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One- and three-dimensional antiferroelectric ordering in $PrCl_3$†

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Electric-susceptibility and specific-heat measurement in $PrCl_3$ show that *electric* dipole ordering occurs at low temperatures. One-dimensional ordering is observed above 0.4 K and is well described by the linear-chain *XY* model. Three-dimensional antiferroelectric ordering occurs at 0.4 K. The electric dipole moments are developed by the non-Kramers-doublet ground states of the praseodymium ions. The nearest-neighbor electric dipole-dipole interaction calculated from the measured dipole moment is of the correct sign and of approximately the correct magnitude to account for the nearest-neighbor interaction deduced from the fitting of the specific heat to the one-dimensional *XY* model. The small change in the magnitude of the specific-heat anomaly (~ 15%) and the small shift of the three-dimensional transition temperature (~ 5%) when a magnetic field of 2.2 T was applied provides further evidence that the ordering in $PrCl_3$ is of nonmagnetic origin.

The low-temperature properties of the rare-earth halides have, up until now, been discussed in terms of magnetic dipole and/or exchange interactions and higher electric and magnetic multipole terms.[1] For ions with an even number of electrons, in certain symmetry sites, electric dipole effects must also be considered.[2] We present electric-susceptibility and specific-heat measurements on the non-Kramers-system $PrCl_3$ which show that electric dipole ordering occurs in this system.

The site symmetry of the Pr^{3+} ion in $PrCl_3$ is C_{3h}, and crystal-field splitting of the $4f^2\,{}^3H_4$ multiplet leaves a doubly degenerate non-Kramers ground state separated by 33 cm^{-1} from the first excited state.[3] Low-temperature specific-heat measurements[4] showed a sharp anomaly at 0.4 K and a broad maximum at 0.85 K. These were attributed to antiferromagnetic ordering in three and one dimensions, respectively.[4] However, subsequent nuclear-quadrupole-resonance measurements[5] showed no magnetic field at the Cl sites below 0.4 K, ruling out magnetic ordering. Furthermore, the crystal symmetry was lowered at 0.4 K, and it was suggested[5] that a cooperative Jahn-Teller transition[6] took place at this temperature. Magnetic-susceptibility measurements,[4] which showed *no* anomaly at the 0.4-K phase transition, also suggest that the ordering is nonmagnetic.

EPR measurements on Pr ions in $LaCl_3$ have provided detailed information on the single Pr ion[7] and on nearest-neighbor Pr pairs.[8] It was pointed out[2] that a non-Kramers doublet in C_{3h} symmetry can have a magnetic dipole moment parallel to the threefold axis, and an electric dipole moment perpendicular to the threefold axis. In the effective $S=\frac{1}{2}$ formalism for the non-Kramers doublet, neglecting hyperfine interactions and random crystal distortions, the single-ion Hamiltonian can be written[9, 10]

$$\mathcal{H}_i = g_{\parallel}\mu_B H^z S_i^z + \gamma(E^x S_i^x + E^y S_i^y)\,,$$

with $g_{\parallel} = 1.031 \pm 0.003$ and $\gamma = (4.0^{+4.0}_{-2.0}) \times 10^{-31}$ C m. The pair measurements[8, 10] showed that the interaction between nearest-neighbor Pr ions, which are situated along the threefold symmetry axis, could be described by

$$\mathcal{H}_{i,\,i+1} = J_{00} S_i^z S_{i+1}^z - J_{1-1}(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)\,,$$

with $J_{00}/k = +0.11 \pm 0.14$ K and $J_{1-1}/k = -2.85 \pm 0.14K$.[10] Hence this interaction is nearly of the ideal *XY* form. No other ion-ion interactions were observed, although sizable ones cannot be ruled out. If only nearest-neighbor interactions are important in $PrCl_3$, its properties should be well described by the linear chain *XY* model.[11, 12] By comparing the specific heat of $PrCl_3$ with Katsura's theoretical specific heat[11] using the above value of J_{1-1}, Pfortmiller[10] obtained a good fit to the broad maximum at 0.85 K, hence identifying this feature with one-dimensional ordering of Pr ions.

