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Low-Temperature Magnetic Transitions in Some Rare-Earth Trichlorides*

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The magnetic susceptibilities of $CeCl_3$, $PrCl_3$, and $NdCl_3$ single crystals and of polycrystalline $SmCl_3$ have been measured in the temperature region between 0.2 and 4.2°K. Each of these compounds exhibits anomalous behavior. $NdCl_3$ has two extremely sharp spikes in its susceptibility-versus-T curve at 1.035 and 1.745°K. These spikes are strongly affected by a weak external field and also depend on the amplitude and frequency of the ac measuring field. $CeCl_3$ has a single sharp spike in its susceptibility at 0.345°K. $PrCl_3$ and $SmCl_3$ have rather broad maxima in their susceptibilities at about 0.7 and 0.4°K, respectively. It is shown, on the basis of a simple molecular field model, that the superexchange coupling between nearest neighbors is ferromagnetic, while that between next-nearest neighbors is antiferromagnetic. The two spikes in the $NdCl_3$ susceptibility curve are ascribed to two successive cooperative magnetic transitions. An attempt is made to correlate in a quantitative way the temperatures of the transitions in $CeCl_3$ and $NdCl_3$, and to explain why no similar transitions were observed in $PrCl_3$.

I. INTRODUCTION

The rare-earth trichlorides form a subclass of one of the major groups of inorganic paramagnetic compounds and would presumably have been as exhaustively studied at low temperatures as the alums, the ethyl sulfates, the tutton salts, and the double nitrates were it not for the difficulty of preparing large, pure crystals. Prior to 1961 there were no published results on the bulk properties of a single crystal specimen.

The susceptibility of powdered $CeCl_3$ was measured[1] down to 14°K in 1931 and the crystal structure of the anhydrous trichlorides was reported by Zachariasen[2] in 1948. Hutchison and Wong[3] have studied the electron spin resonance in dilute solid solutions of vairous rare-earth ions in $LaCl_3$. Dieke and others[4–17] have made extensive investigations of the optical spectra of the dilute trichlorides.

Despite the paucity of experimental work on the concentrated trichlorides they are very appealing as a subject for study because of their simple chemical formula (only two different ions) and their simple crystal structure (hexagonal).

In 1961 it was discovered[18] that a $GdCl_3$ single crystal becomes ferromagnetic at 2.2°K. These experiments were the first on a bulk property of a single crystal. More recently[19] the susceptibility of $CeCl_3$ and $PrCl_3$ has been measured in the temperature range between 4.4 and 300°K.

The ferromagnetism of $GdCl_3$ could be satisfactorily explained in terms of the combined effects of the dipole-dipole coupling and a somewhat stronger isotropic ferromagnetic exchange interaction between neighboring rare-earth ions. We were led to speculate that the remaining isomorphic rare-earth trichlorides (of cerium through europium) would also become ferromagnetic, but at lower temperatures than 2.2°K because of their smaller magnetic moments and larger ionic volumes. Since the dipolar interaction can be calculated one might obtain valuable information about the exchange interaction. Moreover since diamagnetic La^{3+} can be substituted for any of the magnetic ions without altering the structure there is a possibility of studying the ferromagnetic properties as a function of concentration.

II. EXPERIMENTAL DETAILS

The specimens were prepared by a method due to Wong.[20] First the hydrated trichloride is prepared in a straightforward manner from the commercially available 99.9% pure oxide. It is then dehydrated by warming the crystals slowly to their melting point under vacuum. Single crystals are grown from the polycrystalline material in quartz tubes containing helium gas at 250 Torr by lowering the tubes slowly through a furnace which is maintained at a constant temperature. All handling of unprotected crystals is, of course, done in a dry box.

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* Work supported in part by Advanced Research Projects Agency, Department of Defense.

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The first susceptibility measurements were made in an ac mutual induction bridge apparatus, the subject salt and coil system being immersed in a bath of liquid helium.[21] When it subsequently became necessary to extend the measurements to temperatures below 1°K the magnetic cooling method was employed. A separate refrigerator salt (either chromic potassium alum or manganous ammonium sulfate) and a thermal link which consisted of many fine copper wires were used. The wires were "potted" in the refrigerator and attached to the specimen by binding them to it with thread and covering liberally with stopcock grease.[22] Separate coil systems surrounded both salts external to a glass vacuum case, the refrigerator thus serving also as a thermometer. The salts could be subjected to the field of a large movable electromagnet, the trichloride being positioned for maximum H while the refrigerator/thermometer, located some 10 cm above, was in the fringing field. Despite this circumstance, the latter salt always cooled initially to much the lower temperature. This behavior is indicative of the large specific heat manifested by the trichlorides in the 0.1 to 1°K temperature region.[23] A Helmholtz pair and a small solenoid, each capable of producing several hundred gauss, were used to study the variation of the differential susceptibility with applied dc field.

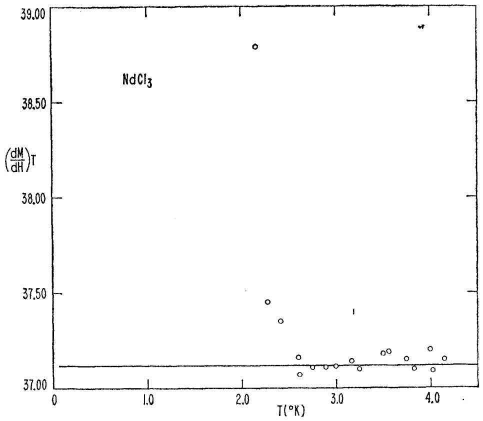

FIG. 2. Deviation of the differential susceptibility of a single crystal of $NdCl_3$ from Curie's law, $(dM/dH)=C/T$. The product of the differential susceptibility and the temperature, $(dM/dH)T$, is plotted in arbitrary units. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The straight line represents Curie law behavior.

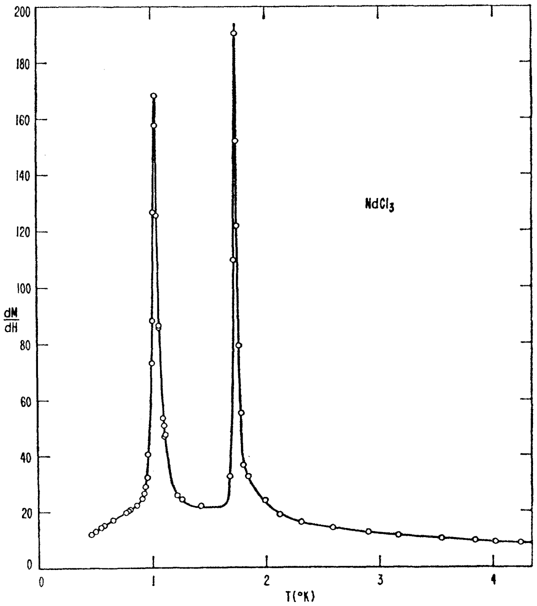

FIG. 1. The temperature dependence of the differential susceptibility, (dM/dH), in arbitrary units, of a single crystal of $NdCl_3$ with the ac measuring field parallel to the crystal c axis. There was zero applied dc field. The ac measuring frequency was 270 Hz. The solid line is drawn through the experimental points. Although no data showing the sharp break in the curve at 1.65°K are presented, that region had been exhaustively studied previously and the temperature dependence of (dM/dH) is as shown by the solid line.

