can also use the Lindeman melting law

$$\Theta_D = B(\rho^{2/3} T_{\text{mp}} / M^{5/3})^{1/2}, \qquad (4)$$

where ρ is the density of the crystal, M the molecular weight, and B is a factor which can be considered nearly constant for $LaCl_3$ [melting point (M. P.) 1025 K] and $CeCl_3$ (M. P. 1075 K). One then predicts a_{CeCl_3} to be 1.6% greater than a_{LaCl_3}.

Combining these two predictions with the value of a measured for $LaCl_3$, we conclude that $a_{CeCl_3} = 6.31 \pm 0.20 \times 10^{-5}$ J/mole. This gives a Debye temperature of $\Theta_D = 154.0 \pm 2.0$ K for one formula unit of $CeCl_3$. As can be seen, this is virtually indistinguishable from the value obtained for $LaCl_3$ when the error limits are considered. Hence, we have simply chosen $\Theta_D = 155.0 \pm 2.0$ K for both $LaCl_3$ and $CeCl_3$.

The specific-heat contribution from the first excited state (the Schottky tail) has the form $C_{\text{Schottky}}/R = (\Delta/T)^2 e^{-\Delta/T}$, where Δ is known from

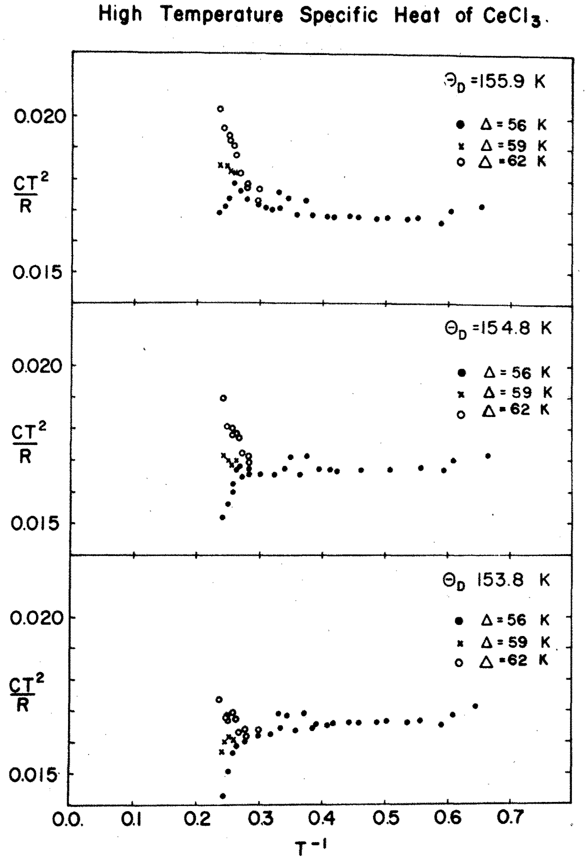

FIG. 6. Specific heat of $CeCl_3$ between 1.5 and 4.2 K corrected for several assumed values of lattice and Schottky contributions. Values of Θ_D and Δ are shown for each of the curves. From these curves limits can thus be set on $\Theta_D = 155.0 \pm 2.0$ °K and $\Delta = 59 \pm 3$ °K.

previous work[1,2] to lie in the range 53–68 K. To obtain an estimate for Δ from the specific-heat data, we tried subtracting lattice and Schottky contributions for several values of Δ and Θ_D to look for a combination which would give the expected smooth variation for the residual magnetic specific heat. This should follow a law of the form $C_M/R = b/T^2 + c/T^3 + \cdots$, with the higher-order terms quite small above 1 K. Figure 6 shows $C_M T^2/R$ plotted as a function of $1/T$ assuming various values of Θ_D and Δ. It can be seen that only a small range of Δ's does not lead to an unreasonable bend in the curve at the highest temperatures and we can conclude that $\Delta = 59 \pm 3$ K. This is in good agreement with the optical[1,2,4] and relaxation[19,20] data. The larger discrepancy with the susceptibility analysis[10,11] is readily explained by the relative insensitivity of the susceptibility to Δ.

All further discussion will be restricted to C_M obtained from the experimental data by subtracting a lattice contribution corresponding to $\Theta_D = 155.0$ K and a Schottky contribution corresponding to $\Delta = 59$ K. Below 3.2 K the uncertainty in C_M corresponding to these corrections should be less than 1%.

To analyze the "high-temperature" behavior of C_M one would like to fit $C_M T^2/R$ to a power series in $1/T$ starting with the constant b. Figure 7 shows $C_M T^2/R$ plotted as a function of $1/T$ between 0.6 and 4.2 K. Unfortunately, the errors are such that one can really only fix the first term in the series, and even the sign of the next-order term remains uncertain. Figure 7 also contains results obtained by Clover[38,39] using a high-frequency relaxation method which measured C_M directly without any corrections for the lattice specific heat. The results are seen to be in excellent agreement with our corrected values, and combining the two sets of data we may finally estimate $b = (170 \pm 10) \times 10^{-4}$ K^2. This value will be used in the analysis of the interactions in Sec. V A.

Below 1 K, the quantitative analysis of C_M becomes more difficult. Near 0.1 K there seems to be evidence of some type or ordering, which would be consistent with nuclear-quadrupole-resonance (NQR) experiments on Cl^{35} in $CeCl_3$, in which a gradual reduction of intensity was observed below about 0.2 K while the signal disappeared completely below about 0.110 K.[8] Unfortunately, no NQR signal could be found below 0.110 K so that there is no indication of the nature of the long-range-ordered state.

B. Specific Heat of $CeCl_3$ in an Applied Magnetic Field

A theoretical expression for the high-temperature specific heat was derived by treating the field exactly and considering the interactions as a perturbation.[25,40] The result will be valid as long as the thermal and Zeeman energies are large with respect to the interaction energy. It can be shown that these criteria should be valid for $CeCl_3$ for temperatures above 0.5 K and fields above 2 kOe. To a sufficient approximation we may write the interactions between the effective spins in the form

$$\mathcal{H}_{\mathrm{int}} = \sum_{\substack{(i>j)\\ \alpha=x,y,z}} K^{ij}_{\alpha\beta} S'_{i\alpha} S'_{j\beta} \tag{5}$$

and neglect off-diagonal terms such as K^{nnn}_{xy} which are small (see Sec. V A and Ref. 5). Expanding the free energy per spin in powers of the interactions divided by kT, we find, correct to second order,

$$\frac{F}{kT} = -\ln\left[2\cosh\left(\frac{W}{kT}\right)\right]^N + \frac{N\langle K_z\rangle}{8kT}\tanh^2\left(\frac{W}{kT}\right) + \frac{N}{64k^2T^2}\left[\langle K_z^2\rangle \operatorname{sech}^4\left(\frac{W}{kT}\right)\right.$$