We measured the specific heat by a heating pulse decay method[13] in zero magnetic field and in a field of 2.2 T applied at 45° to the threefold axis to study the effect of a magnetic field upon the ordering behavior. Figure 1 shows our results and a fit to Katsura's linear chain model with $|J_{1-1}|/k = 2.5$ K. The dashed curve is for the same model but for the case of an applied magnetic field such that $mH/J = 0.3$ (Katsura's notation). While not perfect, a reasonable fit is obtained if H is taken to be the magnetic field component along the threefold axis and if $g_{\parallel} = 0.7 \pm 0.1$,[14] in particular, the magnetic Zeeman effect *depresses* the maximum. The linear chain *XY* model does therefore describe $PrCl_3$ above 0.4 K reasonably well. It is further noted that the effect of a 2.2-T magnetic field which pro-

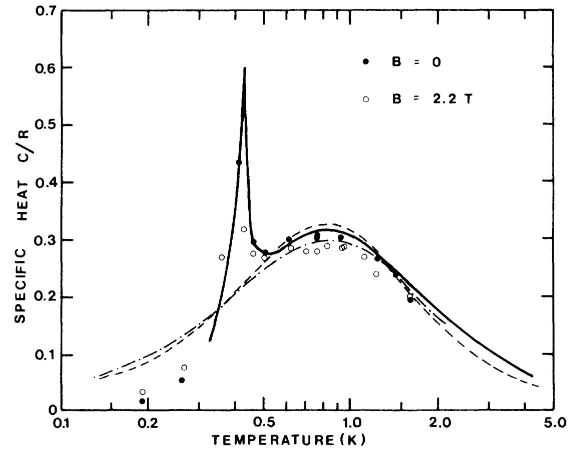

FIG. 1. Specific heat of $PrCl_3$ as a function of temperature in zero field and in a field of 2.2 T applied at 45° to the threefold axis. The solid line represents the data of Colwell *et al.* in zero field, except that their lower anomaly has been redrawn at 0.43 K instead of 0.41 K to correspond to our sample. The dashed line is the specific heat calculated by Katsura for the *XY* linear chain model with $|J_{1-1}|/k = 2.5$ K. The dash-dot line is the same model, but for an applied field such that $mH/J = 0.3$.

duces an interaction energy with the magnetic moment of ~0.35 K causes only a small decrease in the critical temperature from 0.43 to 0.41 K. These effects provide further evidence that the ordering in $PrCl_3$ is not magnetic.

Since the magnetic moment can only lie along the threefold axis, it is unlikely that magnetic moments can be responsible for the *XY* interaction. We propose that this interaction is due to Pr electric dipole moments. The possibility of electric dipole interactions in this system and its *XY* form in the $S = \frac{1}{2}$ representation have been previously suggested.[15] To test this proposal, the electric susceptibility of $PrCl_3$ was measured as a function of temperature and orientation. The susceptibility was determined from the capacitance of a capacitor formed by two copper plates sandwiching the crystal. The capacitor was thermally anchored to, but electrically isolated from, the sample chamber of a dilution refrigerator. Measurements were made on three samples cut so that the E field across the capacitor was parallel, perpendicular, and at 45° to the crystalline axis. The cross-sectional areas of the samples were about 30 mm^2 and the thickness about 0.5 mm. The dielectric constant ϵ of each sample was deduced from the capacitance and from the dimensions of the sample (area A and thickness d), the capacitance being equal to $\epsilon\epsilon_0 A/d$ +const. The electric susceptibility is then $\chi = \epsilon - 1$. Since a covering of mineral oil was required to prevent sample deterioration, and the oil filled part of the capacitor not filled by crystal, the constant in the equation for capacitance is not known. Thus, the dielectric constant and electric susceptibility have to be presented with an arbitrary origin. Figure 2 shows the dielectric constant, or electric susceptibility, of the three samples measured at 2 kHz with an excitation voltage of 200 mV, and of one of the samples at 200 Hz. Clearly, the temperature-dependent part of the electric susceptibility is highly anisotropic and implies an electric dipole moment within the perpendicular plane. Furthermore, in the plane the susceptibility showed approximate Curie-law behavior down to about 2 K, with a broad maximum at about 1 K. These features, when considered with the other evidence, must imply the ordering of the electric dipoles as the temperature is lowered.