III. EXPERIMENTAL RESULTS

(a) $NdCl_3$

The free Nd^{3+} ion is in a $^4I_{9/2}$ state which is split by the crystalline electric field (point symmetry C_{3h}), leaving a ground-state doublet about 115 cm^{-1} below the next level.[6,8] The ion therefore behaves as an effective spin $S'=\frac{1}{2}$; paramagnetic resonance experiments by Hutchison and Wong[3] on $LaCl_3$ containing 0.2% Nd^{3+} gave $g_{\parallel}=3.996$ and $g_{\perp}=1.763$, the reference direction being the crystalline c axis.

(i) $\chi_{\parallel}$: *c Axis Parallel to the ac Measuring Field*

The zero-applied-field differential susceptibility below 4.2°K is shown in Fig. 1.

Between 2.5 and 4.2°K the susceptibility follows the Curie law, $\chi=C/T$, very accurately as shown in Fig. 2. The experimental uncertainties would permit a Curie–Weiss θ in the range ±0.01°. Below 0.9°K the susceptibility decreases with decreasing temperature. Between 0.9 and 2.5°K the susceptibility exhibits two extremely narrow and highly anomalous spikes, one at 1.035±0.005°K and the other at 1.745±0.005°K. The magnitude of these peaks depends on the measuring frequency (Fig. 3) and on the amplitude of the ac measuring field (Fig. 4); note that the susceptibility increases with increasing measuring field. The loss component χ'' of the susceptibility, $\chi=\chi'-i\chi''$, is zero except in the vicinity of the peaks where it also exhibits two extremely narrow spikes. Its maxima occur at the points of maximum slope on the low-temperature

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[21] R. P. Hudson and B. W. Mangum, in *Proceedings of the Eleventh Colloque AMPERE, Eindhoven, 1962* (North-Holland Publishing Company, Amsterdam, Netherlands, 1963), p. 135.

[22] We are indebted to J. F. Schooley for this simple, effective, and nondestructive method of mounting.

[23] It also indicates a failure to achieve an isentropic demagnetization. The experiments suggested that the thermal link diminished rapidly in effectiveness below 0.2°K.

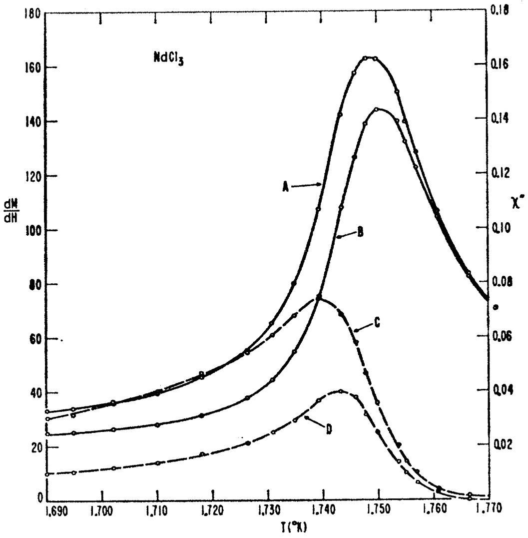

FIG. 3. The dependence of the differential susceptibility (dM/dH) shown as solid lines, and the loss component of the susceptibility χ'' shown as dashed lines, both quantities given in arbitrary units, of a single crystal of NdCl$_3$ on the measuring frequency and on the temperature. Curves A and C show (dM/dH) and χ'', respectively, obtained using a measuring frequency of 75 Hz. Curves B and D show (dM/dH) and χ'', respectively, obtained using a measuring frequency of 270 Hz. The measurements were made in zero applied dc field. The ac measuring field was parallel to the crystal c axis and had an amplitude of 0.14 Oe.

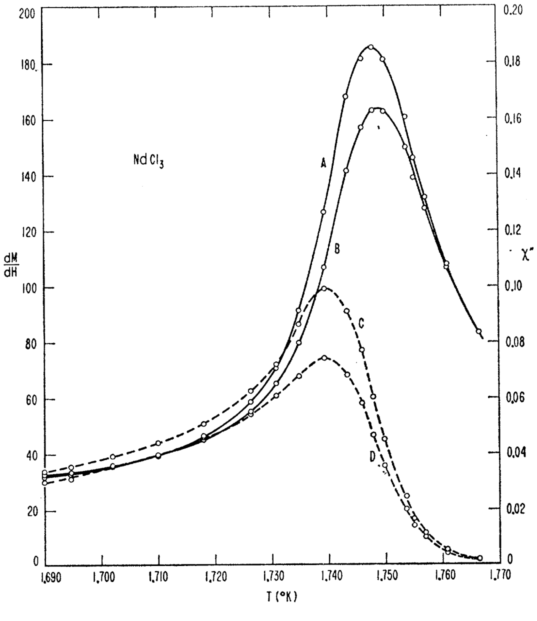

FIG. 4. The dependence of the differential susceptibility (dM/dH) shown as solid lines, and the loss component of the susceptibility χ'' shown as dashed lines, both quantities given in arbitrary units, of single crystals of NdCl$_3$ on the ac measuring field and on the temperature. The measuring frequency was 75 Hz. Curves B and D show (dM/dH) and χ'', respectively, obtained using an ac measuring field of 0.14 Oe. Curves A and C show (dM/dH) and χ'', respectively, obtained using an ac measuring field of 0.52 Oe. The measurements were made in zero applied dc field and the ac measuring field was parallel to the crystal c axis.

