Using high-resolution small-angle X-ray scattering, we observed a new type of the columnar phase with a simple rectangular ($R_S$) structure in colloidal goethite dispersions. Furthermore, it displays a martensitic transition into the usual centered rectangular ($R_C$) structure in an external magnetic field. The findings are rationalized in terms of entropic freedom on the delicate balance between the space available for particle translations and rotations within the two structures.

**Results and Discussion**

In the work presented here, a dispersion of chromium (Cr)-modified goethite particles (5:95 Cr:Fe) was studied. The particle dimensions are $L \times W \times T = 227 \times 68 \times 22$ nm, with a polydispersity of about 30% in all directions. Because of the

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**Introduction**

Suspensions of inorganic anisometric colloidal particles are able to self-organize into various liquid crystalline phases. They are very susceptible to external fields, have a high thermal stability, and are potentially suitable for applications such as photonics. Lyotropic mineral liquid crystals were found for the first time by Zocher in 1925, who observed a nematic phase in suspensions of vanadium pentoxide particles. In addition to the nematic phase, which possesses only the particle orientational order, smectic or columnar phases can also be formed, which are positionally ordered in one or two dimensions, respectively. A recent intriguing example is boardlike goethite particles, which show rich liquid crystalline phase behavior, including nematic, smectic, and columnar phases. The inherent polydispersity of the particles, which is usually considered to be a disadvantage of colloids, in this case enriches their phase behavior. It was found to induce the columnar phase, which coexists with a smectic phase and acts as a “waste bin” for the particles that do not fit within the smectic structure. The coexistence of columnar and smectic phases is rather unusual. The majority of known columnar phases are formed by flat molecules or plateletic particles. A columnar phase can also be formed by, for example, long cylindrical micelles which do not have a fixed length. For rodlike particles, apart from a few rare exceptions such as the columnar phase in suspensions of DNA molecules or fd viruses, a strong tendency toward smectic rather than columnar phases is observed.

In addition to their unusual phase behavior, goethite particles also have peculiar magnetic properties. They possess a considerable permanent magnetic moment along their long axis, presumably due to uncompensated surface spins within their antiferromagnetic crystal structure. At the same time, their magnetic easy axis is orthogonal to the permanent magnetic moment, along the shortest particle dimension. Therefore, particles align parallel to a small external magnetic field but perpendicular to a larger magnetic field ($>250$ mT). These alignment and reorientation phenomena open wide possibilities for easy manipulation of the liquid crystalline phases by an external magnetic field. Apart from the magnetic-field-induced isotropic to nematic phase transition, which has been extensively studied in various systems, goethite also shows a nematic to columnar phase transition under the influence of a magnetic field. Furthermore, the particle properties can be tuned by various modification methods.

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**Simple Rectangular Columnar Phase of Goethite Nanorods and Its Martensitic Transition to the Centered Rectangular Columnar Phase**

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Using high-resolution small-angle X-ray scattering, we observed a new type of the columnar phase with a simple rectangular ($R_S$) structure in colloidal goethite dispersions. Furthermore, it displays a martensitic transition into the usual centered rectangular ($R_C$) structure in an external magnetic field. The findings are rationalized in terms of entropic freedom on the delicate balance between the space available for particle translations and rotations within the two structures.
incorporation of Cr, the particles have a slightly smaller \( L/W \) ratio than usually found for goethite: 3.3 while > 4 is normal.\(^4\) Except for the difference in particle dimensions, normal and modified goethite also have different magnetic properties.\(^1\) The critical field strength \( (H_C) \) where the particles change orientation from parallel to perpendicular to the magnetic field is higher \( \sim 550 \) mT for the modified particles. These modified goethite particles show the same type of phase behavior as normal goethite and have the same surface charge. In a capillary with an overall volume fraction of 7.8\%, four different phases were observed: an isotropic, nematic, smectic A, and columnar phase upon establishment of the sedimentation equilibrium profile.

In a small-angle X-ray scattering (SAXS) experiment, the pattern displayed in Figure 1a was observed; the integrated intensity profile is shown in Figure 1b. The sharp peaks at a small angle originate from the periodicity of a smectic A phase. There is also a broad peak at a larger angle, which corresponds to the liquidlike interactions within the smectic layers. On top of this broad peak, one can see sharp and inhomogeneous scattering rings, which indicate that there is also a columnar phase present. The \( q \)-values corresponding to the first three rings are 0.062, 0.074, and 0.097 nm\(^{-1}\). Since \( 0.0062^2 + 0.074^2 \approx 0.097^2 \), these reflections can originate from a simple rectangular \( (R_S, p2nm \) symmetry group) columnar phase with unit cell dimensions of 85 and 101 nm (Figure 1c, one particle per cell).

