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Magnetic Ordering in $CrCl_3$ at the Phase Transition

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The Faraday-rotation of $CrCl_3$ crystals is investigated in the temperature range from 7 to 23.5 K and in fields up to 320 kA/m. The magnetic ordering sets in at $T = 16.8$ K whereas the maximum of the susceptibility is observed at $T = (15.5 \pm 0.2)$ K. Consequently during cooling first a two-dimensional ferromagnetic ordering at $T_c = 16.8$ K occurs in the hexagonal layers of the crystal, and the antiferromagnetic ordering between the layers appears at a somewhat lower temperature at $T_N = (15.5 \pm 0.2)$ K. A spin-flop is found in the antiferromagnetic state. It shows that $CrCl_3$ is not a metamagnet as often assumed. The flop-field is $H_{sf} = (13.0 \pm 0.5)$ kA/m at $T = 7$ K, corresponding to an anisotropy field of 780 A/m in the layer plane.

Es wird die Faraday-Drehung von $CrCl_3$-Kristallen im Temperaturbereich 7 bis 23,5 K und in äußeren Feldern bis 320 kA/m gemessen. Die magnetische Ordnung setzt bei $T = 16.8$ K ein, während das Maximum der Suszeptibilität bei $T = (15{,}5 \pm 0{,}2)$ K beobachtet wird. Die Untersuchungen lassen den Schluß zu, daß in $CrCl_3$ bei $T_c = 16{,}8$ K zunächst eine zweidimensionale ferromagnetische Ordnung in den hexagonalen Schichten des Kristalls auftritt und erst bei $T_N = (15{,}5 \pm 0{,}2)$ K die antiferromagnetische Ordnung zwischen den Schichten erscheint. Im antiferromagnetischen Zustand wird ein Spin-Flop beobachtet, der zeigt, daß $CrCl_3$ kein Metamagnet ist, wie vielfach angenommen wird. Die Spin-Flop-Feldstärke beträgt $H_{sf} = (13{,}0 \pm 0{,}5)$ kA/m bei $T = 7$ K, entsprechend einer Anisotropiefeldstärke von 780 A/m in der Schichtebene.

1. Introduction

Many investigations concerning $CrCl_3$ deal with the magnetic ordering in these crystals [1 to 6]. These measurements were made in a wide temperature range from about 0.4 K to room temperature and in external fields up to 30 kOe. The paramagnetic susceptibility exhibits a Curie-Weiss dependence with a positive paramagnetic Curie temperature near 29 K [7, 8]. The specific heat shows a λ-type anomaly at $T = 16.8$ K [9 to 11] related to a magnetic transition. A conspicuously strong field-dependent susceptibility is observed in the magnetic ordered state in these hexagonal layer-type crystals [7]. This behaviour is explained by a ferromagnetic coupling within each layer and a relatively weak antiferromagnetic coupling between adjacent layers, that can be disturbed in relatively weak external fields [6].

The crystals are suitable for measurements of magnetooptical rotation since they are moderately transparent in the visible spectral range and exhibit a sufficiently strong Faraday rotation [12 to 14]. Under certain circumstances this rotation is proportional to the magnetization of the crystal. In the investigations presented here the Faraday rotation as a function of temperature and external field in the range of the phase transition was measured. From that conclusions are drawn to the magnetic ordering in $CrCl_3$.

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2. Crystal Structure and Physical Properties

X-ray analysis of anhydrous $CrCl_3$ shows that the crystal consists of honeycomb layers of Cr^{3+} ions sandwiched between two close-packed layers of Cl^- ions [15]. Crystals grown from the vapour by sublimation undergo a polymorphic phase transition at about 240 K from monoclinic symmetry C2/m to rhombohedral symmetry $R\bar{3}$ with the space group C_{3i}^2. This transformation is strongly affected by crystal imperfections [16]. Fig. 1a shows the low-temperature form $R\bar{3}$. Four planes in an ABCA —— stacking are required to complete the unit cell containing six Cr^{3+} ions. The lattice constants of the form $R\bar{3}$ are $a_0 = 5.942$ Å and $c_0 = 17.33$ Å at 225 K [16], corresponding to nearest-neighbour distances for intralayer Cr^{3+} ions of 3.43 Å and for interlayer Cr^{3+} ions of 5.78 Å.