$$- 2\langle K_z\rangle^2 \tanh^2\left(\frac{W}{kT}\right)\operatorname{sech}^2\left(\frac{W}{kT}\right) - \langle K_x^2\rangle + \langle K_y^2\rangle \operatorname{sech}^2\left(\frac{W}{kT}\right)\Bigg] , \quad (6)$$

where $W = g_{\parallel}\mu_B H$, $\langle K_\alpha\rangle = \sum_j K_{\alpha\alpha}^{ij}$ and $\langle K_\alpha^2\rangle = \sum_j (K_{\alpha\alpha}^{ij})^2$. Because the spins are all magnetically equivalent, the lattice sums $\langle K_\alpha\rangle$ and $\langle K_\alpha^2\rangle$ are independent of the chosen starting spin i. The entropy and specific heat are immediately derived from F,

$$S = -\left(\frac{\partial F}{\partial T}\right)_H ,$$

$$C_H = - T\left(\frac{\partial^2 F}{\partial T^2}\right)_H . \quad (7)$$

To the first order in the interactions, we find

$$C_H/R = [(W/kT)^2 \operatorname{sech}^2(W/kT)] \times \{1 - \langle K_z\rangle / W [2\tanh(W/kT) + (W/kT)(1 - 3\tanh^2(W/kT)]\} . \quad (8)$$

The corresponding second-order terms are rather complicated and have been given by Landau,[25] but since they are all small under the conditions of the present experiments they will be neglected here. In fact, substituting values for the various parameters, it soon becomes clear that even the first-order correction terms are very small and that CeCl$_3$ in a field should approximate well to an ideal two-level Schottky system described by the first term in Eq. (8). Figure 8 shows a comparison of Eq. (8) with and without the interaction terms for the case of $H = 12.14$ kOe. It may be seen that the differences are very small and that both curves agree well with the experimental results. Similarly good agreement was found for other field values.

In the present case, the parameters in Eq. (8) were all known from previous experiments, but it is of interest to note that specific-heat measurements in applied magnetic fields may in fact be used to determine g values. Two approaches are possible, their applicability being dictated by the relative magnitudes of the interactions, W, and kT.

If kT is large compared to the other quantities, then the asymptotic form of the specific heat will be described by

$$C/R = b/T^2 + b'H^2/T^2 , \quad (9)$$

where b is the zero-field coefficient (see Sec. III) and $b' = g_{\parallel}^2\mu_B^2/4k^2$. Hence, a plot of the asymptotic values of $C_M T^2/R$ vs H^2 should give a straight line with intercept b and slope proportional to $g_{\parallel}^2$.

If, as is frequently the case, the interactions are small compared with kT but larger fields are used such that W is comparable with kT, then the specific heat will resemble a modified Schottky curve, as described by Eq. (8). By treating W and $\langle K_z\rangle$ as adjustable parameters, $g_{\parallel}$ may again be found.

It was possible to illustrate both methods using our results for CeCl$_3$, the first for fields of 4.55 and 6.53 kOe and the second for fields of 9.20 and 12.14 kOe. A consistent value of $g_{\parallel} = 4.00 \pm 0.06$ was obtained, in excellent agreement with the value from optical measurements on CeCl$_3$[4] and from EPR on Ce^{3+} in LaCl$_3$.[5-7]

C. Zero-Field Entropy as a Function of Temperature

By integrating a smooth curve of C_M/T vs T, one can readily obtain an entropy versus temperature relation between ~ 0.080 and 4.2 K, as shown in

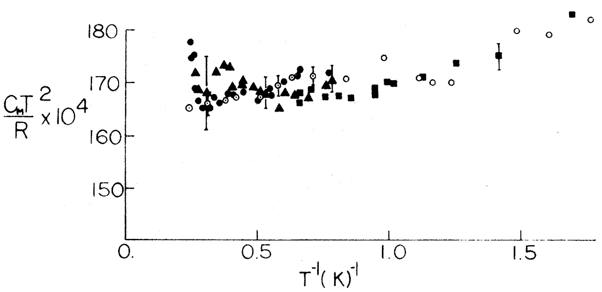

FIG. 7. Magnetic specific heat of CeCl$_3$ between 0.6 and 4.2 °K. Results of the present work are shown by the symbols ■, ○, △; results of Clover use the high-frequency relaxation method and are shown by ⊙. The intercept at $1/T = 0$ of a straight line passing through the points gives $b = (170 \pm 10) \times 10^{-4}$.

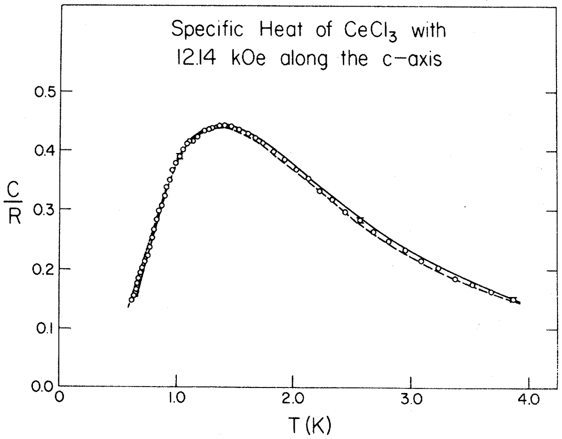

FIG. 8. Specific heat of CeCl$_3$ in a strong applied magnetic field: Experimental values for $H = 12.14$ kOe (○); theory excluding interactions (i.e., two-level Schottky anomaly) calculated for $\Delta E = g_{\parallel}\mu_B H_0$ with $g_{\parallel} = 4.04$ (---); theory including interactions as a perturbation (——) (see Sec. IV B) $\frac{1}{4}\langle K_\alpha\rangle = 0.06$ K.

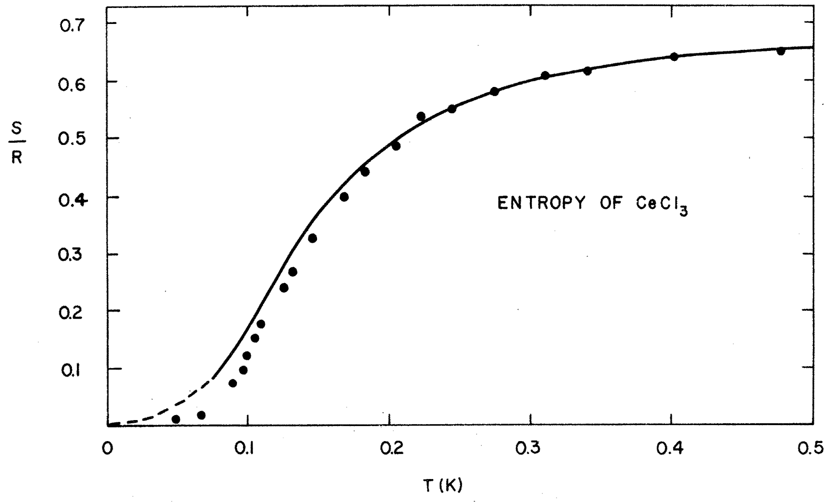

FIG. 9. Entropy vs temperature of $CeCl_3$ in zero field. Results of adiabatic demagnetization (●), integrated specific heat (——). The critical entropy $(S_\infty - S_c) = 0.51R$.

