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Magnetic ordering processes in the quasi-one-dimensional metamagnets RbFeCl₃·2aq and CsFeCl₃·2aq (aq=H₂O,D₂O)

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The static and dynamic properties of the quasi-one-dimensional canted Ising antiferromagnets RbFeCl₃·2aq and CsFeCl₃·2aq (aq=H₂O,D₂O) are investigated in the ordered phases by neutron diffraction and magnetization measurements. For $2\text{ K} \leq T \leq 3\text{ K}$ the magnetic behavior in varying field H may be explained by a sequence of collective reversals of all moments in separate long-range-ordered chains, each chain reversal being initiated by a thermally excited moment reversal at one of the chain ends. The behavior at low T is characterized by nonexponential relaxation towards a partly disordered array of long-range-ordered chains. The properties for $4.2\text{ K} < T < T_N$ were studied for RbFeCl₃·2D₂O only. Two different ferrimagnetic (FI) structures were observed in distinct regions of the (H,T) phase diagram, separated by a boundary at $T \approx 7\text{ K}$. Along the phase boundary $H_{c1}(T)$ between the FI and the antiferromagnetic phase a crossover from first-order to second-order behavior occurs at $T \approx 6.5\text{ K}$. Along the boundary $H_{c2}(T)$ between the FI and pseudoferrimagnetic phase the crossover occurs at $T \approx 9.0\text{ K}$.

I. INTRODUCTION

The compounds RbFeCl₃·2aq (RFC) and CsFeCl₃·2aq (CFC) with aq=H₂O or D₂O are well known as quasi-one-dimensional (1D) metamagnets. Their magnetic properties have been studied by a variety of experiments which include specific heat,¹ spin-cluster resonance,² spin-cluster excitation,³ Mössbauer spectroscopy,⁴ susceptibility,⁵ and T_1^{-1} measurements.⁶ The results indicate a predominance of strongly anisotropic (Ising) magnetic interactions along the chains containing the Fe²⁺ moments.

At lower temperatures, 3D long-range order is induced by the weaker interchain interactions ($T_N = 11.96\text{ K}$ for RFC, $T_N = 12.75\text{ K}$ for CFC). When an increasing magnetic field is applied along the crystallographic c axis below T_N , two metamagnetic phase transitions take place between the antiferromagnetic (AF) phase, the ferrimagnetic (FI) phase, and the pseudoferrimagnetic (F) phase. The magnetic structure in the FI phase is not known, although three possible structures have been proposed.^{2,5} In order to elucidate this point and to study the relaxation phenomena observed in preliminary experiments⁷ more extensively, we performed a neutron scattering study and additional magnetization measurements in the ordered phases.

In this paper we will show that the overall long-range structure in the FI phase is in agreement with the proposed models. Moreover, it is found that the establishment of the long-range order is accompanied with relaxation effects which can be considered as typical for quasi-1D Ising systems^{8,9} and can be interpreted in the framework of the so-called nucleation model suggested by Tinkham.¹⁰ It turns out that the magnetic FI and AF states are partly disordered, which may be understood on the

basis of the same model.

The organization of this paper is as follows: Section II contains the relevant available data on the magnetic properties of the compounds and a short description of the experimental equipment. In Sec. III the characteristic behavior at low T is exemplified by the field dependence of the magnetization and susceptibility which is interpreted on the basis of Tinkham's nucleation model. Sections IV and V contain, respectively, the results bearing on the magnetic disorder and relaxation phenomena in the FI phase. In Sec. VI the magnetic (H,T) phase diagram of RFC will be presented with particular emphasis on the high- T region ($6\text{ K} < T < T_N$). Finally, a general discussion of the experimental results and their interpretation is given in Sec. VII.

II. SAMPLE PROPERTIES AND EXPERIMENTAL TECHNIQUES

Single crystals of RFC and CFC were grown by slow evaporation at 37°C of a solution of anhydrous FeCl₂ and RbCl or CsCl in a molar ratio of, respectively, 3.2:1 (Rb) and 1:2 (Cs). A 0.03N solution of DCl or HCl was used to prevent oxidation of the crystals. Following this procedure single crystals were obtained with typical dimensions $2 \times 2 \times 0.5\text{ cm}^3$. The pale brown crystals may be easily cleaved parallel to the largest crystal face, which corresponds to the a - b plane.

Previous neutron-diffraction experiments¹¹ have shown that the crystal structure of both RFC and CFC is orthorhombic [with space group $Pcca$ (D_{2h}^8)]. The structure consists of *cis*-octahedra which are coupled along the a axis by a shared chlorine ion. The resulting chains are separated in the b direction by layers of Rb (Cs) ions and

TABLE I. The various parameters for RFC and CFC.

Parameter	RFC	CFC
J_a/k	$-35 \text{ K}^a, -39 \text{ K}^b$	-42 K^b
J_b/k	-0.76 K^a	-0.47 K^a
J_c/k	-0.21 K^a	-0.15 K^a
J_{bc}/k	-0.13 K^a	-0.06 K^a
$\mu = \mu_{a-c}$	$4.5\mu_B,^a 4.6\mu_B^c$	$4.4\mu_B^c$

^aSpin-cluster resonance (Refs. 2, 5, and 12).^bMagnetic specific heat (Refs. 1 and 12).^cNuclear magnetic resonance (Ref. 11).

in the c direction by hydrogen (deuterium) bonds. The relevant interaction parameters in RFC and CFC, deduced from the experimental results on the basis of an effective $S' = \frac{1}{2}$ Ising formalism, are listed in Table I. These parameters include the dominant intrachain interaction J_a along the a axis and the three interchain interactions J_b , J_c , and J_{bc} .