The covalent bonding within the "sandwiches" is much stronger than the interaction between them which is predominantly of van der Waals type. This fact accounts for the flake-like form of the crystals, as well as for the pronounced two-dimensional character of the magnetic ordering in the "isolated" sandwiches. Each Cr^{3+} ion has three nearest neighbours of Cr^{3+} ions in the hexagonal layers and is surrounded by six Cl^- ions in an octahedral coordination. There is a reasonably large overlap between the Cr^{3+} single electron 3d-orbitals and the Cl^- p-orbitals [17]. Via superexchange this leads to a ferromagnetic ordering inside the hexagonal Cr^{3+} ion layers, characterized by a positive exchange integral J_T. Neutron diffraction investigations [4] confirmed that at low temperature (4.2 K) the magnetic moments lie in the (001) planes with adjacent ferromagnetic layers being antiparallel, Fig. 1b, characterized by a negative exchange integral J_L. The measured g-value of 2.00 shows that the Cr^{3+} orbital moment is almost completely quenched in the predominantly octahedral crystal field. Therefore, the expected magnetocrystalline anisotropy should be small. Using the 225 K lattice constants and the spin-only moment of $3\mu_B$ per Cr^{3+} ion (16.750 e.m.u./mol) a saturation magnetization $I_s = 0.392$ Vs/m² is calculated.

Spin-wave analysis of NMR measurements [5, 6] yielded "isotropic" exchange constants $J_T/k_B = 5.25$ K and $J_L/k_B = -0.018$ K (corresponding molecular field $H_L \approx$

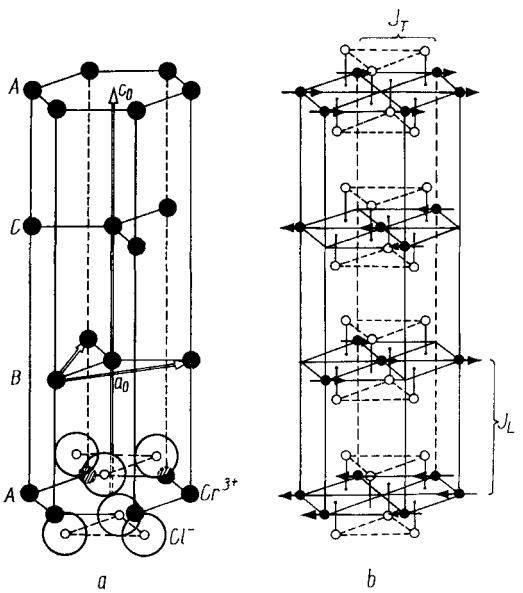

Fig. 1. a) Unit cell of $CrCl_3$ in the low temperature $R\bar{3}$ structure with lattice constants a_0 and c_0 (only two Cl^- ion layers are illustrated). b) Magnetic ordering of the Cr^{3+}-ion spins in the antiferromagnetic state (Cl^- ion places are indicated by hollowed circles)

≈ 67 kA/m) in the presence of a weak effective anisotropy field [18] in the antiferromagnetic state of $H_a(0) = 650$ Oe (≈ 52 kA/m) at 0 K. Furthermore a weak in-plane anisotropy corresponding to an anisotropy field in the (001) plane of about $H_{an} = 10$ Oe (800 A/m) is estimated; the preferred direction of sublattice magnetization in this plane, however, is not known. A nearly linear temperature dependence of sublattice magnetization is observed below $T = 8$ K, due to the two-dimensional nature of the magnetic ordering characterized by the ratio $(J_T Z_T / J_L Z_L) \approx 425$ ($Z_T = 3$; $Z_L = 2$).

The weak antiferromagnetic interaction between the layers can be overcome in moderate external fields. The spins in neighbouring sublattices become aligned parallel (ferromagnetic state) in a field of about 134 kA/m (≈ 1.68 kOe) lying in the (001) plane of the crystal. In fields perpendicular to this plane shape anisotropy has to be considered on account of the preferred flake-shaped habit of the crystals. In the ferromagnetic state $CrCl_3$ is found to be practically isotropic.

3. Experimental Details

Single crystals were grown from dehydrated fine-grained $CrCl_3$ by vacuum sublimation in a quartz tube at a temperature of about 700 °C. A temperature gradient of 1 K/cm guaranteed for the necessarily slow growth. Crystals obtained had an area up to 7×7 mm^2 and a thickness up to 300 μm. Water-free crystals are strongly hygroscopic. $CrCl_3$ crystals show two transmission windows in the visible spectral range, one between 700 and 570 nm and the other between 480 and 390 nm, combined with an absorption coefficient of about 10/mm each at $T = 4.2$ K. The crystals are uniaxial double-refracting, according to their crystal structure. The optical axis lies parallel to the hexagonal c-axis, which is also the surface normal of the crystals.