Fig. 9. As explained in Sec. II C, the entropy can be put on an absolute basis by assuming the highest-temperature points to be given by Eq. (1), where we now have a value for $b = (170 \pm 10) \times 10^{-4}$. Figure 9 shows that a large amount of entropy ($\sim 0.66R \ln 2$) is associated with short-range order above the "critical temperature" which is near 0.115 K.

An independent check of the entropy-temperature relation was obtained from a series of adiabatic demagnetizations to zero field starting at a temperature of about 1.25 K. The results are shown as circles in Fig. 9. For each starting field the initial entropy was calculated using the tables of Hull and Hull[33] for noninteracting spins, and the error involved in neglecting the interactions estimated from Eqs. (7) and (8). In each case the error in entropy was less than $0.003R$.

Below a temperature of ~0.16 K, the demagnetization points are seen to fall consistently below the solid line. The largest discrepancies in S occur at the lowest temperatures and amount to approximately $0.05R$. There are a number of factors which may contribute to these differences, but it is uncertain which is primarily responsible.

The first is the possibility of irreversibilities during demagnetizations. From a number of successive demagnetizations and magnetizations, it was estimated that the irreversible change in entropy was $\Delta S \lesssim 0.01R$ for $T \gtrsim 0.11$ K. Below this temperature, magnetizations were not carried out and the magnitude of irreversibilities in this region is therefore unknown.

The second possibility is that errors were present in the temperature calibrations. These would have affected both the measured specific heat and

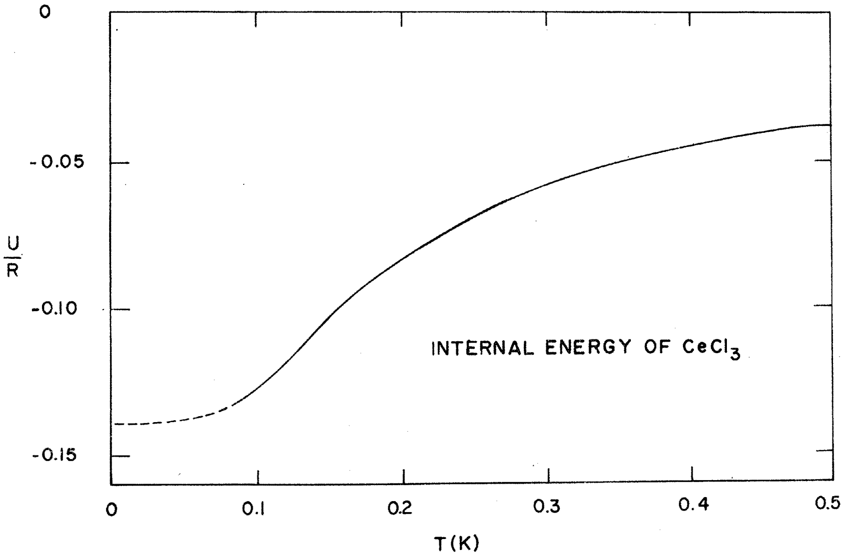

FIG. 10. Internal energy vs temperature for $CeCl_3$ in zero field. The straight line is from the integrated smoothed specific heat. The internal energy at absolute zero is estimated as $U_0/R = -0.139 \pm 0.015$ K.

TABLE I. Entropy contributions above the highest measured temperature T_{max} in applied magnetic fields.

H (kOe)	T_{max} (K)	$S_\infty - S_{T_{max}}$
4.55	4.043	0.012 ± 0.001
6.53	4.038	0.025 ± 0.002
9.20	3.765	0.053 ± 0.004
12.14	3.890	0.080 ± 0.006

the temperature indicated by the carbon resistor after a demagnetization.

A third, and most likely, factor could be errors in the measured values of the specific heat. The entropy is extremely sensitive to such effects, especially at the lower temperatures where the scatter in the data was largest.

D. Internal Energy in Zero Field

The magnetic internal energy U can be calculated in a similar way by integrating the specific heat,

$$U = \int_T^\infty C_M \, dT . \tag{10}$$

The contribution above 4.2 K can again be obtained by extrapolating the specific heat according to a b/T^2 law. For the energy zero we take the fully disordered state ($T \to \infty$) so that all energies due to the interactions will be negative. Figure 10 shows U/R as a function of T down to 0.076 K. Below 0.076 K the curve was extrapolated by assuming a smooth variation of C_M with T consistent with the constraint that the total entropy should be $R \ln 2$. The resulting contribution to U in this region was quite small, $0.006R$, and its uncertainty about $\pm 0.002R$. The corresponding total internal energy at $T = 0$ K is $U_0/R = -0.139 \pm 0.015$ K.

E. Entropy in Applied Magnetic Fields

The isothermal entropy of magnetization was measured at 1.25 K using the feedback arrangement described in Sec. II C. The experiment gives the time derivative $(\partial S/\partial t)_T$ as the magnetic field is swept at a rate $\partial H/\partial t$. This is readily integrated to give S as a function of H at the chosen temperature T. The result is shown in Fig. 11, which also includes the theoretical curve calculated for negligible spin-spin interactions. It can be seen that the agreement is very good, in accord with our expectations that the effect of the interactions is very small.

The temperature dependence of the entropy in applied magnetic fields was obtained by integrating the measured specific-heat curves. For temperatures greater than those actually measured the curves were extrapolated using a $1/T^2$ approximation [Eq. (9)], or the complete expression of Eq. (8) as appropriate. The contributions to the entropy from this region are given in Table I. The results are summarized in Fig. 12. Entropy values taken from these curves may be compared with the isothermal entropy determined at 1.25 K and may be used to test the consistency of the whole procedure. The values thus obtained are shown as crosses in Fig. 11 and it can be seen that the agreement is excellent.