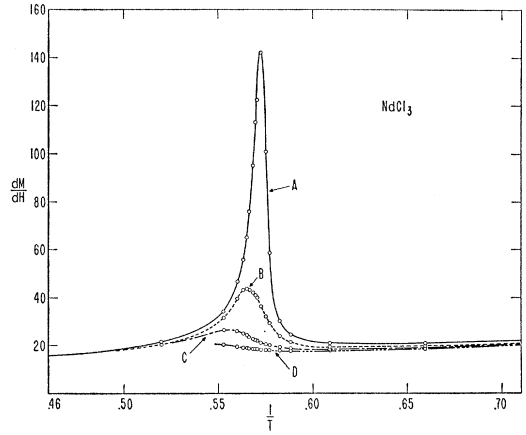

FIG. 5. The dependence of the differential susceptibility (dM/dH) given in arbitrary units, of a single crystal of NdCl$_3$ on a dc field applied parallel to the crystal c axis (with the ac measuring field also parallel to the c axis) and on the temperature. Curve A gives (dM/dH) in zero applied dc field. Curve B gives (dM/dH) in an applied dc field of 5 Oe. Curve C gives (dM/dH) in an applied dc field of 20 Oe and curve D gives (dM/dH) in an applied dc field of 50 Oe. The ac measuring frequency was 270 Hz and the ac measuring field was 0.14 Oe.

side of the peaks in χ'. The behavior of χ'' is also shown in Figs. 3 and 4.

The magnitudes of the peaks in χ' are very sensitive to a dc field applied parallel to the c axis as shown in Fig. 5. It can be seen that a field of 50 Oe nearly removes the spikes. A dc field applied perpendicular to the c axis has a somewhat smaller effect but one which is still very pronounced as shown in Fig. 6. The positions of the peaks are moved toward higher temperatures with increasing dc fields. The magnetization of a given specimen at 1.745°K is approximately the same as would be

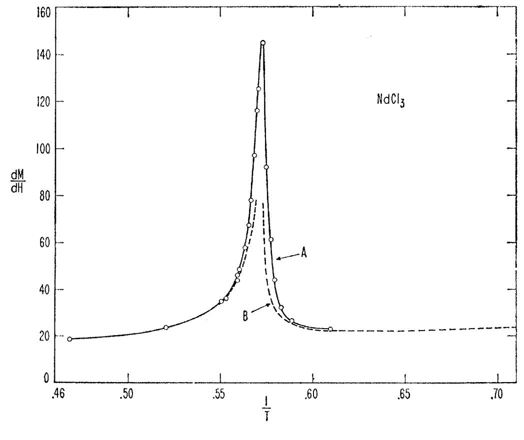

FIG. 6. The dependence of the differential susceptibility ((dM/dH) given in arbitrary units, of a single crystal of NdCl$_3$ on a dc field applied perpendicular to the crystal c axis (with the ac measuring field parallel to the c axis) and on the temperature. Curve A gives (dM/dH) in zero applied dc field. Curve B gives (dM/dH) in an applied dc field of 50 Oe. The ac measuring frequency was 270 Hz and the ac measuring field was 0.14 Oe.

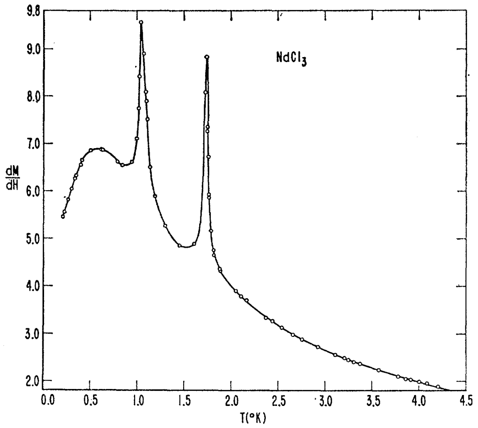

FIG. 7. The temperature dependence of the differential susceptibility (dM/dH) in arbitrary units, of a single crystal of NdCl$_3$ with the ac measuring field perpendicular to the crystal c axis. There was zero applied dc field. The ac measuring frequency was 270 Hz and the ac measuring field was 0.14 Oe.

obtained if 0.1% of the Nd^{3+} ions in the specimen had reached saturation.

The effect of slight dilution of the NdCl$_3$ with LaCl$_3$ is that the peaks occur at somewhat lower temperatures but the amplitudes of the peaks remain about the same. For example, a NdCl$_3$ single crystal containing 1% LaCl$_3$ exhibits the same features as a pure NdCl$_3$ crystal except that the positions of the peaks occur 5 mdeg lower in temperature. In addition, between 2.5 and 4.2°K Curie's law is still obeyed.

Although the amplitude of the low-temperature peak was always approximately the same for the various crystals studied, the amplitude of the high-temperature peak varied from crystal to crystal. Crystals taken from a batch all of which were grown from the same melt exhibited the same amplitude for the high-temperature peak. However, crystals taken from batches which were grown from different melts, although the melts were taken from the same batch of dehydrated NdCl$_3$, exhibited quite different peak amplitudes. The high-temperature peak of one crystal was unusually small; its amplitude was 24 times smaller than that shown in Fig. 1.

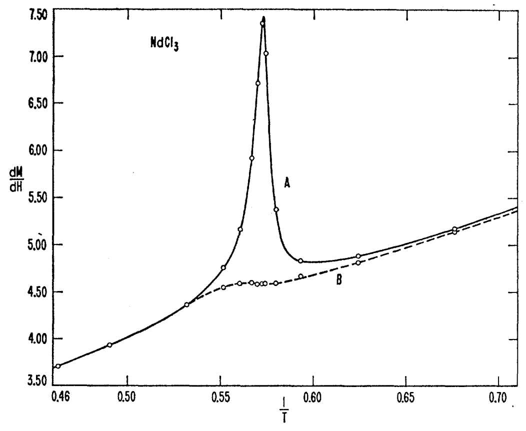

FIG. 8. The dependence of the differential susceptibility (dM/dH), given in arbitrary units, of a single crystal of NdCl$_3$ on a dc field applied parallel to the crystal c axis (with the ac measuring field perpendicular to the c axis) and on the temperature. Curve A gives (dM/dH) in zero applied dc field. Curve B gives (dM/dH) in an applied dc field of 50 Oe. The ac measuring frequency was 270 Hz and the ac measuring field was 0.14 Oe.

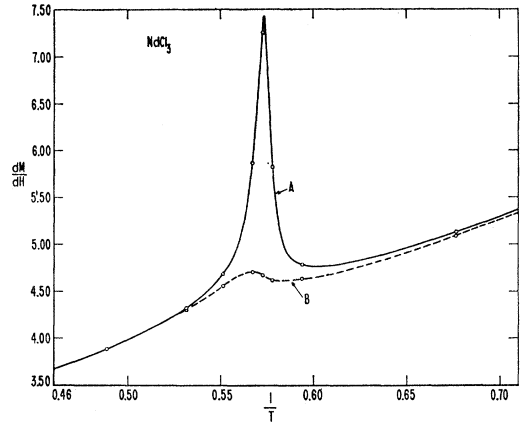

FIG. 9. The dependence of the differential susceptibility (dM/dH), given in arbitrary units, of a single crystal of NdCl$_3$ on a dc field applied perpendicular to the crystal c axis (with the ac measuring field also perpendicular to the c axis) and on the temperature. Curve A gives (dM/dH) in zero applied dc field. Curve B gives (dM/dH) in an applied dc field of 50 Oe. The ac measuring frequency was 270 Hz and the ac measuring field was 0.14 Oe.