Those crystals were selected for the measurements that appeared free from defects under the microscope and showed the undisturbed interference pattern of concentric rings with a dark cross in the conoscopic beam path between crossed polarizers. The crystal thickness t was determined according to $t = t^* n$, where t^* is the apparent thickness when measured under the microscope between top and bottom side of the crystal and n is the refractive index, which is $n = 1.96$ for the used wavelength $\lambda = 432$ nm [13]. The following measurements were carried out at four selected crystals of thicknesses: 125, 160, 195, and 290 μm. The uncertainty of the thickness measurement was $\pm 2\%$ each. The corresponding demagnetizing factors N_c are in the range of 0.96 to 0.92.

The crystal investigated was mounted together with two thermometer probes on a cooling finger of an evaporator cryostat situated between bored pole pieces of an electromagnet [19]. The desired temperature in the range of 7 to 23.5 K was adjusted by electronic control of the liquid He flow. The errors of the specimen temperature were ± 0.2 K in stationary operation.

Linearly polarized monochromatic light, sent out from a xenon high pressure lamp XBO 150 combined with a narrow-band filter ($\lambda = 432$ nm) and a Glan-Tompson prism, was passed through the crystal. The Faraday rotation of the crystal was measured, depending on temperature and external field, by the aid of a second polarizer and a sensitive photometer. The obtained values were automatically recorded. The errors were smaller than 0.1°. A direct measure of the applied field was obtained from a suitably adjusted Hall probe taped to the pole pieces of the magnet.

The Faraday rotation β may be described by the equation

$$\beta = \varrho(\lambda)\, t \boldsymbol{I} \cdot \boldsymbol{n}_l \,. \tag{1}$$

$\boldsymbol{I} \cdot \boldsymbol{n}_l$ represents the effective part of the magnetization $\boldsymbol{I}$ along the line of sight $\boldsymbol{n}_l$. t is the thickness of the sample and ϱ a factor depending on the wavelength λ of light. At fixed λ the specific Faraday rotation $\beta' = \beta/t$ is a measure of the magnetization of the sample [20].

4. Results and Discussion

4.1 Measurements parallel to the hexagonal c-axis of the crystal

For these measurements the line of sight and the direction of the field were arranged normal to the crystal surface. The crystals were cooled down to 7 K in zero field and then slowly warmed up to 23.5 K with $\Delta T \approx 0.1$ K/s in a constant external field. A reduced external field $H_{ex} = HN_c$ was chosen to achieve comparable results for the four examined crystals with different N_c. H is therefore the field valid for a thin infinitely extended layer with $N_c = 1$. The field H was increased from zero up to 320 kA/m (≈ 4.0 kOe) in steps of 20 kA/m in successive measurements. The Faraday rotation β was measured.

It was observed that no hysteresis effects showed up during a cycle of warming up and cooling in constant field. From the recorded values β the specific Faraday rotation β' was attained and drawn as a function of the temperature T, Fig. 2. The curves obtained for the different crystals are the same for the same H. A negative β' results for the used wavelength $\lambda = 432$ nm [14]. A magnetization of about $I = 0.23$ Vs/m^2 corresponds to a specific rotation $\beta' = -1.0$ degree/cm [7].

First with decreasing temperature the magnetization curves run through the paramagnetic region until they reach their point of inflection lying on the (—·—·—)-line at $T_c = (16.7 \pm 0.2)$ K for all curves. With further decreasing temperature the magnetization curves show a temperature dependence typical for ferromagnetic materials until they reach their maximum. Beyond these maxima the curves decline with decreasing temperature, typical for antiferromagnetic materials. The maxima are connected by the dashed line that leads to a transition temperature of $T_N = (15.5 \pm 0.2)$ K for vanishing external field.

Measurements of the Faraday rotation as a function of the field are shown in Fig. 3. Again the obtained specific Faraday rotation β' is drawn as a function of the field H, now for different constant temperatures T. Starting from zero the magnetization increases linearly with the field until it reaches the spontaneous magnetization in a ferromagnetic state (parallel alignment of the ferromagnetic sublattices), then it bends to the region of increasing ferromagnetic saturation in the field. The initial gradient, a measure of the initial susceptibility, first increases with decreasing tem-