In the 3D ordered AF phase ($T < T_N$, $H = 0$), the magnetic array can be described as a compensated four-sublattice system with space group $P_{2b}c'ca$ (RFC) and $P_{2b}cca'$ (CFC).¹¹ These space groups allow a canting of the magnetic moments in the a - c plane with a net magnetization of each chain along the c direction. The canting angle θ_M (see Fig. 1) amounts to $\theta_M \simeq 19^\circ$ for RFC and $\theta_M \simeq 15^\circ$ for CFC.¹¹

According to earlier magnetization and susceptibility measurements,³ two metamagnetic phase transitions at $H_{c1}(T)$ and $H_{c2}(T)$ can be observed in the (H, T) parameter plane ($H \parallel c$). Each phase transition is associated with a steplike variation of the magnetization by an amount of $M_F/2$, where M_F is the magnetization in the F phase. The reported phase diagram for RFC is shown in Fig. 2. Theoretically, three different magnetic FI structures have been proposed,^{2,5} which will be denoted as FI(I), FI(II), and FI(III). These structures can be characterized by the stacking of the chains in the b - c plane as shown in Fig. 3 and are energetically equivalent when only nearest-neighbor interactions are taken into account.

The magnetization measurements were performed on hydrated samples with a commercial vibrating-sample magnetometer. The sample temperature was controlled by regulating the pressure of a ^4He bath ($T < 4.2 \text{ K}$), thermal contact with the sample being established by ^4He gas. For the experiments on CFC a conventional electromagnet ($H_{\max} = 11 \text{ kOe}$) was used, whereas a superconducting magnet was employed for the investigation of RFC in view of the larger transition field H_{c2} .

The diffraction measurements were carried out mainly

FIG. 1. The orientation in the a - c plane of the canted magnetic moments in a chain.

FIG. 2. Magnetic (H, T) phase diagram of $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$ for $H \parallel c$ (Ref. 3). AF, FI, and F denote, respectively, the antiferromagnetic, ferrimagnetic, and ferromagnetic ordering between the net moments of the chains. M_F is the magnetization in the F phase.

on deuterated RFC with a double-axis instrument. The incident neutron beam, having a wavelength $\lambda = 1.478 \text{ \AA}$, was collimated to $30'$ both in the horizontal and vertical directions, while a $30'$ horizontal collimator was mounted

FIG. 3. Stacking in the b - c plane of the net magnetic moments of the chains for the various structures. For each structure, the magnetic unit cell is indicated by dashed lines, whereas the crystallographic unit cell is indicated by solid lines. The FI(I) and FI(II) structures are characterized by "antiferromagnetic" ($a, \bar{a}$) and "ferromagnetic" (f) stacking in adjacent a - c planes.

between sample and detector. Scans in three reciprocal-lattice planes were made to determine the actual FI structure and the correlation lengths along principal crystal axes (cf. Table IV). For the scans in the $(1\bar{2}0)$ and $(50\bar{1})$ planes in horizontal field a conventional electromagnet was used in combination with a ^4He -bath cryostat ($H < 15$ kOe; $T < 4.2$ K). The scans in the (001) plane in vertical field were performed by means of a variable-temperature cryostat with a split-coil superconducting magnet.

III. MAGNETIZATION AND SUSCEPTIBILITY

A closer inspection of the magnetization and susceptibility data reveals that abrupt changes in the magnetization occur not only at H_{c1} and H_{c2} . As an example, we show in Figs. 4(a) and 4(b) the field dependence of M and χ , respectively, observed in CFC at low T and $\mathbf{H} \parallel \mathbf{c}$.

Apart from the phase transitions at H_{c1} and H_{c2} , a number of additional transitions are observed at discrete field values H_i . A comparison of the $M(H)$ curves in decreasing and increasing field sweeps reveals that the field values H_i remain constant in spite of the irreversible variation of the magnetization. These observations clearly demonstrate that changes in the magnetization occurring at H_i arise from local reorientations of moments.

FIG. 4. Typical field dependence of (a) the magnetization M and (b) the susceptibility χ in CFC with $\mathbf{H} \parallel \mathbf{c}$ at low T . The field values at which an instability occurs in M are not affected by the direction of the field sweep. Note the shift in the vertical χ axis.

Qualitatively, the same phenomena have been observed in RFC and in some other quasi-1D Ising systems, and have been interpreted on the basis of a nucleation model suggested by Tinkham.¹⁰ In the framework of this model, the 3D structure at low T ($k_B T \ll |J_a|$) is approximated by a 2D array representing the stacking of perfectly ordered chains of moments as shown in Fig. 3. Consequently, a change in the magnetic order (e.g., a metamagnetic phase transition) can only be realized by reversals of entire chains. Each chain reversal is subject to the so-called nucleation condition,¹⁰ which states that it will occur only if it is energetically favorable to reverse all moments within the chain (domino style) after one individual moment in that chain has been reversed thermally. For the present systems this results in the condition

$$dE/dm = (n_b J_b + n_c J_c + n_{bc} J_{bc} + 2\mu_c \cdot \mathbf{H}) < 0, \quad k_B T \ll |J_a| \quad (1)$$

where dE/dm is the energy required to enlarge a reversed cluster of m moments along the chain with one moment. The values for $n_b = \pm 2, 0$, $n_c = \pm 2, 0$, and $n_{bc} = \pm 4, \pm 2, 0$ reflect the relative orientations of the moments in the neighboring chains with respect to the chain under consideration (for one pair of chains, $n_i = +1$ or -1 for a

FIG. 5. Variation of the magnetization in RFC and CFC in decreasing field scans (700 Oe/min) at various temperatures. The transition fields H_{c1} , H_{c2} , and the fields H_i are determined by linearizing the curves, as is shown schematically in the inset.