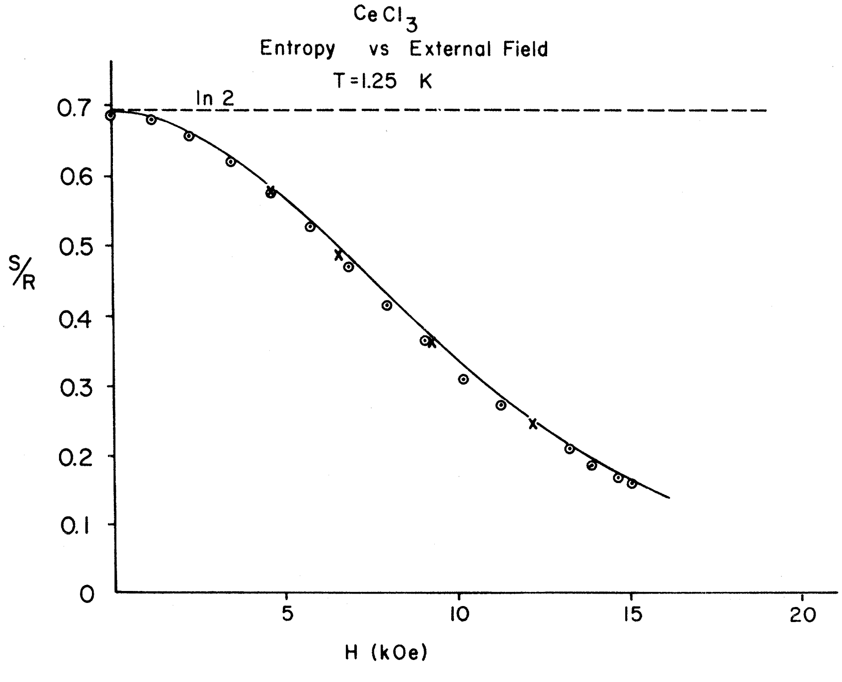

FIG. 11. Entropy vs applied magnetic field at $T = 1.25\,^\circ$K: experimental values from isothermal magnetization (⊙); values calculated from integration of measured C_M/T in various magnetic fields (×) (see Fig. 13); theory for noninteracting spins (——).

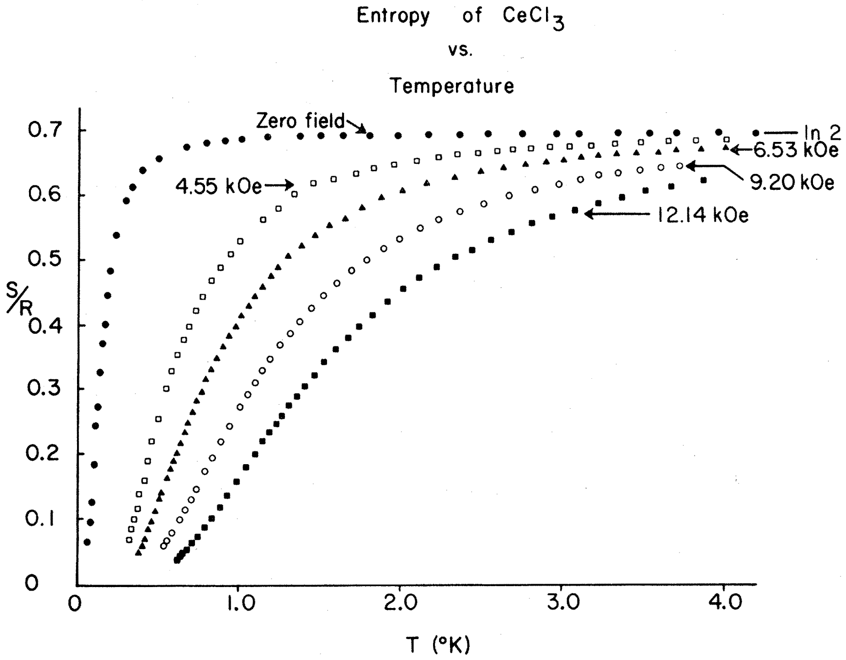

FIG. 12. Entropy vs temperature of $CeCl_3$ for constant magnetic field applied parallel to the c axis.

F. Susceptibility

While it is customary to analyze the high-temperature susceptibility in terms of a Curie–Weiss Law of the form

$$\chi = C/(T-\Theta), \qquad (11)$$

it is also known that the true asymptotic form for

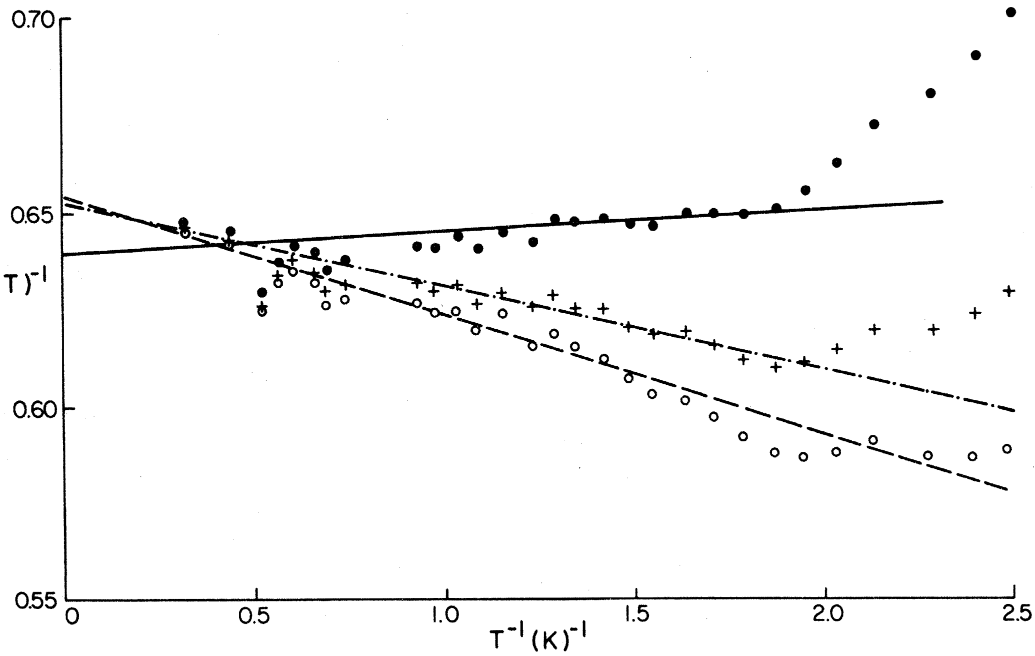

FIG. 13. Magnetic susceptibility of $CeCl_3$: Variation of $(\chi T)^{-1}$ vs T^{-1} uncorrected data ●●●, corrected data $(\chi' T^{-1})$: using parameters of solution I (○○○), using parameters of solution II (+++). Best fits to the data yield $\Theta = +0.05$ K for solution I and $\Theta = +0.30$ K for solution II. Data were corrected using Eq. (14) with $B_2 = 0.027$ for solution I and $B_2 = 0.017$ for solution II.

the susceptibility is a power series,

$$\chi = (C/T)(1 + A_1/T + A_2/T^2 + \cdots) . \qquad (12)$$

This means that the inverse susceptibility can be written

$$(\chi T)^{-1} = (1/C)(1 + B_1/T + B_2/T^2 + \cdots) , \qquad (13)$$

where $B_1 = -\Theta$. We may therefore determine Θ directly from the experimental data from the slope of a plot of $(\chi T)^{-1}$ vs T^{-1} such as the one shown in Fig. 13. The best fit yields a value $\Theta_{\text{sphere}} = -0.01$ K although it is clear that the data do not obey a linear relationship over a very wide temperature range. The small value of Θ and the curvature in the data suggest that the next-order term in Eq. (13), i.e., B_2/T^2, is not negligible. Fortunately, a fairly reliable estimate can be obtained for B_2 in the following manner. Using an approximate value for Θ the interaction parameters can be determined in a manner described in Sec. V. From these interaction parameters we determine B_2[41,42] and then calculate the corrected susceptibility χ' where

$$(\chi' T)^{-1} = (\chi T)^{-1} - B_2/CT^2 . \qquad (14)$$

From a plot of $(\chi' T)^{-1}$ vs T^{-1} we obtain a new value of Θ and by continuing this process we obtain a self-consistent solution.[43] Fortunately, the value of B_2 does not vary greatly as the interaction parameters change and the convergence should be quite good. In Fig. 13 we also show the final corrected susceptibility. Since *two* possible solutions are obtained from the analysis (cf. Sec. V A) two different values of B_2 are available to correct the susceptibility. Not only are the resultant plots linear over a wider temperature range, but the slopes have the *opposite* sign from that obtained from the uncorrected susceptibility. If one fits the final "corrected" values of χ to a plot of $(\chi T)^{-1}$ vs T^{-1}, a value of $\Theta = 0.040 \pm 0.020$ K is obtained, where we have taken the average of the values from the two corrected curves.