(ii) $\chi_\perp$: *c Axis Perpendicular to the ac Measuring Field*

The zero-applied-field differential susceptibility below 4.2°K is shown in Fig. 7. As in the parallel case the sus-

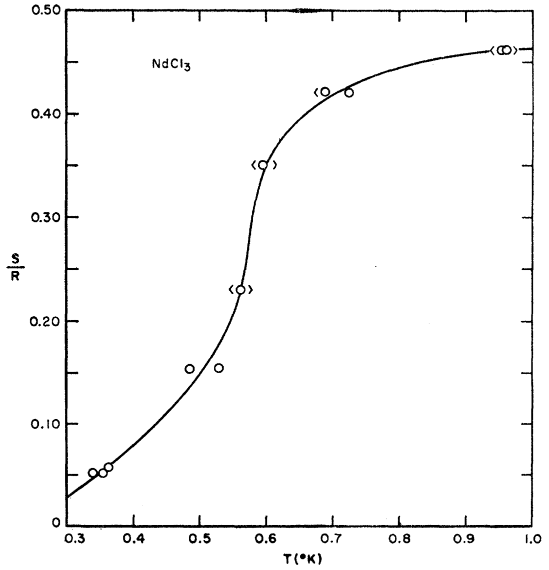

FIG. 10. Entropy as a function of temperature for a single crystal of NdCl$_3$.

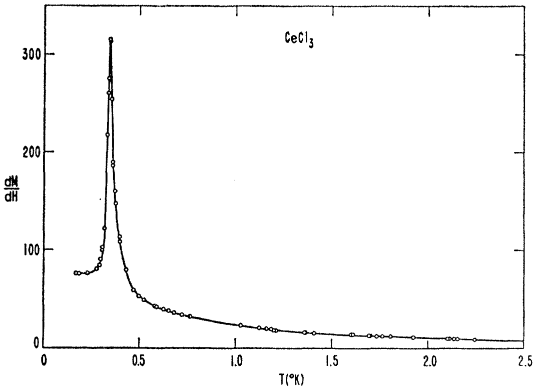

FIG. 11. The temperature dependence of the differential susceptibility (dM/dH), in arbitrary units, of a single crystal of CeCl$_3$. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The ac measuring frequency was 270 Hz.

ceptibility obeys the Curie law very accurately between 2.5 and 4.2°K. Again between 0.9 and 2.5°K the susceptibility exhibits two extremely narrow spikes at the same temperatures at which they occurred in the parallel case. Below 0.9°K the behavior is quite different from that of ordinary antiferromagnets in that the susceptibility goes through a maximum and decreases quite rapidly below 0.5°K. As in the parallel case the magnitude of the two spikes is dependent on the measuring frequency and on the amplitude of the ac measuring field. Again, the loss component of the susceptibility is zero except in the vicinity of the peaks and there it has two very narrow spikes with their maxima at the points of maximum slope on the low-temperature side of the peaks in χ'.

The magnitudes of the peaks in χ' are very sensitive to a dc field applied either parallel to the c axis (Fig. 8) or perpendicular to the c axis (Fig. 9). Unlike the $\chi_{\parallel}$ case, $\chi_{\perp}$ is relatively insensitive to the direction of the applied dc field; a field of 50 Oe nearly removes the spikes whether the field be parallel or perpendicular to the c axis. As in the $\chi_{\parallel}$ case the peaks are moved to higher temperatures by a dc field.

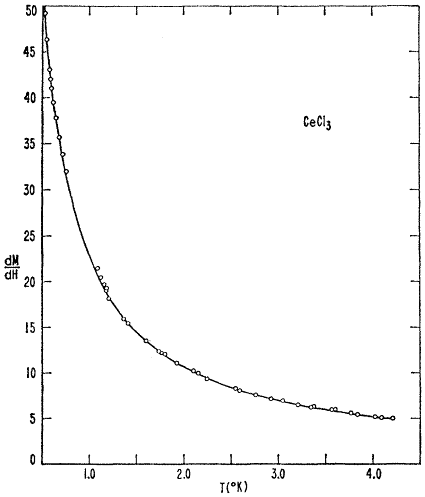

FIG. 12. The temperature dependence of the differential susceptibility (dM/dH), in arbitrary units, of a single crystal of CeCl$_3$. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The ac measuring frequency was 270 Hz.

(iii) *Specific Heat*

By adiabatically demagnetizing a NdCl$_3$ specimen (in this case not attached to a refrigerator salt) from various values of H/T the entropy versus temperature curve (Fig. 10) was obtained. In these experiments the dc field was parallel to the c axis and the ac measuring field was perpendicular to the c axis. The final temperature reached upon demagnetization was obtained by comparing the value of the differential susceptibility with the dM/dH versus T curve (Fig. 7). It should be noted that the temperature at which the entropy increases sharply is the same temperature at which the relatively broad maximum in $\chi_{\perp}$ occurs.

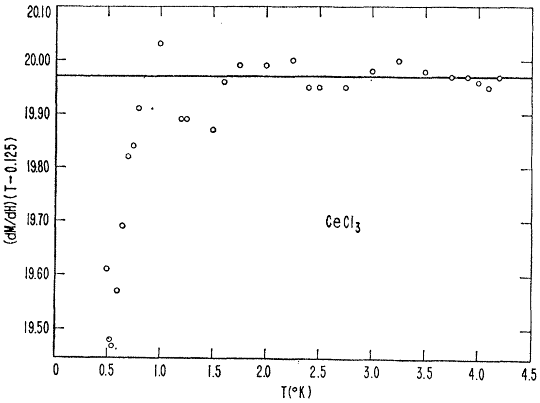

FIG. 13. Deviation of the differential susceptibility of a single crystal of CeCl$_3$ from the Curie-Weiss law, $(dM/dH) = C/(T-0.125)$. The product $(dM/dH)(T-0.125)$ is plotted in arbitrary units. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The straight line represents the Curie-Weiss law behavior.

(b) CeCl$_3$

The free Ce^{3+} ion is in a $^2F_{5/2}$ state. In the trichloride this state is split by the crystalline field into three Kramers doublets, the ground-state doublet being about 47 cm^{-1} below the first excited level.[19] The Ce^{3+} ion has an effective spin $S'=\frac{1}{2}$ and its spectroscopic splitting factor, measured by Hutchison and Wong,[3] has the principal values $g_{\parallel}=4.0366$ and $g_{\perp}=0.17$.