More (higher order) rings can also be observed with longer exposure times. From the basis vectors, the other peak positions can be calculated and they are shown as dots and crosses in Figure 1b. The peaks corresponding to the dots are clearly observed, and they correspond to the following reflections: 10, 01, 11, 21, 12, and 22. The 20 reflection is weakly present as can be seen in the circles in Figure 1a, but it is not strong enough to be observed in the profile in Figure 1b. The 02 reflection was not observed, presumably due to a minimum of the particle form factor and a close vicinity of the stronger 21 reflection. The \( R_S \) structure of the columnar phase is further supported by the fact that in this powderlike pattern a few sets of reflections can be identified as originating from particular domains; one of them is highlighted in Figure 1a.

For comparison, in Figure 2, we present the results measured in a similar suspension of ordinary goethite, without doping by Cr \( (282 \times 68 \times 25 \) nm, volume fraction of 6\%). Here only the centered rectangular \( (R_C, c2nm \) symmetry group) phase has been observed; see also refs 5 and 6. The \( R_C \) columnar structure appears as less rings in a SAXS pattern (see Figure 2a,b). The rectangular cell of the \( R_C \) columnar phase can be seen in Figure 2c. In the powderlike pattern, particular domains can be found; one of them is underlined in the figure.

The origin of the \( R_S \) structure in this Cr-modified system instead of \( R_C \) (as in ordinary goethite) is not clear yet. It is known
that $H_C$ is significantly different for normal and modified goethite.\textsuperscript{18} The change of $H_C$ might be related to the effect of the Cr substitution on the permanent magnetic moment as well as on the induced moment (by changing the susceptibility anisotropy). However, it is expected that the dipole–dipole interactions between the particles are too weak to play a significant role when there is no field applied. Furthermore, there is a difference in the length of the particles, which could make a difference, but the effect of the particle shape should be further studied.

Interestingly, by applying a magnetic field of 1.5 T to the Cr-modified system, which is above the critical field where particles align with their shortest axis along the field, the R$_S$ phase transforms into the R$_C$ columnar phase (Figure 3). The rectangular cell dimensions are now 130 and 132 nm (two particles per cell), and the particle density remained the same within experimental error. Since the transformation breaks the symmetry of the intercolumnar structure, one can expect that the transition between R$_S$ and R$_C$ ordering is of first order. It occurs via a martensitic transition, where particles only move within the unit cell by a fraction of the cell size. This externally controlled transformation is interesting from a fundamental point of view and can prove useful for possible applications of goethite self-organization, since no long-scale diffusion and no rotation of the long particle axis are involved in this transition.

Furthermore, the structure goes back to the initial (R$_S$) structure after removal of the field, which was observed two months later. Repeating the experiments in a magnetic field, similar behavior was observed. Waiting again for a few months, a part of the phase remained in the R$_C$ structure, but mostly R$_S$ was observed. A combined pattern is shown in Figure 4. The R$_S$ phase seems to be the stable phase without an external field.

To elucidate the competition between both phases, a simple cell model was developed. Within this approach, the 3D space inside the crystal is split into Voronoi cells. The particles are assumed to be confined within the cells. Using the average particle dimensions ($L \times W \times T = 227 \times 68 \times 22$ nm), the configurational space $\Omega$ per particle is estimated as the product of the particle translations $\Delta x$ and $\Delta y$ possible in two orthogonal directions within the cell multiplied by the amplitudes $\alpha$, $\beta$, and $\gamma$ of the particle rotations within the cell around three orthogonal axes. The $\alpha$ rotation is around the long axis $L$, $\beta$ around the shortest axis $T$, and $\gamma$ around the $W$ axis (see Figure 5). This simple cell model was used to estimate the entropy difference $\Delta S = k_B(\ln \Omega_S - \ln \Omega_C)$ between the R$_S$ and R$_C$ columnar structures.

It is found that the R$_S$ phase has a slightly higher entropy with $\Delta S = 0.32k_B$ per particle. Moreover, the difference becomes certainly more pronounced if one accounts for the electrostatic repulsion between the particles. By simply adding the Debye length of 10 nm to all particle sizes, one gets an upper estimate of $\Delta S = 3.4k_B$. In the presence of a strong magnetic field, one can assume that the $\alpha$ and $\gamma$ fluctuations are frozen to ensure that the shortest particle axis stays in the field direction. In this case, the cell model predicts that $\Delta S = -0.14k_B$ for bare particles and $\Delta S = -0.22k_B$ after accounting for the Debye length. This result is mostly caused by the fact that the R$_C$ structure leaves more room for particle $\beta$ rotations which are not frozen by the external field.

We note that this cell model is presumably far too simple for exact quantitative predictions of the excluded volume entropy. Moreover, possible fractionation was not taken into account which would lead to the formation of columnar phase.\textsuperscript{7} Yet, the cell model does qualitatively confirm that while the phase with R$_S$ structure is more stable without the external field, the one with the R$_C$ structure wins after particle alignment in a strong external magnetic field.