Below 0.4 K, additional terms in the susceptibility become increasingly apparent. There is a broad peak in the susceptibility near 0.18 K (see Fig. 5) and near 0.1 K there is a weak inflection corresponding to a maximum gradient in χT. This point of maximum slope occurs at the same temperature, within experimental error, as the peak in the specific heat. All this suggests that CeCl$_3$ orders antiferromagnetically along the c axis (or in the xy plane) near 0.1 K with a large amount of short-range order in the temperature region above the onset of long-range order. This is also consistent with the variation of entropy above the critical temperature.

One alternative which had to be excluded was the possibility that the ordered state was actually ferromagnetic along the c axis and that the decrease of susceptibility at lower temperatures was due to relaxation effects associated with domain motion. However, if this were true one would expect χ to exhibit a maximum value close to $1/N$ near the Curie point. For a sphere this gives $3/4\pi$ emu/cm^3 or 14.8 emu/mole of CeCl$_3$. The experimental peak, on the other hand, was almost a factor of 3 smaller than this. Moreover, we may also note that the change in the out-of-phase component of the susceptibility χ'' was much smaller than that usually encountered in ferromagnets in the region of their Curie points.

We conclude from all this that the cooperative transition near 0.1 K is in fact antiferromagnetic in nature, though we shall see that the actual spin configuration cannot be inferred readily from the present measurements.

V. DETERMINATION OF INTERACTIONS AND THE ORDERED STATE

A. Interaction Parameters

The general interaction between any two effective spins $S' = \frac{1}{2}$ has the form

$$\mathcal{H}_{ij} = \sum_{\alpha,\beta = x,y,z} S'_{i\alpha} K^{ij}_{\alpha\beta} S'_{j\beta} , \qquad (15)$$

with nine independent constants $K^{ij}_{\alpha\beta}$. In any particular case, the actual number may be limited by either symmetry or a knowledge of the actual interaction mechanisms. Both of these are useful in the case of CeCl$_3$.

For the third and more distant neighbors, EPR experiments on Ce^{3+} pairs in LaCl$_3$[6] have shown that the effective interactions are well explained by magnetic-dipole interactions alone, and because of the large g-value anisotropy these are characterized by just one constant per pair,

$$K^{ij}_{zz} = g_{\parallel}^2 \mu_B^2 (r_{ij}^2 - 3z_{ij}^2)/r_{ij}^5 , \qquad (16)$$

where r_{ij} and z_{ij} represent the relative coordinates of spins i and j. These interactions are all quite weak, the largest being those between third and sixth nearest neighbors for which one finds

$$\begin{aligned} K^{3n}_{zz} &= 0.025 \text{ K (antiferromagnetic)} , \\ K^{6n}_{zz} &= -0.032 \text{ K (ferromagnetic)} . \end{aligned} \qquad (17)$$

The sum of all interactions from the third neighbor out to an effectively infinite sphere was calculated by direct summation of Eq. (15) and this gives $\frac{1}{4}\sum{}' K_{zz} = 0.0077$ K, where the prime indicates the fact that the first- and second-neighbor contributions have been excluded.

For both the nearest and next-nearest neighbors there are clear indications that the interaction mechanisms are quite complex with significant contributions from electric quadrupole coupling and anisotropic exchange.[5,6] Since the magnitude of these cannot be predicted, one must use symmetry to reduce the number of unknowns and experimental

TABLE II. Interaction constants for $CeCl_3$ (K). In addition to the experimental uncertainty, the error limits include an allowance for the estimate $|K_{xy}^{\text{nnn}}| < 0.05$ and for the unknown value of the asymmetry parameter η which was arbitrarily allowed to vary between ± 1.

	Solution I	Solution II
$K_{\parallel}^{\text{nn}}$	$0.33^{+0.05}_{-0.09}$	$-0.06^{+0.07}_{-0.03}$
$K_{\perp}^{\text{nn}}$	$0.03^{+0.05}_{-0.11}$	$-0.36^{+0.04}_{-0.02}$
K_{zz}^{nnn}	$-0.15^{+0.03}_{-0.04}$	$-0.01^{+0.02}_{-0.03}$
$K_{\perp}^{\text{nnn}}$	$-0.14^{+0.03}_{-0.04}$	$0.00^{+0.03}_{-0.05}$
	$\lvert K_{\text{nnn}}^{xz}\rvert$, $\lvert K_{\text{nnn}}^{yz}\rvert < 0.002$	

data to estimate their actual magnitudes. For the nearest neighbors (nn), symmetry demands only two nonzero constants K_{zz}^{nn} $(\equiv K_{\parallel}^{\text{nn}})$ and $K_{xx}^{\text{nn}} = K_{yy}^{\text{nn}}$ $(\equiv K_{\perp}^{\text{nn}})$. For the next-nearest neighbors (nnn) there is only a center of inversion and six nonzero terms are allowed. Of these, EPR experiments have shown that two are very small (K_{xz}^{nnn} and K_{yz}^{nnn}). If we define

$$\eta = (K_{xx}^{\text{nnn}} - K_{yy}^{\text{nnn}})/(K_{xx}^{\text{nnn}} + K_{yy}^{\text{nnn}})$$

then the Hamiltonian for the nearest and next-nearest neighbors may be written

$$\mathcal{H} = \sum_{\text{nn}} [K_{\parallel}^{\text{nn}} S_i^z S_j^z + \tfrac{1}{2} K_{\perp}^{\text{nn}} (S_i^+ S_j^- + S_i^- S_j^+)] + \sum_{\text{nnn}} [K_{zz}^{\text{nnn}} S_i^z S_j^z + \tfrac{1}{2} K_{\perp}^{\text{nnn}} (S_i^+ S_j^- + S_i^- S_j^+) + \tfrac{1}{2} \eta K_{\perp}^{\text{nnn}} (S_i^+ S_j^+ + S_i^- S_j^-)] \quad (18)$$

and is specified by five parameters which must be determined from an analysis of the experimental data.