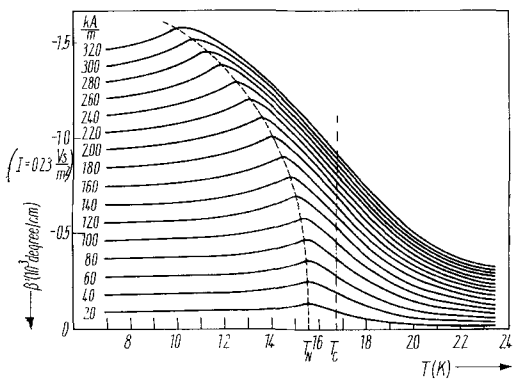

Fig. 2. Specific Faraday rotation β' of $CrCl_3$ versus temperature T for different applied fields H normal to the crystal surface, measured with blue light of wavelength $\lambda = 432$ nm

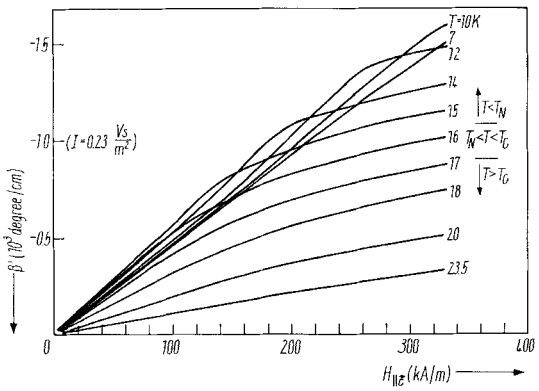

Fig. 3. Specific Faraday rotation β' of $CrCl_3$ versus applied field H normal to the crystal surface at different temperatures T, $\lambda = 432$ nm

perature, reaches a maximum at about $T = 15.5$ K, and then drops again with further decrease of temperature.

Magnetization curves of $CrCl_3$ measured by Bizette et al. [7] and Bizette and Terrier [8] show the same tendency. These authors have additionally measured the magnetization perpendicular to the c-axis and noticed that their specimen became magnetically anisotropic beyond the temperature of $T = 16.8$ K. The limiting line, passing through the maxima of all their magnetization curves analogous to Fig. 2, enters into a transition temperature of about $T = 14.5$ K for vanishing external field. Accordingly they found the maxima of the initial susceptibilities $\chi_{\parallel c}$ and $\chi_{\perp c}$ at $T = 14.5$ K. Since these authors did not indicate the shape of their specimen, a direct comparison of their curves and those shown here is impossible. The transition temperatures for vanishing field, however, are not affected by the crystal shape.

Measurements of the specific heat of $CrCl_3$ carried out by Kostryukova and Lukyanova [21] in the temperature range 2 to 20 K, yielded a linear term of the magnetic specific heat, typical for a two-dimensional ferromagnetic system. The maximum of the specific heat remained practically unshifted at $T = 16.8$ K in external fields up to 5800 Oe (≈ 460 kA/m). At 8100 Oe (≈ 645 kA/m) the maximum of the specific heat curve disappeared [11], an indication of the vanishing phase transition in this field [22].

All these observations lead to the conclusion that below the transition temperature $T_C = 16.8$ K (points of inflection that lie on the (—·—·)-line in Fig. 2) the crystal first reaches a two-dimensional ferromagnetic ordering in the sublattices with "ferromagnetic single layer domains" [3]. The weak magnetic dipole field between the layers is overcome by the thermal agitation, resulting in a random distribution of the two-dimensional magnetic layers along the c-axis. With decreasing temperature the magnetization in the layers increases, and so does the susceptibility, until reaching $T_N = (15.5 \pm 0.2)$ K, where the antiferromagnetic coupling between the sublattices appears and the net magnetization in a field decreases and therewith the susceptibility.

The magnetic behaviour in the antiferromagnetic state can be estimated by the use of a molecular-field approximation. Assuming two ferromagnetic sublattices A and B with magnetizations I_A and I_B, the molecular field of one sublattice at the place of the other is $H_A^m = \alpha_{AB} I_B/\mu_0$ and $H_B^m = \alpha_{BA} I_A/\mu_0$, respectively. The negative molecular field parameters α_{AB} and α_{BA} have to be assumed temperature dependent, however, as indicated by the measured temperature-dependent susceptibility $\chi_\perp$ [17].