TABLE II. Comparison of the values $\mu_c H_i/k$ at which steplike variations occur in the experimental $M(H)$ curves with calculations based on the nucleation condition. For RFC the transitions observed in the simulation experiments are listed too.

RFC Field	Experimental $2\text{ K} \leq T \leq 3\text{ K}$			Calculated		$\mu_c H_i/k$	Simulations $T^* > 1\text{ K}$
	$\mu_c H_i/k$	n_b	n_c	n_{bc}			
H_{c2}	1.23	2	2	4		1.23	H_{c2}
H_3	1.10	2	2	2		1.10	H_3
H_4	1.00	2	0	4		1.02	H_4
H_5	0.96	2	2	0		0.97	
H_6	0.88	2	0	2		0.89	H_6
H_{c1}	0.79	2	-2	4		0.81	H_{c1}
H_8		2	0	0		0.76	H_8
H_{22}		0	-2	4		0.05	H_{22}

CFC Field	Experimental $3\text{ K} \leq T \leq 3.5\text{ K}$			Calculated		$\mu_c H_i/k$	
	$\mu_c H_i/k$	n_b	n_c	n_{bc}			
H_{c2}	0.74	2	2	4		0.74	
H_3	0.68	2	2	2		0.68	
H_4	0.62	2	2	0		0.62	
H_6	0.56	2	2	-2		0.56	
H_{c1}	0.50	2	2	-4		0.50	
H_8	0.47	2	0	0		0.47	
H_{11}	0.38	2	-2	2		0.38	
H_{14}	0.27	0	2	4		0.27	
H_{16}	0.21	0	2	2		0.21	
H_{18}	0.15	0	2	0		0.15	
H_{19}	0.12	0	0	4		0.12	
H_{21}	0.06	0	0	2		0.06	

parallel or antiparallel ordering, respectively). For the given set of exchange constants, condition (1) defines 23 field values $H_i \geq 0$ (H_{c1} , H_{c2} , H_i , $i=3,4,\dots,23$) at which a chain in a certain local configuration, labeled by (n_b, n_c, n_{bc}) becomes unstable [$dE/dm(H_i)=0$]. These values may be compared with the field values at which steplike variations are observed in $M(H)$. Since the F phase is well defined, in contrast to the AF phase, we will confront the nucleation model with the $M(H)$ curves obtained in a decreasing field sweep, starting from the F phase at $H > H_{c2}$.

The experimental data for RFC and CFC at various temperatures are shown in Fig. 5. At low T , the response of the system is very slow and no equilibrium is reached at the sweep rate used in the experiments (700 Oe/min). At higher T the transitions at H_i become detectable. The results for RFC indicate that these additional transitions become less pronounced if the temperature is raised above 4.2 K. All the experimentally determined values $\mu_c H_i/k$ are listed in Table II and can be identified with local configurations, labeled by n_b , n_c , and n_{bc} . Apparently, only a subset of the 23 possible values for H_i are observable, which suggests that not all configurations are actually realized with a detectable statistical weight.

Qualitatively this can be understood on the basis of the nucleation condition. Starting from the F structure, the nucleation condition implies that at $H \leq H_{c2}$ all chains become simultaneously unstable. A single chain which reverses will stabilize its neighboring chains. These rever-

sals are randomly distributed in the array since all chains are potentially unstable, and therefore a disordered FI array will result. This disordered array will accommodate a number of different local configurations which are not necessarily equally abundant. Since it is extremely complicated to sort out the abundancy of the different configurations analytically, we performed a computer simulation process on the basis of the nucleation model.

The magnetic ordering in RFC in a decreasing field sweep was simulated for a 2D array of $N=48 \times 48$ elements, each element corresponding to a perfectly ordered chain. According to Tinkham,¹⁰ the probability P for a reversal of an arbitrary element that satisfies the nucleation condition is given by $P \propto \exp(-\Delta E/k_B T)$, where ΔE is the energy required for the first moment reversal in the corresponding chain. As the probability P was normalized to 1 for the minimum value of ΔE ($H < H_{c2}$), the parameter T should not be identified with the thermodynamic temperature. In order to avoid confusion, we will denote this parameter by T^* . The field sweeps were simulated by changing the field in steps (0.2 kOe) and fixing the number of Monte Carlo shots (MCS) at $40N$ for each field value.

The results of the simulations at two extreme conditions are shown in Fig. 6. For $T^* > 1\text{ K}$, the results do not depend on T^* , since the arrays attain a locally stable state ($dE/dm > 0$), whereas at $T^* = 0.2\text{ K}$ the process is very slow and no significant variations occur. It is obvious from Fig. 6 that the magnitude of the steps in $M(H)$

FIG. 6. Simulated $M(H)$ for RFC in a decreasing field sweep. The curve for $T^* > 1$ K represents the behavior when the array reaches its equilibrium state at each field value. The steplike variations at H_i are indicated by the label i . For $T^* = 0.2$ K the variations are invisibly small.

varies considerably and that some steps (e.g., $i=20,21$) can hardly be detected. In Table II we have listed the most significant simulated instabilities in M . The agreement with the observed steps at $T=2.49$ K and $T=3.25$ K is fair and indeed confirms that not all the configurations are realized with an observable statistical weight.