Such an analysis has been discussed in an earlier publication[18] using two preliminary results of the present work, the values of b and Θ_{sphere}. Our final values are only slightly different and the corresponding K values are therefore not changed significantly. The results are shown in Table II.

B. Choice of Solutions

As discussed in Ref. 18, there are two different solutions which cannot be distinguished by the asymptotic high-temperature bulk data and the EPR pair measurements. While the parameters characterizing solution I in Table II corresponded more closely to the set of values predicted for magnetic-dipole-dipole (MDD) and electric-quadrupole-quadrupole (EQQ) interactions, this correspondence should not be regarded as definitive evidence for the correctness of the particular solution. The possibility of additional anisotropic exchange sufficient to account for the parameters of solution II cannot be ruled out.

Nor was it possible to distinguish between solutions by an examination of higher-order terms in the specific heat or susceptibility.[44] While these may be calculated in terms of the relevant parameters, the experimental accuracy was not sufficient to allow a useful comparison to be made.

A potentially appealing approach is to analyze the behavior of $CeCl_3$ in terms of a one-dimensional linear xy or linear Ising model,[45,46] and indeed this has been done previously.[47–49] However, it will now be shown that such an analysis is inadequare. We may begin by considering the characteristics of the two sets of solutions.

An examination of solution II shows that all of the interaction parameters save one are relatively small. The one large parameter is $K_{\perp}^{\text{nn}}$ and is seen to act only between nearest neighbors. Since these neighbors are located along a chain parallel to the c axis of the crystal, it appeared that the one-dimensional linear xy model might prove to be a good approximation to the physical system.

The situation for solution I is somewhat more complicated. However, as a first approximation, the near-neighbor interactions are dominated by an antiferromagnetic interaction in the z direction. This suggests that the basic structure to be considered is a series of antiferromagnetic linear chains. If this is indeed the case, then the next-nearest-neighbor interactions will tend to cancel in pairs. As a result, $CeCl_3$ might be expected to divide itself into two noninteracting sublattices, each composed of independent antiferromagnetic linear chains, and such a situation can be approximated by the linear Ising model.

Before proceeding any further with this approach, it is important to interject several notes of caution. The first is that the models considered are one dimensional in nature. It is therefore probably quite invalid to expect them to describe the behavior of $CeCl_3$ below the ordering point. For this reason, although the behavior of these models will be indicated even for $T \to 0$, it would be misleading to expect good quantitative agreement between experimental and model data at the lowest temperatures. Second, the models are only approximations to the real Hamiltonian in that they also neglect certain nonzero interactions. The importance of such omissions will be considered later when appropriate. Finally, in all discussions it will be assumed that η has been set equal to zero, unless other indicated. There is no *a priori* reason why this should be true, but it introduces one simplifying factor into an already complex situation.

1. Specific Heat

The first quantity to be considered is the specific heat. Figure 14 shows the smoothed experimental curve, together with predictions of the linear *xy* and Ising models[45,47] with $K_{\perp}^{nn}$ and $K_{\parallel}^{nn}$ chosen from solutions II and I, respectively, as the appropriate parameters for the two models. As can be seen, neither model describes the observed behavior very well.

This is not so surprising for the Ising model, since this approximation neglects a number of important interactions. For example, at high temperatures, $C_M/R = b/T^2 + \cdots$, where $b = \frac{1}{32}\sum_j (K_{\alpha\beta}^{ij})^2$ (and the $K_{\alpha\beta}^{ij}$ are now expressed in units of temperature). Experimentally, $b = 1.70 \pm 0.10 \times 10^{-2} K^2$, while for the Ising model, $b = \frac{1}{16}(K_{\parallel}^{nn})^2 = 0.69 \times 10^{-2} K^2$. The effect of neglecting the non-Ising interactions is apparent.

For the linear *xy* model, the situation is quite different. In this case, the approximation of solution II by such a model should be rather good since the neglected interactions are quite small. This can be seen by noting that $b = \frac{1}{8}(K_{\perp}^{nn})^2 = 1.62 \times 10^{-2} K^2$, in close agreement with the observed value. However, the specific heat predicted by this model shows serious discrepancies with the experimental values below 0.5 K.

This lack of agreement suggests two possibilities. The first is that solution II is, in fact, incorrect and should be eliminated. The second possibility is that solution II is correct but is not well represented by the linear *xy* model. On the basis of the specific-heat data, however, no definite conclusion can be drawn.

2. *Susceptibility*

The experimental susceptibility may also be compared with the behavior predicted by Katsura[45,47] for the two model Hamiltonians. In doing this, however, a modification of the model results is necessary. In Katsura's calculations, it was assumed that only nearest-neighbor interactions were present, while for $CeCl_3$ more-distant-neighbor interactions in the chain have a non-negligible effect. The effect of these more distant neighbors can be approximated by an effective field $H_e = \gamma M$, where M is the moment of the sample. If χ_k is the exact susceptibility of the nearest-neighbor linear *xy* or Ising model, then the susceptibility χ which is modified by the effective field is given by $\chi^{-1} = \chi_k^{-1} - \gamma$, where

$$\gamma = -\sum z_i K_i / N g_{\parallel}^2 \mu_B^2 , \tag{19}$$

where z_i is the number of *i*th neighbor spins and K_i is the *i*th-neighbor interaction.

For the case of $CeCl_3$, one can write

$$\chi^{-1} = \chi_k^{-1} + \frac{6K_{zz}^{nnn}}{N g_{\parallel}^2 \mu_B^2} + \frac{1}{N g_{\parallel}^2 \mu_B^2} \sum_{i \geq 3} z_i K_i . \tag{20}$$

The last two terms on the right-hand side above can also be written in the form

$$\gamma = (-1/C)(\tfrac{3}{2} K_{zz}^{nnn} + \Theta_{dip}) , \tag{21}$$

where C is the Curie constant and Θ_{dip} is the dipolar contribution from third and more distant neighbors. This result can also be found from a consideration of a high-temperature expansion for χ where it is exact to order $1/T^2$. As noted earlier, Θ_{dip} for a spherically shaped specimen is 0.0077 K.