In our recent experiment, which was performed one year later than the measurement shown in Figure 4, the structure did not return back anymore to the R$_S$ columnar phase after its field-induced transformation to the R$_C$ structure. This observation suggests the occurrence of slow processes, which can affect the delicate balance between the phases with the R$_S$ and R$_C$ structures. A possible explanation is the slow densification of the system due to sedimentation, which can slowly arrest the
dynamics of the system. This has been observed before in goethite samples. Additionally, it is known that fractionation plays a role which slows changes in the system. One could also speculate that a slow release of ions from the goethite particles and/or capillary walls might have increased the ionic strength, thereby screening the charge of the particles. This will make them more “barelike”. As one can see from the results of the simple cell model, this will reduce ∆τ and, therefore, will shift the equilibrium toward the R_C structure. Further study with better control over the ionic strength would be useful.

Conclusions
In this work, we have studied a suspension of Cr-modified goethite particles. Cr substitution modifies the magnetic properties and slightly influences the particle shape. In this dispersion, we found a novel columnar phase with a different structure. The most common structure of a columnar phase is the hexagonal one (p6mm symmetry group), as in, for example, gibbsite dispersions. For goethite particles with a rectangular cross section, a centered rectangular structure has been observed (R_C, p2mm symmetry group), which can also be seen as a hexagonal structure deformed along one of the symmetry planes. This type of columnar phase is also found frequently in molecular liquid crystals.23 We have with flexible lateral chains.25 It is rather rare and has not been found in molecular liquids, such as in, for example, gibbsite dispersions.27 For goethite particles with a rectangular cross section, a centered rectangular structure has been observed (R_C, p2mm symmetry group), which can also be seen as a hexagonal structure deformed along one of the symmetry planes.8 This type of columnar phase is also found frequently in molecular liquid crystals.23 We have found a self-assembled simple rectangular columnar structure (R_S, p2mm symmetry group), similar to those seen before in a system of helical dendrimers24 and in a system of bolaamphiphiles with flexible lateral chains.25 It is rather rare and has not been observed in colloidal systems before. Moreover, we have found that the columnar phase can also be switched between different structures via a magnetic-field-induced martensitic transition. The different structures can lead to different properties which can be useful for applications of goethite self-organization. A simple cell model was used to rationalize the observation. The results suggest that it is the competition for free space needed for particle translations and rotations that determines which phase is the most stable. The subtle balance between the two structures can easily be affected by external fields.

Experimental Section
Synthesis. The normal goethite particles were obtained by hydrolysis of iron nitrate at high pH according to Lemaire et al., already described in detail in ref 17. The Cr-modified particles were synthesized in a slightly adjusted way. A solution of 1 M NaOH (Merck, p.a.) was added dropwise, under stirring, to a 0.1 M iron/chromium nitrate (Acros, p.a./Merck, p.a. molar ratio Cr:Fe 9:1) solution until a pH of 9 was reached. After this, the precipitate was redispersed in fresh Millipore (mp) water before raising the pH further to 11–12. Aging took place at 70 °C for 10 days. After aging, the supernatant was removed and the sediment was washed twice with mp water and charged with 3 M HNO_3 (Merck, 65%, p.a.). After centrifuging and redispersing in mp water for three times, the particles were redispersed in mp water to obtain a stable dispersion in water of pH = 3. It is assumed that after many centrifugation steps the salt concentration was determined by the 1^+ and charge-compensating NO_3^- concentrations. The Debye length is then 10 nm at most.

Characterization. Particle size distributions were determined by transmission electron microscopy (TEM) using a Technai 10 (FEI company) electron microscope. The length and width of about 300 particles was measured with iTEm imaging software to determine the average length (L) and width (W) and their standard deviation (δ_L and δ_W). The length polydispersity is then defined as δ_L = δ_W/L. The thickness was difficult to measure because hardly any particles lay on their side on the TEM grid. For each sample, about 10 particle thicknesses were measured. Inductively coupled plasma optical emission spectroscopy (ICP OES) was used to determine the amount of Cr in the goethite particles.

SAXS. The sample was prepared in flat glass capillaries (Vitrocom W3520-100) with internal dimensions of 0.2 × 4.0 × 100 mm. The capillaries were closed by melting and kept in a vertical position to allow the establishment of the sedimentation equilibrium profile. SAXS measurements were performed at the BM26 DUBBLE beamline26 and the ID2 high brilliance beamline27 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A variable permanent magnet was used, with which a magnetic field up to 1.5 T could be reached. Two stacks of NdFeB permanent magnets generated the field, and the distance between them could be adjusted to reach the desired field strength. At the BM26 beamline, the microradon resolution setup28 was used.

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