(i) $\chi_{\parallel}$: *c Axis Parallel to the ac Measuring Field*

The zero-applied-field differential susceptibility below 4.2°K is shown in Figs. 11 and 12. Between 0.80 and

4.2°K the susceptibility obeys the Curie-Weiss law, $\chi=C/(T+\theta)$, with $\theta=-0.125\pm0.01°$, very accurately as shown in Fig. 13. Between 0.49 and 0.80°K the susceptibility departs from the Curie-Weiss law in an "*antiferromagnetic*" manner as is also shown in Fig. 13. Below 0.49°K the susceptibility exhibits a very narrow and highly anomalous spike at 0.345±0.005°K (Fig. 11). From 0.25°K to the lowest temperature reached the susceptibility appears to be independent of temperature somewhat like the case for $NdCl_3$ immediately below its high-temperature peak (Fig. 1).

The magnitude of the $CeCl_3$ peak depends on the measuring frequency and on the amplitude of the ac measuring field in the same way as the magnitude of the $NdCl_3$ peaks. Likewise, the loss component of the susceptibility, χ'' is zero except in the vicinity of the peak and there it also manifests a very narrow spike with its maximum at the point of maximum slope on the low-temperature side of the peak in χ'.

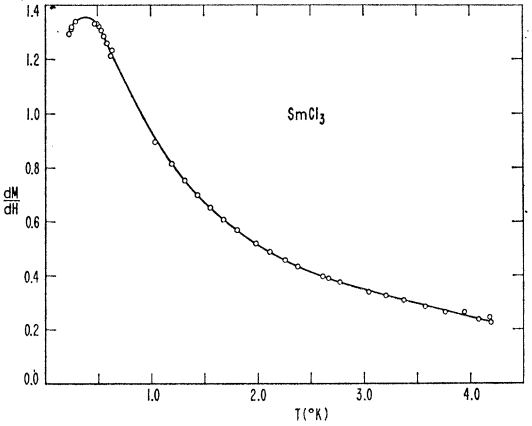

FIG. 14. The temperature dependence of the differential susceptibility (dM/dH), in arbitrary units, of a polycrystalline sample of $SmCl_3$. The ac measuring frequency was 270 Hz and there was zero applied dc field.

The detailed dependence of the magnitude of the peak on an applied dc field was not studied but, as was the case for the $NdCl_3$ peaks, a field of approximately 100 Oe completely eliminates the spike.

(*ii*) $\chi_\perp$: *c Axis Perpendicular to the ac Measuring Field*

We were unable to measure the perpendicular susceptibility because of the small value of $g_\perp$.

(c) $SmCl_3$

The free Sm^{3+} ion is in a ${}^6H_{5/2}$ state which is split by the crystalline electric field into three Kramers doublets. The ground state doublet is 41 cm^{-1} below the first excited level.[10] The Sm^{3+} ion has an effective spin $S'=\frac{1}{2}$ and its g values are[3]: $g_\parallel=0.5841$ and $g_\perp=0.6127$.

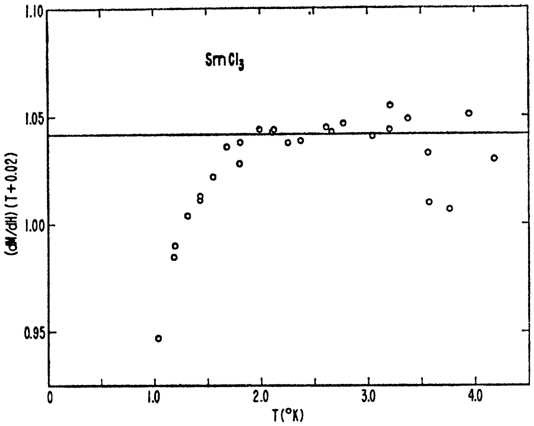

FIG. 15. Deviation of the differential susceptibility of a polycrystalline sample of $SmCl_3$ from the Curie-Weiss law, $(dM/dH)=C/(T+0.02)$. The product $(dM/dH)(T+0.02)$ is plotted in arbitrary units. The ac measuring frequency was 270 Hz and there was zero applied dc field. The straight line represents the Curie-Weiss law behavior.

(*i*) χ

We were unable to grow single crystals of $SmCl_3$, the crystals either undergoing some kind of decomposition during growth or containing a large amount of Sm^{2+}. In all cases the dehydrated $SmCl_3$, which was used for the melt, had neither of these defects.

Since $g_\parallel$ and $g_\perp$ are not very different, the susceptibility of a polycrystalline sample should be almost the same as that for a single crystal at temperatures above any cooperative transition. Only at temperatures below such a transition should there be an appreciable difference. Also any cooperative transition exhibited by a single crystal would also be exhibited at the same temperature by a polycrystalline sample. In view of these facts it was decided that measurements on polycrystalline $SmCl_3$ would be worth doing.

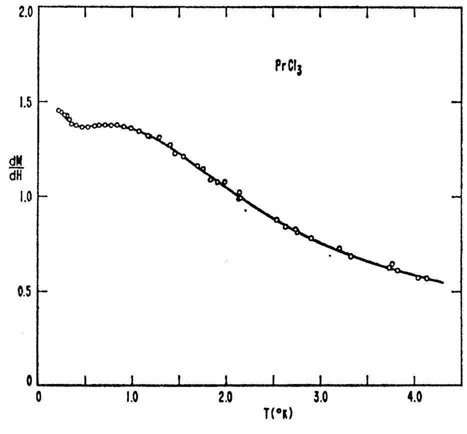

FIG. 16. The temperature dependence of the differential susceptibility (dM/dH), in arbitrary units, of a single crystal of $PrCl_3$. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The ac measuring frequency was 270 Hz.

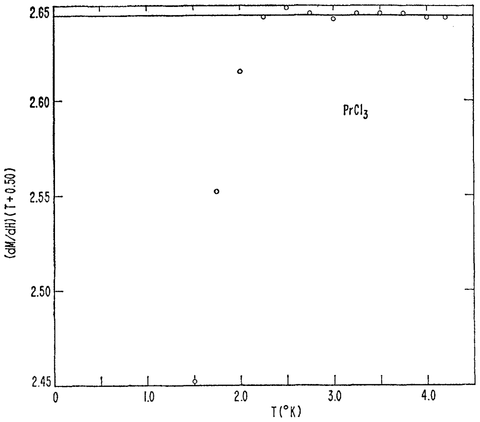

FIG. 17. Deviation of the differential susceptibility of a single crystal of PrCl$_3$ from the Curie-Weiss law, $(dM/dH) = C/(T+0.50)$. The product $(dM/dH)(T+0.50)$, is plotted in arbitrary units. The ac measuring field was parallel to the crystal c axis and there was zero applied dc field. The straight line represents the Curie-Weiss law behavior.