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}) \propto F_L f_Q^2 \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \hat{\mathbf{Q}}_\alpha \hat{\mathbf{Q}}_\beta) \sum_{\mathbf{R},\mathbf{R}'} \langle \mu^\alpha(\mathbf{R}) \rangle \langle \mu^\beta(\mathbf{R}') \rangle \exp[i\mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')], \quad (2)$$

where $\alpha, \beta = a, c$ ($\langle \mu^b(\mathbf{R}) \rangle = 0$), $\mathbf{Q}$ is the scattering vector, $\hat{\mathbf{Q}}$ is the unit vector $\mathbf{Q}/Q$, f_Q is the magnetic form factor, and $F_L = 1/\sin 2\theta$ is the Lorentz factor. By using the fractional coordinates of the Fe^{2+} ions within the unit

cell, the relative Bragg intensities can be calculated for the three proposed long-range-ordered FI structures. The results for a selected set of reflections, with indices based on the crystallographic unit cell, are shown in Table III.

For values $T^* < 1$ K, it is found that after 40N MCS there are still nonstable configurations ($dE/dm < 0$) present in the simulated array, and consequently the $M(H)$ curves become more smooth, in agreement with the experimental data in Fig. 5. In the extreme case $T^* = 0.2$ K, this results in an almost constant magnetization.

In conclusion, the qualitative agreement between the variation of $M(H)$ observed for $T=3.25$ and 2.49 K, and simulated for $T^* \geq 1$ K may be considered as an indication of the occurrence of a nucleation process in RFC at sufficiently low T . The simulations for RFC fail to describe the observed gradual disappearance of the transitions at H_i for $T > 4$ K.

The observation of the variations in M at $H_i \neq H_{c1}, H_{c2}$ implies the presence of local configurations that do not fit into the regular structures shown in Fig. 3. In the following sections, we will investigate these imperfectly ordered structures of RFC and CFC in the FI phase (Sec. IV) and the relaxation phenomena associated with chain reversals in the magnetic arrays (Sec. V).

IV. LONG-RANGE ORDER AND DISORDER IN THE FI PHASE

The cross section for elastic magnetic Bragg scattering of neutrons by an assembly of magnetic moments $\mu(\mathbf{R})$ is given by the expression

TABLE III. Theoretical intensities derived from Eq. (2) for the various structures, normalized with respect to the $(1 \frac{1}{2} 4)$ and $(1 \frac{1}{2} 3)$ reflections for the AF structure in RFC and CFC, respectively. For the FI(I) and FI(II) structures the contributions from the $(a, \bar{a})$ and (f) planes are listed separately (cf. Fig. 3).

$(h\ k\ l)$	AF	(f)	FI(I)	$(a, \bar{a})$	(f)	FI(II)	$(a, \bar{a})$	FI(III)	F
RFC			+			+			
$(1\ \frac{1}{2}\ 4)$	100	25	+	0.004	25	+	0	0	0
$(1\ \frac{1}{2}\ \frac{7}{2})$	0		0			0		31.2	0
$(1\ \frac{1}{2}\ 3)$	0.05	0.01	+	31.9	0.011	+	0	0	0
$(1\ \frac{1}{4}\ 5)$	0		0		0	+	18.1	0	0
$(0\ \frac{1}{2}\ 0)$	100.4	25.1	+	3.8	25.1	+	0	0	0
$(0\ \frac{9}{4}\ 0)$	0		0		0	+	9.7	0	0
$(\bar{1}\ 1\ 0)$	0	55.5	+	0.48	55.5	+	0	56.0	222.2
$(\bar{1}\ \frac{3}{2}\ 0)$	171.5	42.9	+	0.7	42.9	+	0	0	0
$(h\ k\ l)$	AF	(f)	FI(I)	$(a, \bar{a})$	(f)	FI(II)	$(a, \bar{a})$	FI(III)	F
CFC			+			+			
$(1\ \frac{1}{2}\ 3)$	100	0.004	+	25	0.004	+	0	0	0
$(1\ \frac{1}{2}\ \frac{7}{2})$	0		0			0		22.8	0
$(1\ \frac{1}{2}\ 4)$	0.01	20.4	+	0.002	20.4	+	0	0	0

TABLE IV. Selected crystal orientations, field directions, and investigated temperature ranges for RFC and CFC ($a||a^*$, $b||b^*$, $c||c^*$).

Scattering plane	Principal axes	Field orientation			Temperature range (K)
		$\angle(H, c)$ (deg)	$\angle(H, b)$ (deg)	$\angle(H, a)$ (deg)	
(1 $\bar{2}$ 0) RFC	$c^*, a^* + \frac{1}{2}b^*$	13.2	82.9	78.9	$T=4.2$
(50 $\bar{1}$) RFC	$b^*, a^* + 5c^*$	17.4	79.8	76.1	$T \leq 4.2$
(001) RFC	a^*, b^*	0	90	90	$T \leq 15$
(1 $\bar{2}$ 0) CFC	$c^*, a^* + \frac{1}{2}b^*$	14.8	82.2	77.5	$T=4.2$

For the observation of the reflections with $l \neq 0$, the magnetic field had to be aligned at an angle with the c axis. The selected scattering planes and corresponding field orientations are listed in Table IV. Because of the high single-ion anisotropy, the phase transitions are almost exclusively determined by the c component of the field.⁵ Therefore, in the following, the applied field is represented by its c component.