Figure 15 shows the experimental susceptibility points between 0.05 and 0.5 K together with the behavior of the two models corrected for the effects of the more distant neighbors as described above. At the higher temperatures, the linear *xy* model seems to give slightly better agreement with the

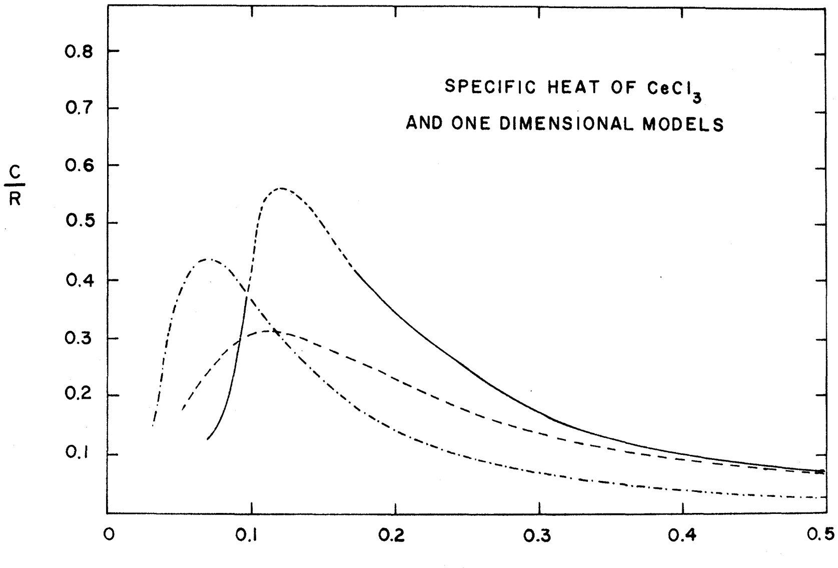

FIG. 14. Specific heat of $CeCl_3$ below 0.4 K. The theoretical curves are for the usual one-dimensional Ising model, $K_z = 0.33$ K (Ref. 46) (•–•–•–) and for the transverse coupled Ising model (Ref. 46), $K_z = 0$, $K_x = K_y = 0.36$ K (–––). The experimental results are shown by a solid line except in the region near 0.11 K where scatter in the data makes it impossible to determine if the curve is rounded or has a spike in it.

data, although in view of the uncertainties in the values of the interaction parameters (cf. Table II), either model can be made to fit the experimental points. At lower temperatures, the qualitative behavior of the data also resembles that of the *xy* model. However, in this region the applicability of one-dimensional models to $CeCl_3$ is more dubious, and a more careful consideration of the experimental behavior is called for.

The situation for solution II is relatively straightforward. The dominant $K_{\perp}^{nn}$ term would be expected to align the spins perpendicular to the *c* axis. Hence, a field applied along the *c* axis would measure a "perpendicular" susceptibility, which should have a finite and nonzero value even at $T=0$.

The possibilities arising from solution I are more complicated. If the large $K_{\parallel}^{nn}$ term produces a spin configuration which is essentially Ising-like, then one would expect a susceptibility characteristic of such a state, and this implies $\chi \rightarrow 0$ as $T \rightarrow 0$. However, the temperature at which this behavior becomes evident depends upon the energy gap between the ground state and any low-lying energy levels. If this gap is small enough, the susceptibility would only vanish at extremely low temperatures. Thus far it has not been possible to construct a state with the required properties, but neither has its existence been ruled out.

In addition, the presence of the non-Ising terms might significantly alter the assumed Ising-like characteristics of solution I. In that case, the ground state would not be an Ising-like one, and the susceptibility as $T \rightarrow 0$ might be modified. For example, if the Hamiltonian contains terms of the form $S_i^z S_j^+$, then the ground state will have admixtures of state $|i\rangle$ such that $\sum S_i^z |i\rangle \neq 0$. It is then possible to have a nonzero susceptibility through the mechanism of a second-order coupling to excited states $|e\rangle$. The process is analogous to the one responsible for Van Vleck temperature-independent paramagnetism, and depends upon matrix elements of the form $\langle e|\sum S_i^z|i\rangle$. The magnitude of terms such as $S_i^z S_j^+$, however, were found to be very small,[6] and it is unlikely that such effects can account for the large susceptibility exhibited by $CeCl_3$ at low temperatures.

Again, the data do not provide sufficient grounds for a definitive choice of the proper solution, although a finite susceptibility at $T=0$ is more easily understood in terms of the parameters of solution II.

In summary, an analysis of the specific heat or susceptibility of $CeCl_3$ in terms of one-dimensional models is inadequate and inconclusive.

3. *Internal Energy*

In the previous discussions of thermodynamic properties below the ordering temperature of $CeCl_3$, the model calculations were of little use since a model which exhibits no ordering at finite temperatures can hardly be expected to describe a real ordered state adequately. In particular, the models fail to include precisely those interactions which are responsible for the finite-temperature ordered state.

The internal energy at $T=0$, however, depends only upon the ground-state spin configuration. If this state consists of a system of ordered one-dimensional linear chains, and if these chains are only weakly interacting, then $U(T=0)/R$ may be well approximated by the result for a one-dimensional system. For solution II, all interactions

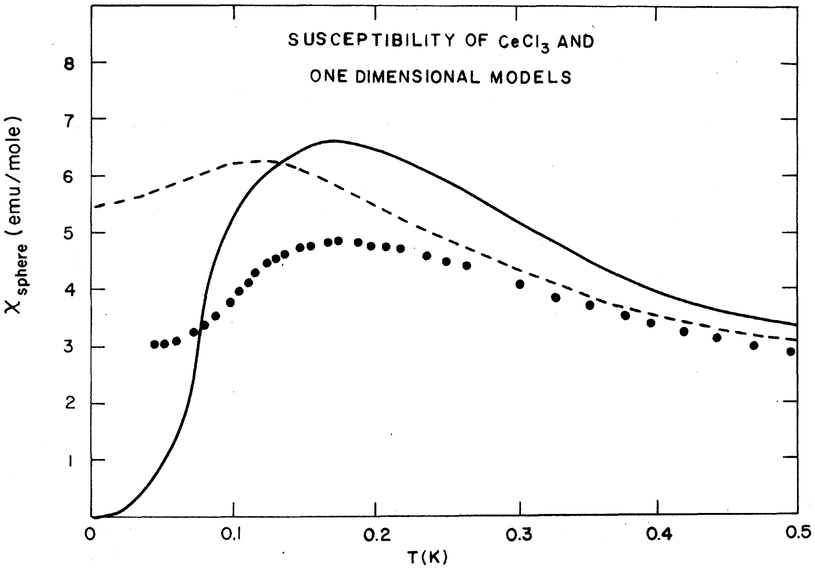

FIG. 15. Susceptibility of $CeCl_3$ for a spherical sample (• ••), theoretical susceptibility of the one-dimensional Ising model (———), theoretical susceptibility of the transverse-coupled Ising chain (----). Both theoretical curves have been corrected for dipolar interactions as described in the text.

except $K_{\perp}^{nn}$ are quite small, and transversely ordered linear chains seem to be a reasonable assumption for the ordered state. For solution I, the tendency of the next-nearest-neighbor interactions to cancel in pairs (giving a basic Ising chain structure) make it reasonable to consider the ordered state at $T=0$ as a system of noninteracting or weakly interacting Ising chains.