Recently, Capel *et al.*[16] formulated a high-tem-

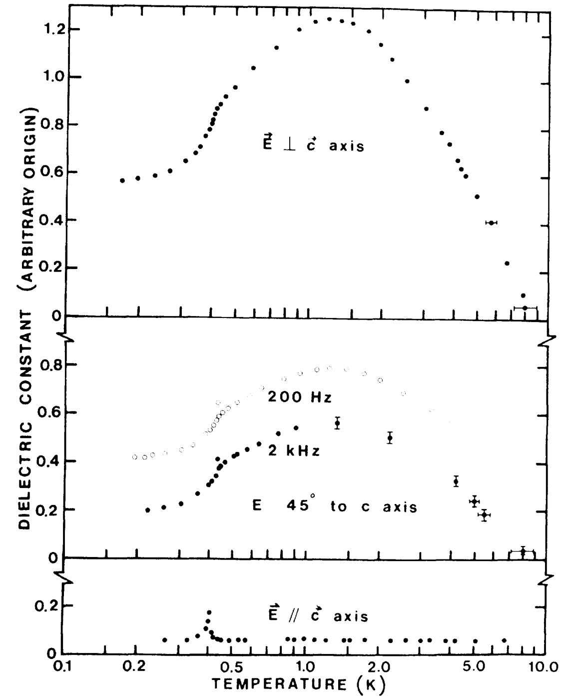

FIG. 2. Dielectric constant of $PrCl_3$ as a function of temperature for three samples such that the E field was parallel to, at 45° to, and perpendicular to the threefold axis. The 45° sample was from the same boule as used for specific-heat and thermal conductivity measurements, and shows a lower transition temperature of 0.43 K. The parallel and perpendicular samples were from a different boule, and show a transition temperature of 0.41 K. The effect of a 2.2-T H field applied along the E field was to decrease the lower transition temperature by 0.03 K for the parallel sample, and to cause no change, within 0.005 K, for the perpendicular sample. For the 45° angle results the 200-Hz and 2-kHz data have been separated for convenience; they do not have the same origin.

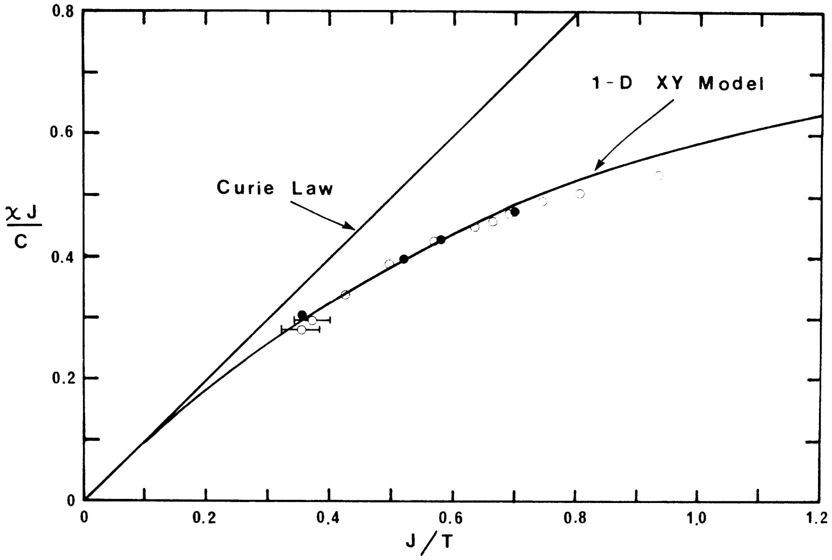

FIG. 3. Matching of the high-temperature experimental susceptibility data to the high-temperature expansion series for the perpendicular susceptibility of the 1-D *XY* model. The solid lines represent the Curie law for noninteracting dipoles ($\chi = C/T$) and the expansion given in the text, with $J = 2.85$K. The matching above 3 K was achieved by allowing the Curie constant to be a variable. The departure of experiment from the theoretical curve for $J/T > 0.8$ is attributed to the phase transition at 0.4 K. The open circles are the perpendicular susceptibility data, with $C = 9.8$ K and the closed circles are the 45° susceptibility with $C = 5.0$ K.