First, we investigated the long-range order established in the FI phase at small sweep rates (< 100 Oe/min). In view of the irreversible behavior observed in CFC (see Fig. 4) the data were collected mainly in decreasing field scans, starting from the regular F structure at $H > H_{c2}$. The long-range order in the FI phase was investigated by recording the field dependence of the $(1\frac{1}{2}3)$, $(1\frac{1}{2}\frac{7}{2})$, and $(1\frac{1}{2}4)$ reflections at $T=4.2$ K. The resulting peak intensities are shown in Figs. 7(a) and 7(b) for RFC and CFC, respectively. At the reciprocal-lattice position $(1\frac{1}{2}\frac{7}{2})$ a

constant intensity was observed, resulting exclusively from nuclear scattering of second-order ($\lambda/2$) neutrons. In contrast to the behavior of RFC, which at 4.2 K is almost independent of the direction and rate of the field sweep, the ordering phenomena in CFC are irreproducible under different scanning conditions. Inspection of Fig. 7(b) shows that the magnetic order of CFC in the FI phase depends on the way in which this phase is entered. Moreover, the perfect AF structure, which is established by cooling in zero field, is not restored after a field scan through the F phase.

A comparison between the experimental results in Fig. 7 and the calculated relative intensities in Table III leads to the following conclusions for the order in the FI phase.

RFC. The structure is predominantly FI(II), with a small number of FI(I) domains giving rise to the $(1\frac{1}{2}3)$ intensity increase with respect to the AF phase.

CFC. The structure depends on the sweep conditions. In decreasing field (5 Oe/min and 100 Oe/min) both FI(I) and FI(II) domains are formed, whereas the structure becomes predominantly FI(I) in increasing field (100 Oe/min). When the FI phase is entered very slowly (5 Oe/min) at H_{c1} the established order does not correspond to any of the three proposed structures.

A more detailed investigation of the disorder in the FI phase was performed by scanning through selected reflections along the a^* , b^* , or c^* direction at constant T and H . In order to reduce relaxation effects, these reciprocal-lattice scans were performed typically a few hours after the FI phase had been entered in a slowly decreasing field (< 100 Oe/min). Since the magnetic ordering in CFC is far more complex than in RFC, these measurements were limited to RFC (with the exception of the scan for CFC shown in Fig. 8). By choosing suitable reflections, a distinction could be made between disorder due to stacking faults of "antiferromagnetic" ($a, \bar{a}$) or "ferromagnetic" (f) a - c planes (cf. Fig. 3 and Table III). The main results may be summarized as follows.

CFC. When the FI phase has been entered at 4.2 K in decreasing field, the $(1\frac{1}{2}3)$ and $(1\frac{1}{2}4)$ reflections are found to be broadened along c^* (see Fig. 8) in comparison with the corresponding instrumental resolution widths, indicating the presence of short-range correlations along the c direction. There are indirect indications that also the correlations along the b direction are short ranged.

FIG. 7. Variation of the $(1\frac{1}{2}3)$ and $(1\frac{1}{2}4)$ magnetic peak intensities at $T=4.2$ K. The data points represent the observations in a decreasing field scan (100 Oe/min). For CFC, the variations observed in an increasing field scan (100 Oe/min) are also shown (dashed curves). Note the different field scales for RFC and CFC and the different intensity scales for the various reflections.

FIG. 8. Profiles of the magnetic $(1 \frac{1}{2} 3)$ and $(1 \frac{1}{2} 4)$ reflections along c^* at $T=4.2$ K in the FI phase in CFC and RFC. The FI phase is entered by decreasing the field below H_{c2} . In CFC the reflections are substantially broadened in comparison with the instrumental resolution function, determined at $H=0$ and indicated by the dashed curves.

RFC. Under the same conditions as above, the profiles of $(1 \frac{1}{2} 3)$ and $(1 \frac{1}{2} 4)$ along c^* are identical to the instrumental resolution functions (Fig. 8) indicating long-range order along the c direction. On the other hand, the reflections $(1 \frac{1}{4} 5)$ and $(0 \frac{9}{4} 0)$, which are due to the “antiferromagnetic” planes in the FI(II) structure (see Fig. 3), are much broader than the instrumental resolution in the b^* direction. The results of several scans at different T , each performed after a slow passage through H_{c2} at constant T , are collected in Fig. 9. Finally, the profile of the $(0 \frac{1}{2} 0)$ reflection along b^* , which reflects the stacking order of the (f) planes in the FI(II) structure (cf. Table III), is resolution limited at $T=4.2$ and 3.7 K but broadened at $T=1.8$ K.

From the above scans, and a number of additional ones along a^* and c^* which have not been specified because they yielded resolution-limited profiles, one may conclude that the order of RFC in the FI phase may be described as a more or less regular stacking of long-range-ordered a - c planes. For decreasing T in the range $T > 2.62$ K, the increasing disorder along b results from stacking faults in the sequence of “antiferromagnetic” $(a, \bar{a})$ planes in between (f) planes stacked correctly over much larger distances. At $T=2.62$ K the $(a, \bar{a})$ planes are stacked almost randomly (Fig. 9), whereas the correlation length for the (f) -plane stacking is still appreciable ($\xi_b/b = 6.6 \pm 0.5$) at $T=1.8$ K. It turns out that the correlation lengths along b are determined exclusively by the temperature at which the phase boundary $H_{c2}(T)$ is traversed; the order or disorder is frozen in at H_{c2} and subsequent variation of H or T within the FI(II) region of the phase diagram has no influence on the reflection profiles.