Presumably there are $\alpha_{AB} = \alpha_{BA} = \alpha$ and $I_B = I_A$ and therefore the molecular fields are $H_A^m = H_B^m = H_L$. At some finite field H below saturation the magnetic energy is a sum of antiferromagnetic coupling energy, energy of sublattice magnetiza-

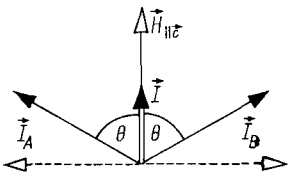

Fig. 4. Behaviour of sublattice magnetizations I_A and I_B in a field H applied along the c-axis of the crystal

tions in the field H, and demagnetizing energy,

$$E = -\frac{\alpha}{\mu_0} \boldsymbol{I}_A \boldsymbol{I}_B - \boldsymbol{H}(\boldsymbol{I}_A + \boldsymbol{I}_B) + \frac{1}{2\mu_0} N I^2 . \tag{2}$$

The weak anisotropy energy is neglected here.

Related to the external field H along the c-axis of the crystal, Fig. 4, one obtains with the net magnetization

$$I = (I_A + I_B) \cos\theta = 2 I_A \cos\theta \tag{3}$$

the energy expression

$$E = \frac{\alpha}{\mu_0} I_A^2 (1 - 2\cos^2\theta) - 2 H I_A \cos\theta + \frac{2N}{\mu_0} I_A^2 \cos^2\theta .$$

The equilibrium angle of the magnetization is found from the condition $\frac{\partial E}{\partial \cos\theta} \stackrel{!}{=} 0$, that yields

$$\cos\theta = \frac{\mu_0 H}{2N I_A - 2\alpha I_A} .$$

The net magnetization in the field is then with (3)

$$I = \frac{1}{N + |\alpha|} \mu_0 H . \tag{4}$$

The susceptibility comes out as $\chi_\perp = \frac{I}{\mu_0 H} = \frac{1}{N + |\alpha|}$, or as

$$\chi_\perp = \frac{1}{|\alpha|} \tag{5}$$

for usually treated negligible demagnetizing field ($N = 0$).

The maximum of the susceptibility results here for disappearing antiferromagnetic coupling, $\alpha = 0$ ($I_A = I_B \neq 0$) at the Néel temperature T_N.

The magnetization increases linearly with field at constant temperature according to (4) until it reaches the ferromagnetic state (parallel alignment of the two sublattices at $\cos\theta = 1$) at a field of

$$H_{\text{ferro}} = \frac{N 2 I_A}{\mu_0} + 2|\alpha| \frac{I_A}{\mu_0} = H_D + 2|H_L| . \tag{6}$$

The magnetizations of the two sublattices turn continuously towards the direction of field H.

At the field H_{ferro} depending on temperature the magnetization curves bend to a region of increasing ferromagnetic saturation in the field, as shown in Fig. 3.

4.2 Measurements perpendicular to the hexagonal c-axis of the crystal

For these measurements the sample holder was turned by an angle of 20° against the line of sight. The external field was arranged in the plane of the crystal to study the magnetization behaviour in this plane. The effective component of magnetization responsible for Faraday rotation is then $I \sin 20° \approx \frac{1}{3} I$. The crystal was cooled to $T = 7$ K in zero field, being in an antiferromagnetic state. The measured Faraday rotation was zero. In an increasing field at this temperature there was a more or less strong increase of Faraday rotation in different experiments. This results from the accidental orientation of the sublattice magnetization each with respect to the field [23]. In some cases there was no measurable rotation in increasing field until a certain field strength H_{sf}, where an abrupt increase of Faraday rotation started, to reach after a short course, the rotation values obtained in the other experiments.

Obviously this was a spin flop. The magnetizations of the two sublattices jump inside the layer plane at the flop field H_{sf} into a perpendicular position with respect to the field, with subsequent rotation towards the field [24]. The measurements yielded an average flop field for the four investigated crystals of $H_{sf} = (13.0 \pm 0.5)$ kA/m ($\approx (163 \pm 6)$ Oe) at $T = 7$ K.

From the known relation [25]

$$H_{sf} = \sqrt{\frac{2K_1}{\mu_0(\chi_\perp - \chi_{||})}}$$

with the anisotropy constant $K_1 = H_{an} I_{A,B}$ per sublattice in the plane, one obtains

$$H_{sf}(T) = \sqrt{\frac{2H_{an}H_L}{1 - \chi_{||}/\chi_\perp}} \,. \tag{7}$$

With $H_L(7\text{ K}) \approx 0.8 H_L(0\text{ K})$ [6], $\chi_{||}/\chi_\perp \approx 1/2$ at $T = 7$ K, and the measured value of H_{sf}, an anisotropy field of $H_{an}(7\text{ K}) = 780$ A/m (≈ 9.8 Oe) in the (001) plane is calculated from (7). The observed spin flop shows that $CrCl_3$ is not a metamagnet [26], as often assumed [4, 27 to 29].

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