The zero-applied-field differential susceptibility below 4.2°K is shown in Fig. 14. Between 1.6 and 4.2°K the susceptibility obeys the Curie-Weiss law with $\theta = 0.02 \pm 0.01°$ quite accurately as shown in Fig. 15. Below 1.6°K there is an "antiferromagnetic" departure from the Curie-Weiss law as is also shown in Fig. 15. The susceptibility goes through a maximum at 0.385±0.005°K but in this case there is no spike as was the case for NdCl$_3$ (Fig. 1) and CeCl$_3$ (Fig. 11). The SmCl$_3$ exhibited no measurable loss (i.e., $\chi'' = 0$) throughout the entire temperature range.

The susceptibility was independent of an applied dc field.

(d) PrCl$_3$

The free Pr^{3+} ion is in a $^3H_4$ state which is split by the crystalline electric field. A ground state doublet lies some 33 cm^{-1} below the first excited state.[4,5] Pr^{3+} is a non-Kramers ion but owing to random deviations from the ideal symmetry $g_\perp$ is not zero. The g values have been measured by means of paramagnetic resonance.[3] They are: $g_{\parallel} = 1.035$ and $g_\perp = 0.1$.

(*i*) $\chi_{\parallel}$: *c Axis Parallel to the ac Measuring Field*

The zero-applied-field differential susceptibility below 4.2°K is shown in Fig. 16. Between 2.1 and 4.2°K the susceptibility obeys the Curie-Weiss law where $\theta = 0.50 \pm 0.05°$, very accurately as shown in Fig. 17. There is a rather flat maximum in the susceptibility at 0.735 ±0.025°K; below 0.45°K the susceptibility increases with decreasing temperature. This salt resembles SmCl$_3$ in exhibiting a susceptibility independent of applied dc field, zero loss component and no susceptibility spike throughout the entire temperature range in which measurements were made.

(*ii*) $\chi_\perp$: *c Axis Perpendicular to the ac Measuring Field*

We were unable to measure the perpendicular susceptibility because of the small value of $g_\perp$.

IV. DISCUSSION

For CeCl$_3$ and NdCl$_3$ the sharp increases in the susceptibility as the temperature is lowered strongly suggest that cooperative transitions associated with magnetic ordering take place. We shall give a semiquantitative interpretation of these transitions; some of the precise details, however, have not yet been fully elucidated. For the present we shall consider only NdCl$_3$ since we believe our data, which reveal the remarkable behavior of this compound, are reasonably complete. We return later to a consideration of the other rare-earth trichlorides.

Figure 18 is a drawing of the trichloride lattice. The nearest-neighbor rare-earth ions to each Nd^{3+} ion are two other Nd^{3+} ions, one above and one below on the c axis at a distance[2] of 4.231 Å. A Nd^{3+} ion is "connected" to each of its nearest-neighbor Nd^{3+} ions by three identical "bridges" with chlorine intermediaries. Each Nd^{3+} ion has as next-nearest-neighbor rare-earth ions six Nd^{3+} ions which lie in two planes perpendicular to the c axis, one above and one below the central ion. A Nd^{3+} ion is "connected" to each of its next-nearest-neighbor Nd^{3+} ions by two identical "bridges" with chlorine intermediaries. The next nearest-neighbor Nd^{3+}-Nd^{3+} distance is 4.758 Å. The smallest distance between two Nd^{3+} ions which are in the same plane perpendicular to the c axis is 7.381 Å. These ions are not "connected" via chlorine "bridges."

We postulate that there are superexchange interactions via the Cl$^-$ ions between a Nd^{3+} ion and its nearest-neighbor and its next-nearest-neighbor Nd^{3+} ions. It seems unlikely that the $4f$ electrons are exchanged. It is more probable that the screening $5s$ and $5p$ electrons are exchanged and that there is a resultant polarization of the magnetic electrons. The absence of any chlorine hyperfine structure in the electron-spin-resonance experiments[24] indicates that the $4f$ wave functions do not overlap the Cl$^-$ ions.

The two superexchange interactions (between nearest neighbors, and between next-nearest neighbors) should have comparable magnitudes. The exchange between neighbors should be stronger than that between next-nearest neighbors by a factor $\frac{3}{2}$ since the former involves three "bridges" and the latter only two. The smaller distance may also relatively enhance the nearest-neighbor interaction.

From the spatial arrangement of the ions it appears as though the next-nearest-neighbor interaction could be either ferromagnetic or antiferromagnetic, but that the nearest-neighbor interaction could only be ferromagnetic.

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[24] C. A. Hutchison, Jr. (private communication).

A simple, two-sublattice, molecular field model can be used to account for some of the features of the susceptibility curve. The Nd^{3+} ions can be divided between two sublattices in such a way that the nearest neighbors of an ion lie on the same sublattice, and the next-nearest neighbors lie on the other sublattice. If we assume that the sublattice magnetizations follow Curie's law at "high" temperatures we can write, in the usual way,

$$\begin{aligned} TM_A&=\tfrac{1}{2}C(H-\lambda' M_B+\lambda'' M_A)\,,\\ TM_B&=\tfrac{1}{2}C(H-\lambda' M_A+\lambda'' M_B)\,. \end{aligned} \tag{1}$$

It will be shown that λ' and λ'' are both positive. It follows from (1) that

$$\chi=\frac{M}{H}=\frac{C}{T-\frac{1}{2}C(\lambda''-\lambda')}\,. \tag{2}$$

The experimental results for $NdCl_3$ indicate that $|\frac{1}{2}C(\lambda''-\lambda')|<0.01°$. Therefore $\lambda''\cong\lambda'$ and it is clear that if one of the sublattice couplings is ferromagnetic the other is antiferromagnetic.

The true Curie temperature, that is the temperature at which a spontaneous sublattice magnetization appears with $H=0$, is given by

$$T_c=\tfrac{1}{2}C(\lambda''+\lambda')\cong C\lambda''. \tag{3}$$

If we identify T_c with either of the susceptibility peaks in $NdCl_3$ it follows that $\lambda''>0$. Consequently we have established, within the framework of this model, that the nearest-neighbor superexchange coupling is ferromagnetic and that the next-nearest-neighbor superexchange coupling is antiferromagnetic.