In view of the fairly successful interpretation of the $M(H)$ curves by the nucleation model, we shall compare the observed magnetic long-range order and disorder with predictions based on the same model. In passing a phase

FIG. 9. (a) Observed profiles of the $(1 \frac{1}{4} 5)$ reflection along b^* in RFC. The double arrow indicates the full width at half maximum of the resolution function. For $T > 2.62$ K, no broadening occurs along the c^* direction. The curves represent the fitted profiles.¹³ (b) Temperature dependence of the correlation length ξ_b/b for the $(a, \bar{a})$ plane stacking in the FI(II) phase.

transition at H_i , the magnetic array in the final state is determined by the array in the initial state and the positions of the chains becoming unstable at H_i . For the perfectly ordered structures AF, FI(I), FI(II), and F, one may distinguish phase transitions at which the condition $dE/dm(H_i)=0$ applies to nonneighboring or neighboring chains (see Table V). In the first case (FI $\rightarrow$ F, FI $\rightarrow$ AF), one expects long-range order after reversal of all unstable chains. In the last case (F $\rightarrow$ FI, AF $\rightarrow$ FI), the reversal of each unstable chain will stabilize the originally unstable neighbor chains, which inevitably will result in a disordered array. In general, such disordered arrays will remain disordered at subsequent transitions H_i , except at H_{c2} where the perfect F structure will be established irrespective of the positions of the “minus” chains for $H < H_{c2}$.

The experimental results are partially in agreement with the above predictions. The FI arrays formed at the phase

TABLE V. Magnetic unit cells of the F, FI, and AF structures, visualized by the stacking of the chains in the b - c plane (b : horizontal; c : vertical). Encircled symbols indicate the chains that are unstable at the field given below the cell.

F	RFC FI(I)	CFC FI(I)	RFC FI(II)	CFC FI(II)	RFC AF	CFC AF
H_{c2}	H_{c1}	H_{c1}	H_{c1}	H_9	H_{c1}	H_{c1}
	H_{c2}	H_{c2}	H_{c2}	H_{c2}		

transitions H_{c1} and H_{c2} are indeed imperfectly ordered, but the degree of ordering is much larger than that found in the simulations. There is a pronounced preference for either the FI(I) or FI(II) pattern, the correlation length being larger than predicted, anisotropic and temperature dependent. The expected formation of the long-range-ordered F array at H_{c2} is confirmed indeed in the experiments. Since the FI arrays formed at H_{c2} are partly disordered, one would expect disordered arrays to be formed in the AF phase. This is indeed the case for CFC. On the other hand, the AF array in RFC turns out to be long-range ordered for $T \geq 2$ K. This unexpected behavior may be related to the long-range correlation for the stacking of the (f) planes in the FI phase, which leads to the correct AF structure at H_{c1} , even if the ($a, \bar{a}$) planes are stacked in a disordered way.

The disagreement between predictions and observations with respect to the degree of disorder is probably due to the strictly local definition of the nucleation condition (1) which, for example, does not take into account simultaneous reversal of two or more chains. The inadequacy of the nucleation model for the description of temperature-dependent features of the magnetic ordering was noticed earlier in Sec. III, and is due to the restricted validity range of the model ($T \ll |J_a|/k$).

V. RELAXATION PHENOMENA

As stated in the Introduction, the relaxation phenomena in quasi-1D Ising systems at low temperatures are related to the ordering process which proceeds by single-chain reversals initiated by a thermally excited moment reversal. Therefore, the dynamic properties at the metamagnetic transitions are determined mainly by the large intrachain interaction, and will be strongly temperature dependent. The relaxation of the magnetic system from the F state towards the equilibrium FI state at fixed H and T was studied by diffraction and magnetization measurements, after a rapid field change from $H > H_{c2}$. Magnetization measurements were used to investigate the short-time behavior, whereas the diffraction technique was employed to study the change in correlation length at large time intervals.

The relaxation curves $M(t)$ shown in Fig. 10(a) were

recorded for CFC at various temperatures and $H=8.3$ kOe. As we may expect by extrapolation of the results at small field sweep rates (cf. Fig. 5), the final FI array will be partly disordered and will have a magnetization $M(\infty) > M_F/2$. Even when these nonequilibrium values $M(\infty)$ are taken into account, the variation of $M(t)$ cannot be described by a single relaxation time τ . In Fig.

FIG. 10. (a) Variation of the magnetization M in CFC with time for different temperatures, after a rapid field change starting in the F phase. (b) The initial relaxation time $\tau'(t=0)$ plotted against T^{-1} . The drawn line corresponds to $\tau'(t=0) \propto \exp(\Delta E/k_B T)$.

10(b) we present the temperature dependence of the initial relaxation time $\tau'(t=0)$ as $\ln\tau'$ versus T^{-1} . In the interval $2.02\text{ K} < T < 3.25\text{ K}$ the relaxation time $\tau'(t=0)$ can be described by the relation

$$\tau'(t=0) \propto \exp(\Delta E/k_B T),$$

which suggests that the initiation of a chain reversal requires an activation energy $\Delta E/k \approx 33 \pm 5\text{ K}$.

The observed relaxation behavior may be explained qualitatively by the nucleation model. It is important to note that the transition probability P for a single-chain reversal does not necessarily define the relaxation behavior of the whole system. A relaxation time

$$\tau = 1/P \propto \exp(\Delta E/k_B T) \quad (3)$$

can be associated with each chain reversal, where $\Delta E = 2|J_a|$ or $|J_a|$ for an initial moment reversal within the chain or at a chain end, respectively.¹⁰ The relaxation of the magnetization is governed by the rate of nucleation moment reversals per time unit dN_{fl}/dt at unstable chains:

$$\frac{1}{M_F} \frac{dM}{dt} = -\frac{2}{N} \frac{dN_{fl}}{dt}, \quad \frac{dN_{fl}}{dt} = \frac{N_{unstable}(t)}{\tau}, \quad (4)$$