perature expansion for the perpendicular susceptibility of the one-dimensional (1-D) *XY* system. There is no exact analytic solution for this susceptibility. This expansion has been used to determine the Curie constant, and hence the dipole moment of the Pr^{3+} ions, from the experimental data. The susceptibility is given by

$$\frac{\chi J}{C} = \frac{J}{T} - \frac{1}{2}\left(\frac{J}{T}\right)^2 + \frac{1}{12}\left(\frac{J}{T}\right)^3 + \frac{1}{96}\left(\frac{J}{T}\right)^4 - \frac{1}{240}\left(\frac{J}{T}\right)^5 - \frac{17}{23040}\left(\frac{J}{T}\right)^6 ,$$

where $J \equiv J_{1\,-1}/k_B$ is the interaction constant and C is the Curie constant. The expansion, which should be accurate for $0 < J/T < 1$ is shown in Fig. 3 and compared with the Curie law for noninteracting dipoles. The perpendicular and 45° experimental results were matched to the theoretical expansion for $T > 3$ K by taking $J = 2.85$ K,[10] and treating the Curie constant as a variable parameter. For $PrCl_3$, departures are expected at low temperatures because of the three-dimensional (3-D) transition. The matching shown in Fig. 3 required Curie constants of 9.5 K for the perpendicular results and 5.0 K for the 45° results. The Curie constant for classical dipoles confined to a plane, as well as for dipoles with three equally likely equilibrium orientations within the plane is

$$C_{\perp} = (Np^2/2\epsilon_0 k_B)(E_{\text{loc}}/E)$$

for the perpendicular susceptibility and for the 45° susceptibility where only a component of p is measured,

$$C_{45^\circ} = (Np^2/4\epsilon_0 k_B)(E_{\text{loc}}/E) ,$$

where p is the electric dipole moment and E and E_{loc} are the applied electric field and the corresponding local field at the Pr ion. Unfortunately, the correct local-field correction for the $PrCl_3$ structure is not known to us and so we take $E_{\text{loc}} = 2E$ which is a typical value for a cubic ionic crystal. The dipole moment obtained in this way was 3.3×10^{-31} C m. The dipole-dipole interaction between two nearest-neighbor Pr ions along the threefold axis then becomes

$$p^2/4\pi\epsilon_0 z^3 k_B = 0.98 \text{ K}.$$

This quantity should be compared with the interaction energy deduced from EPR pair measurements of $|J_{1\,-1}|/2k = 1.43$ K. In view of the uncertainty in the local-field corrections, the agreement can be considered very good and we conclude that the electric dipole-dipole interaction is sufficient to describe the 1-D *XY* interaction in $PrCl_3$ above 0.4 K both in magnitude and sign. A similar dipole moment of $p = (2.0^{+2.0}_{-1.0}) \times 10^{-31}$ C m was determined from EPR spectra for the Pr ions when in $LaCl_3$.[8]

Both the specific-heat and electric susceptibility anomalies in the vicinity of 0.4 K are sharp and may accordingly be identified with 3-D ordering. The features of interest in the electric susceptibility are the sharp peak when the field is along the threefold axis, repeated to a smaller extent in the 45° data, and the sharp fall at the transition temperature and horizontal intercept with the zero-temperature axis when the field is perpendicular to the threefold axis. This behavior is compatible with 3-D antiferroelectric ordering[17] but we cannot deduce the nature of the ordered state without further knowledge of interchain interactions and single-ion anisotropies.

The suggestion of Hessler and Carlson that $PrCl_3$ undergoes cooperative Jahn-Teller ordering seems quite compatible with our demonstration of electric dipole ordering, if it is assumed that the electric dipole is associated with some kind of transverse distortion which splits the Pr ground-state doublets. The effective ion-ion interactions would then be generated by a cooperative lattice distortion, but should be roughly described by the crude point-dipole interaction we have discussed, just as in the rare-earth vanadates,[18] the effective spin-spin interaction may be attributed to distortion-induced electric quadrupole moments.

An interpretation along these lines requires an investigation of these distortions and the symmetry of the ordered state.

Finally, as we remarked earlier it is clear that similar electric dipole effects may be expected in other even-electron rare-earth compounds. Pr ethyl sulfate is an obvious possibility, and we have observed 1-D antiferroelectric ordering which will be reported shortly.

After the initial submission of this manuscript, we noted that Washimiya and Naito[19] also have recently suggested the possibility of electric dipolar ordering in $PrCl_3$.

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