We shall now consider the susceptibility in a somewhat better approximation than that afforded by the molecular field theory. We write the Hamiltonian as

$$\mathcal{H}=\mathcal{H}_0+H\mathcal{H}_M\,, \tag{4}$$

where $\mathcal{H}_0$ includes all the terms that do not depend explicitly on the applied field H. By expanding the partition function and differentiating we obtain, in the usual way,

$$\frac{dM}{dH}=\frac{1}{kT}\left(a_1-\frac{a_2}{kT}+\frac{a_3}{k^2T^2}-\cdots\right), \tag{5}$$

where

$$a_1=\langle\mathcal{H}_M{}^2\rangle\,,$$
$$a_2=\langle\mathcal{H}_0\mathcal{H}_M{}^2\rangle\,,$$

$$\begin{aligned} a_3=\tfrac{1}{3}\langle\mathcal{H}_0{}^2\mathcal{H}_M{}^2\rangle+\tfrac{1}{6}\langle\mathcal{H}_0\mathcal{H}_M\mathcal{H}_0\mathcal{H}_M\rangle \\ -\tfrac{1}{2}\langle\mathcal{H}_M{}^2\rangle\langle\mathcal{H}_0{}^2\rangle+\tfrac{1}{2}H^2\langle\mathcal{H}_M{}^4\rangle-\tfrac{3}{2}H^2\langle\mathcal{H}_M{}^2\rangle^2. \end{aligned}$$

The Curie constant is given by

$$C=\langle\mathcal{H}_M{}^2\rangle/k\,, \tag{6}$$

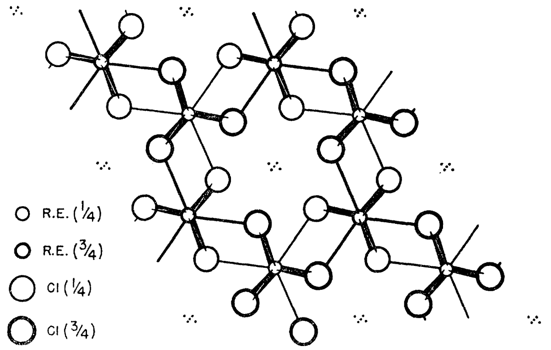

FIG. 18. The crystal structure of the rare-earth trichlorides (La through Gd).

and the Weiss constant[25] is given by

$$\theta=\langle\mathcal{H}_0\mathcal{H}_M{}^2\rangle/k\langle\mathcal{H}_M{}^2\rangle\,. \tag{7}$$

We shall assume that the superexchange interaction between rare-earth ions is isotropic, and has the form

$$-\sum_{i<j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j\,.$$

J_{ij} is positive for ferromagnetic exchange and negative for antiferromagnetic exchange. The true Hamiltonian also contains the terms

$$-\sum_i \boldsymbol{\mu}_i\cdot\mathbf{H}+\sum_{i<j}\left(\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j-3\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij}\boldsymbol{\mu}_j\cdot\frac{\mathbf{r}_{ij}}{r_{ij}{}^2}\right)r_{ij}{}^{-3}\,,$$

where

$$\boldsymbol{\mu}_i=-\beta(\mathbf{L}_i+2\mathbf{S}_i)\,.$$

$\mathcal{H}$ operates within the complete manifold of states.

At the temperatures of interest here only a few of the lowest states are occupied. It is therefore advantageous to replace the true Hamiltonian by an effective or spin Hamiltonian which operates only within the ground multiplet. For the compounds $CeCl_3$ through $EuCl_3$ the ground multiplet is a doublet; for $GdCl_3$ it is an octet but since $L=0$ the effective spin operator is identical with the true spin operator. These fortunate circumstances make it possible to write the effective Hamiltonian as[26]

$$\begin{aligned} \mathcal{H}_{\text{eff}}=-\sum J_{ij\alpha}S_{i\alpha}{}'S_{j\alpha}{}'+\beta\sum g_\alpha H_\alpha S_{i\alpha}{}' \\ +\beta^2\sum g_\alpha g_\beta S_{i\alpha}{}'S_{j\beta}{}'\left\{\delta_{\alpha\beta}-\frac{3r_{ij\alpha}r_{ij\beta}}{r_{ij}{}^2}\right\}r_{ij}{}^{-3}\,. \end{aligned} \tag{8}$$

$\mathbf{S}'$ is the effective spin operator. The coefficients $J_{ij\alpha}$ and g_α are chosen to make

$$J_{ij}\langle|S_{i\alpha}S_{j\alpha}|\rangle=J_{ij\alpha}\langle|S_{i\alpha}{}'S_{j\alpha}{}'|\rangle$$

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[25] With this choice of sign we have $\chi=C/(T+\theta)$.

[26] Latin indices refer to ions; Greek indices refer to coordinate axes.

TABLE I. Values of the lattice sum

$$\sum_{j\,(i<j)} \left(1-\frac{3z_{ij}^2}{r_{ij}^2}\right) r_{ij}^{-3}$$

for spheres of various radii about a Nd^{3+} ion in $NdCl_3$.

Radius (Å)	Sum (cm^{-3})
5	-15.07×10^{21}
10	-11.91
15	-14.14
20	-12.73
25	-13.54
30	-13.46
35	-12.92
40	-13.32

and

$$\langle |L_{i\alpha}+2S_{i\alpha}|\rangle = g_\alpha \langle |S_{i\alpha}'|\rangle .$$

The states on the left are the ground eigenstates of the true Hamiltonian; the states on the right are the eigenstates of S_z'.

Even though the exchange coupling has been assumed to be isotropic one can expect that it will appear anisotropic when expressed in terms of the effective spin operators. We shall set

$$\begin{aligned} J_{ij\alpha} &= J_{1\alpha} \quad \text{for } i,\, j \text{ nearest neighbors},\\ &= J_{2\alpha} \quad \text{for } i,\, j \text{ next-nearest neighbors},\\ &= 0 \quad\;\; \text{otherwise}. \end{aligned}$$

One then obtains

$$C = N\beta^2 g_H{}^2 S'(S'+1)/3k\,, \tag{9}$$

$$\theta = \left[\frac{2S'(S'+1)}{3k}\right] \times \sum_{\substack{j\\(i<j)}} \left\{ -J_{ijH} + \beta^2 g_H{}^2 \left(1-\frac{3r_{ijH}{}^2}{r_{ij}{}^2}\right) r_{ij}{}^{-3} \right\} . \tag{10}$$

Here the subscript H refers to the direction of the applied field which is assumed to be along one of the coordinate axes.

The contribution of the dipole-dipole interaction to the Weiss constant can be calculated. Table I contains values of

$$\sum_{\substack{j\\(i<j)}} \left(1-\frac{3z_{ij}{}^2}{r_{ij}{}^2}\right) r_{ij}{}^{-3}$$

for spheres of various radii about a Nd^{3+} ion in the $NdCl_3$ lattice. The sum appears to converge to a value of approximately -13×10^{21} cm^{-3}. The corresponding contribution of the dipolar interaction to the Weiss constant in $NdCl_3$ is $-0.065°$.