where N denotes the total number of chains. Since the experiments were performed at a constant field in the interval $H_3 < H < H_{c2}$, only "plus" chains surrounded by eight parallel chains ($n_b=2$, $n_c=2$, $n_{bc}=4$; cf. Table II) were unstable. As a result of each chain reversal n chains are stabilized (i.e., the reversed chain and $n-1$ neighbor chains), and in general $N_{fl}(t)$ and $N_{unstable}(t)$ will vary as

$$dN_{unstable}/dt = -\bar{n}(t)dN_{fl}/dt. \quad (5)$$

At $t=0$ the chains form the F array, which implies that $\bar{n}(0)=9$. As the number of reversed chains increases, $\bar{n}(t)$ will decrease to a minimum $\bar{n}(\infty)=1$: A combination of (4) and (5) yields the differential equation for $M(t)$:

$$d^2M/dt^2 = -(1/\tau')dM/dt, \quad (6)$$

$$\tau'(t, T) = \tau(T)/\bar{n}(t) = [1/\bar{n}(t)]\exp(\Delta E/k_B T). \quad (7)$$

From the above expressions it is obvious that $M(t)$ cannot be described by a simple exponential function, and that the effective relaxation time $\tau'(t, T)$ will increase by a factor 9 in the course of time. The experimental data in Fig. 10 are in qualitative agreement with the expected variation of $\tau'(t, T)$. The activation energy $\Delta E/k = 33 \pm 5\text{ K}$ derived from the observed temperature dependence of $\tau'(t=0, T)$ suggests that nucleation at chain ends dominates the relaxation for $2\text{ K} < T < 3\text{ K}$: $|J_a|/k = 42 \pm 3\text{ K}$.

The same kind of experiments as described above have been performed by means of neutron scattering at $T=4.2\text{ K}$. In these experiments, the change of the long-range order in the FI phase has been studied at large time intervals. In RFC, a typical value of the growth of the corre-

lation length with time is $d(\xi_b/b)/dt = 0.08/\text{h}$ for $t > 30\text{ min}$, whereas for CFC at this time scale practically no variation in the correlation length occurs.

Concluding this section, we may state that, qualitatively, the nonexponential and strongly temperature-dependent relaxation behavior in CFC is in agreement with the theoretical model, again confirming the occurrence of a nucleation process in the present quasi-1D Ising system. However, with respect to the slowing down of the relaxation rate with time, the data are not accurate enough to make a quantitative comparison between theory and experiment.

VI. THE MAGNETIC PHASE DIAGRAM OF $\text{RbFeCl}_3 \cdot 2\text{D}_2\text{O}$

In the preceding sections interest was focused on the deviations from perfect structures and the associated reversals of unstable chains at field values $H_i \neq H_{c1}, H_{c2}$. In some cases the experimental procedure was even chosen specifically to enhance the deviations from thermal equilibrium. It should be emphasized, however, that the metamagnetic transitions at $H_{c1}(T)$ and $H_{c2}(T)$ remain well-defined in spite of the disorder present in the AF and FI arrays, provided that T is not too low (see Fig. 5). Observation of these transitions, which correspond to the equilibrium phase boundaries, may be facilitated by performing scans at small field sweep rates.

In order to compare the phase diagrams for RFC (aq= H_2O and D_2O), neutron-diffraction measurements were performed on the deuterated compound in the a^*-b^* plane (cf. Table IV). The phase transitions, derived from the intensity variation of the reflections $(0 \frac{1}{2} 0)$, $(0 \frac{3}{4} 0)$, and $(\bar{1} \frac{3}{2} 0)$ for increasing H or increasing T , are plotted in Fig. 11. In general, there is a fair agreement with the phase boundaries for the hydrated compound, determined previously by susceptibility measurements (cf. Fig. 2), with two exceptions that will be discussed below.

For $\text{RbFeCl}_3 \cdot 2\text{D}_2\text{O}$ we obtain $T_N = 11.85(1)\text{ K}$ and, by extrapolation, $H_{c1}(T=0) = 7.85(5)\text{ kOe}$ and $H_{c2}(T=0) = 12.0(1)\text{ kOe}$. These values deviate only little from the corresponding ones for $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$: $T_N = 11.96\text{ K}$, $H_{c1}(T=0) = 7.8(1)\text{ kOe}$, and $H_{c2}(T=0) = 11.7(1)\text{ kOe}$, the transition fields being corrected for demagnetization.⁵ At low T the transitions $H_{c1}(T)$ and $H_{c2}(T)$ are of first order, resulting in approximately linear intensity variations in a narrow field interval $\Delta H = 350\text{ Oe}$, from which we may derive the demagnetization factor $N_D = \Delta H/(M_F/2) = 8.3$ by using the value $M_F = 8.7 \times 10^3\text{ emu/mol}$ from the magnetization measurements.¹¹ The crossover from first-order to second-order behavior for increasing T will result in a gradual change of the intensity versus H curves, the intensity variation becoming non-linear in a larger interval below the transition. Taking the increase in ΔH as an indication for the crossover, we conclude that the transitions $H_{c1}(T)$ and $H_{c2}(T)$ are of second order for $T \gtrsim 6.5 \pm 0.2\text{ K}$ and $T \gtrsim 9.0 \pm 0.5\text{ K}$, respectively.