The energies of both the linear Ising and *xy* model systems have been determined and may be compared with the experimentally observed result. For the *xy* model,[45]

$$U_0/R = -(1/\pi)\left|K_{\perp}^{nn}\right|. \tag{22}$$

In the presence of a perturbation of the form $K_{\parallel}^{nn}S_i^z S_j^z$, it has also been shown that[47]

$$\frac{U_0}{R} = -\frac{1}{\pi}\left|K_{\perp}^{nn}\right| + \frac{1}{\pi^2}K_{\parallel}^{nn} - \frac{8}{\pi^3}\left(\tfrac{1}{6} - \tfrac{1}{14}\pi^2\right)\left(\frac{(K_{\parallel}^{nn})^2}{(K_{\perp}^{nn})^2}\right)\left|K_{\perp}^{nn}\right|. \tag{23}$$

Applying this model to $CeCl_3$ and substituting the appropriate parameters from solution II into the above expression, one finds $U_0/R = -0.120$ K. Experimentally, U_0/R was found to be $-(0.139 \pm 0.015)$ K.

For the nearest-neighbor linear Ising model, the ground-state energy is given by $U_0/R = -\frac{1}{4}K_{\parallel}^{nn}$. It has already been seen, however, that this model fails to include a number of interactions in solution I which are comparable in magnitude with $K_{\parallel}^{nn}$. The effect of such interactions on the ground-state energy can be estimated by assuming a ground state of antiferromagnetically ordered chains, and considering the effect of couplings to states with two or more spins flipped by terms in the Hamiltonian such as $S_i^+S_j^-$. It can then be shown that this leads to a correction in the ground-state energy of magnitude

$$\Delta E = \frac{(K_{\perp}^{nn})^2}{4K_{\parallel}^{nn}} + \frac{3(K_{\perp}^{nnn})^2}{8(2K_{\parallel}^{nn} - K_{zz}^{nnn})} + \frac{3\eta^2(K_{\perp}^{nnn})^2}{8(2K_{\parallel}^{nn} + K_{zz}^{nnn})}. \tag{24}$$

Substitution of the *K* values for solution I gives

$$U_0/R = (-0.093 - 0.015\eta^2)\,\mathrm{K}. \tag{25}$$

For $\eta = 0$, the result for solution I does not agree with the measured value as well as the result for solution II, but neither falls within the error limits of the experimental value. Moreover, it can be shown that if η is increased from zero to provide a larger correction term, then $K_{\parallel}^{nn}$ decreases, so the discrepancy with the experimental result cannot be easily removed in this manner. Thus, the internal energy of $CeCl_3$ is not adequately accounted for by either of the two model calculations.

Since the obvious defect of the above models is that they are one dimensional, one would hope to use the two solutions to draw some conclusions regarding the actual three-dimensional ordered state. The solutions are really quite similar in that both predict basically the formation of linear chains along the *c* axis, each of which has three identical nearest-neighbor chains. Moreover, for solution I the coupling between these chains cancels to a first approximation (due to symmetry), and for solution II the interaction itself between chains is essentially zero. The long-range order would then be determined by interactions with more distant chains. If these interactions are dipolar, as the resonance results indicate, they would favor antiparallel alignment between *z* components of spins in the same plane. Because of symmetry this is possible for only four out of six neighbors (this is similar to the problem of producing an ordered state on an Ising-plane triangular lattice[50]), and it therefore appears likely that the actual spin configuration will be an antiferromagnetic state (possibly complex) produced by the small off-diagonal terms in the Hamiltonian.

In summary then, an unambiguous choice between the two sets of interaction parameters is not yet possible. In particular, the treatment of $CeCl_3$ in terms of one-dimensional models is not justified on the basis of the available data, but we cannot predict what the three-dimensional spin arrangement will be.

VI. SUMMARY AND CONCLUSIONS

An extensive collection of magnetothermal data for $CeCl_3$ is now known for temperatures ranging from 0.05 to 4.2 K. Above 0.5 K, $CeCl_3$ was found to behave as an almost ideal paramagnet in the presence of a magnetic field. The susceptibility could be closely approximated by Curie's law and the specific heat in an applied field could be well represented by a Schottky anomaly calculated for a paramagnet without interactions.

Below 0.5 K, $CeCl_3$ shows evidence of undergoing an ordering process, but the nature of the ordered state remains unknown.

It is interesting to consider what other types of measurements might be sufficient to resolve the problem of the proper choice of solutions.

A nuclear-quadrapole-resonance experiment on $CeCl_3$ has been carried out by Colwell *et al.*[8] They found that below 0.2 K, the resonance line decreased in intensity without broadening until it disappeared at 0.11 K. Efforts to locate the line below this temperature were in vain, although it was looked for down to 54 mK. They speculated that 0.11 K marked the onset of short-range order within the chains, while long-range order presumably occurred at some lower temperature. While this is a possible explanation, it is not easily understood in view of the rather sharp decrease of the specific heat in the region below 0.1 K. The specific-heat peaks found in the ordering of either linear Ising or *xy* chains are more rounded than the experimentally observed one for $CeCl_3$ and of a significantly smaller magnitude. It seems more reasonable that long-range-order sets in near 0.1 K, but it is not clear how the behavior of the resonance line is related to this.

If the spins align perpendicular to the *c* axis below the ordering temperature, then the small *g* value in this direction will result in only a small internal field. This would be expected to leave the main resonance line essentially unaffected. On the other hand, spins aligned along the *c* axis would produce a significantly larger field, and this might be sufficient to shift the resonant frequency beyond the range studied. On this basis, solution I appears to be the more likely one. A repetition of the experiment, but with a wider frequency range and extended to lower temperatures would be desirable.

Neutron-diffraction experiments pose another possibility, and perhaps hold the most promise for determining the nature of the ordered state. However, even this method has potential difficulties. In addition to the technical problems posed by working at 0.1 K or below, there is also the small value of $g_\perp$ to cope with. If the spin configuration in the ordered state is perpendicular to the *c* axis, the magnetic moment will be quite small, and the scattering intensity correspondingly weak. It is therefore possible that no magnetic superlattice lines would be seen upon cooling through the transition temperature, leaving the nature of the ordered state undetermined.

A final possibility is to examine the resonance spectrum of Ce^{3+} triplets in $LaCl_3$. Wu (private communication) has shown that the spectrum for solution I differs from solution II. However, he has also shown that the intensities of the triad lines are at least a factor of 10 smaller than the intensity of a nearest-neighbor-pair line. Moreover, a number of the triad lines would be obscured by the single ion line or by pair lines. While it is therefore possible that a triplets experiments could be used to distinguish the solutions, it would be quite a difficult task to accomplish.

$CeCl_3$ thus remains an intriguing material for further study. A more refined statistical mechanical treatment of problem of this nature would be most useful, and might yet provide a means of resolving the ambiguities still present.

ACKNOWLEDGMENTS

The authors wish to express their thanks to S. Mroczkowski for his painstaking efforts to grow pure high-quality $CeCl_3$ and $LaCl_3$ single crystals and to C. Sneider for his skillful work in constructing the cryostats used in these experiments. It is also a pleasure for them to thank Dr. C. Y. Wu and Dr. R. J. Birgeneau for helpful discussions, and they wish particularly to acknowledge Dr. A. T. Skjeltorp for his advice and insight concerning the analysis of the susceptibility. They also wish to thank Professor W. P. Wolf for his constant advice and encouragement throughout the course of this work.

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