If we ignore the dipole-dipole interaction in $NdCl_3$ we can relate the exchange constants to the molecular field parameters. We find

$$\begin{aligned} J_{1z} &= \tfrac{1}{4} N\beta^2 g_z{}^2 \lambda'' > 0\,,\\ J_{2z} &= -\tfrac{1}{12} N\beta^2 g_z{}^2 \lambda' < 0\,. \end{aligned}$$

Since, according to the molecular field theory, $\lambda' \cong \lambda''$ we have $|J_{1z}| \cong 3|J_{2z}|$, in reasonable agreement with the estimate made earlier ($|J_1| = \frac{3}{2}|J_2|$).

The description of the magnetic behavior of $NdCl_3$ to which we are led is, then, the following. The exchange interaction between nearest neighbors is about three times as strong as that between next-nearest neighbors. It is ferromagnetic and causes the alignment of ions in chains parallel to the *c* axis. We associate the susceptibility peak at 1.745°K with this ferromagnetic ordering. The next-nearest-neighbor interaction is relatively ineffective at this temperature so that there is no correlation between the aligned chains; one would expect equal numbers to have their moments parallel and antiparallel to the *c* axis. The total moment of a sample is indeed small. The variation of the height of the susceptibility peak at 1.745°K in different samples can possibly be ascribed to unequal numbers of chains aligned parallel and antiparallel to the *c* axis. This inequality might be produced by impurities, strains or surface effects.

The susceptibility decreases on the low-temperature side of the peak because the individual spins are locked into the chains.

When the temperature is lowered sufficiently the antiferromagnetic interaction between next-nearest neighbors becomes important. Its effect is to cause neighboring chains to become antiferromagnetically aligned. We associate the susceptibility peak in $NdCl_3$ at 1.035°K with the cooperative antiferromagnetic ordering of the previously aligned chains.

The antiferromagnetic ordering is completely consistent with the ferromagnetic ordering at the higher temperature. Another way of describing the order below 1.035°K is by saying that the ions are aligned in sheets which are perpendicular to the *c* axis. All ions in one sheet are parallel to the *c* axis, and all ions in the two neighboring sheets are antiparallel to the *c* axis.

We can account qualitatively for the dependence of the differential susceptibility on the amplitude of the measuring field, and on the applied constant field by assuming the material, when alignment occurs, is hysteretic and saturates at low fields.

It we ignore the dipole-dipole interaction we can, without undue difficulty, obtain the first few of the higher order terms in the expression for the susceptibility. We do not quote the results we have obtained here because they have very limited usefulness in the analysis of the experimental data.

What has been said about $NdCl_3$ should presumably apply to the other rare-earth trichlorides as well. To see why only one susceptibility spike has been observed in

$CeCl_3$ and none at all in $PrCl_3$ and $SmCl_3$ we must try to apply some quantitative considerations.

The quantities to be considered are the dipole-dipole interaction and the superexchange interaction. The former can be calculated for one of the compounds and then scaled by the g values and the volume factors for the others. Approximate values for the contribution of the dipole-dipole interaction to the Weiss constant are given in Table II. The dipole-dipole interaction is probably unimportant in all the compounds, with the possible exception of $CeCl_3$.

The superexchange interaction may increase slightly from $CeCl_3$ to $GdCl_3$ due to the lanthanide contraction and may involve rather complicated shielding and polarization effects. Our intuitive expectation is that the exchange interaction is nearly the same in all compounds under investigation. However, it is not the "true" exchange but the "effective" exchange which appears in the formulas for the susceptibility and the latter depends on the matrix elements within the ground multiplet of the true spin operator. We have used wave functions we had available[27–29] to calculate these matrix elements for $CeCl_3$, $PrCl_3$, and $NdCl_3$; the results for the relative values of the effective exchange in the axial direction are also given in Table II.

If we ignore the dipole-dipole interaction, and if the general basis of the theory is correct, then we can infer from Table II that the susceptibility of $CeCl_3$ should have peaks similar to those of $NdCl_3$ but at temperatures lower by a factor 5.1. That is, they should be at approximately 0.20 and 0.34°K. A peak actually occurs at 0.345°K in $CeCl_3$ while 0.20° is at the lower limit of the experimental temperature range. The position of the lower peak in $CeCl_3$ may be affected by the dipolar interaction which, relative to the superexchange interaction, is stronger in $CeCl_3$ than in $NdCl_3$.

The susceptibility peaks which one might expect for $PrCl_3$ should occur at temperatures below 0.12°K. In the absence of reliable ground-state wave functions it is difficult to estimate where the susceptibility peaks for $SmCl_3$ should lie.

TABLE II. Contribution of dipole-dipole interactions to the Weiss constant in the axial direction, and relative values of the contribution of the superexchange interaction to the Weiss constant for various rare-earth trichlorides.[a]

	Dipole-dipole	Exchange
$CeCl_3$	−0.066°	0.56
$PrCl_3$	−0.004°	0.19
$NdCl_3$	−0.065°	2.88
$SmCl_3$	−0.001°	
$GdCl_3$	−0.34°	

[a] The contribution of the dipole-dipole interaction to the Weiss constant in the axial direction is taken to be −0.065° for $NdCl_3$ and scaled by the relative g values and spins for the other compounds.

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APPENDIX

We have considered and rejected quite a few hypotheses about the origin of the sharp susceptibility peaks in $CeCl_3$ and $NdCl_3$:

(1) The peaks are not due to rare-earth impurities. If they were they should occur at the same temperature in $CeCl_3$ and $NdCl_3$ and one would expect to find them in the other rare-earth trichlorides.

(2) They are not due to an audiofrequency resonance since they occur for all measuring frequencies.

(3) The peaks are not due to the Dzialoshinsky phenomenon. The threefold symmetry precludes any antiferromagnetic ordering perpendicular to the c axis. Therefore the appearance of a small ferromagnetic moment due to a canting of the antiferromagnetically aligned spins can be ruled out.

(4) The peaks are not due to vacancies or La^{3+} in the rare-earth sites. We demonstrated this fact experimentally by substituting 1% La in $NdCl_3$. The susceptibility was nearly unaffected.

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[27] J. C. Eisenstein, unpublished calculations on $CeCl_3$.

[28] J. C. Eisenstein, in *Proceedings of the First International Conference, 1962* (Academic Press, Inc., New York, 1963), Vol. 1.

[29] J. C. Eisenstein, J. Chem. Phys. **39**, 2134 (1963).