There appear two striking differences between the phase boundaries shown in Figs. 2 and 11. The neutron-diffraction data reveal the existence of an additional boun-

FIG. 11. Magnetic (H, T) phase diagram of $\text{RbFeCl}_3 \cdot 2\text{D}_2\text{O}$ with $\mathbf{H} \parallel \mathbf{c}$ as determined from neutron-diffraction experiments. The data points denote transitions in increasing field (Δ) and increasing temperature ($\circ$).

dary within the FI phase, and fail, on the other hand, to detect the final approach of the boundary $H_{c1}(T)$ towards the point where it is expected to join the boundary between the AF and F phases. The additional phase boundary, which meets the boundaries $H_{c1}(T)$ and $H_{c2}(T)$ at $T=6.3(1)$ and $7.7(1)$ K, respectively, is most clearly observed by the sudden disappearance of the $(0 \frac{9}{4} 0)$ peak intensity in scans at constant H and increasing T . A typical illustration of the irreversible behavior at the transition is given in Fig. 12(a) for $H=9.38$ kOe. A similar irreversible transition is observed in field scans at constant T at the $(0 \frac{9}{4} 0)$ reflection [see Fig. 12(b)].

When the steplike intensity changes observed for decreasing H or increasing T are compared with the relative intensities in Table III, it may be concluded that the FI(II) structure is transformed into the FI(I) structure at a well-defined phase boundary, shown in Fig. 11. The reverse transition, however, is only partly achieved. The long-range FI(I) order was investigated by measuring the widths of Bragg reflections in the a^*-b^* plane at one fixed combination $H=9.38$ kOe, $T=7.2$ K, close to the phase boundary [see Fig. 12(a)]. No broadening was observed, which indicates a regular FI(I) pattern along the a and b directions. The order along the c direction has not been established.

The occurrence of the FI(I)-FI(II) transition implies that the two structures are energetically inequivalent. This may be due to various causes that have not been considered so far. Firstly, long-range dipole-dipole interactions or exchange interactions beyond nearest neighbors may favor one of the structures. For example, the inclusion of the dipolar energy, which may be calculated for the perfectly ordered FI structures at $T=0$, indeed yields a minimum energy for the FI(II) structure in RFC.¹⁴ On the other hand, at higher temperatures ($T \geq 6$ K) the gradual variation of the transition fields $H_{c1}(T)$ and $H_{c2}(T)$ indicates that the entropy term TS in the free energy is becoming important. To evaluate the influence of this term separately, the free energy of the three FI structures

FIG. 12. Typical variations of magnetic peak intensities across the phase boundary $T_c(\text{II} \rightarrow \text{I})$. (a) Temperature scans at constant field ($H=9.38$ kOe). (b) Field scans at constant temperature. The indicated F, FI(II), FI(I), and AF phases refer to the decreasing field scan.

was calculated in the molecular field approximation for an Ising system.¹⁵ From these calculations, which do not include dipolar interactions, it appears that the FI(I) structure will have the lowest free energy for $T > 0$. Hence, it is conceivable that the phase boundary in the FI regime is due to a competition between different terms in the free energy of the system.

In contrast to the AF-FI and F-FI transitions, the FI(I)-FI(II) transition cannot be explained by a successive reversal of single unstable chains. It may be seen from Fig. 3 that the transition between the two perfect FI structures requires reversal of all moments in each fourth b - c plane. However, in both FI structures all chains are locally stable between H_{c1} and H_{c2} . The same applies to the partly disordered FI arrays below $T=6$ K, in which some "antiferromagnetic" ($a, \bar{a}$) planes are not stacked in the regular sequence between correctly stacked "ferromagnetic" (f) planes. Hence, the transition can take place only by a collective reversal of chains.

The irreversible behavior at the transition might be related to the larger number of stacking faults in the FI(II) phase. Actually, each irregular sequence of "antiferromagnetic" planes corresponds to an FI(I) domain of at least seven layers that may initiate domain growth at the FI(II) $\rightarrow$ FI(I) transition. The reverse nucleation and growth process is less probable because the FI(I) array is better ordered.

FIG. 13. Temperature dependence of the $(\bar{1} 1 0)$ and $(\bar{1} \frac{3}{2} 0)$ intensities at constant field. The inset shows the path followed in the (H, T) phase diagram.

The observation of the FI(I) $\rightarrow$ AF transition for $T > 8$ K in field scans is severely hampered by the unfavorable scanning paths with respect to the boundary. Moreover, temperature scans at reflections that are sensitive to the FI(I) $\leftrightarrow$ AF transition, for example, at $(\bar{1} \frac{3}{2} 0)$, give the impression that the FI(I) structure is transformed directly into the F structure (Fig. 13). No well-defined intensity increase is observed at $T \approx 9$ K where one would expect the FI(I) $\rightarrow$ AF transition to occur on the basis of the susceptibility results. The only observable irregularity in Fig. 13 is a shallow minimum in the $(\bar{1} 1 0)$ intensity at $T \approx 9$ K, corresponding to a small decrease in the magnetization. Apparently, this part of the boundary between the FI and AF phase is observed more easily in susceptibility or magnetization measurements than by diffraction in the a^*-b^* plane.

The absence of the expected increase in the $(\bar{1} \frac{3}{2} 0)$ intensity at the FI $\rightarrow$ AF transition may be a consequence of the large magnetization in the AF phase for these values of H and T , which implies that the calculated relative intensities for the perfect AF structure ($M=0$) are not applicable. When a fraction p of the "down" chains in the perfect AF array is reversed ($M=pM_F$), the intensities listed in the second column of Table III should be multiplied with a factor $(1-p)^2$. For $p = \frac{1}{2}$ the $(\bar{1} \frac{3}{2} 0)$ intensity will be constant at the FI(I)-AF transition.

VII. SUMMARY AND DISCUSSION

From the present investigation one may conclude that the magnetic ordering of the quasi-1D metamagnets RFC and CFC depends strongly on the temperature and the scanning procedure. When the samples are cooled below $T \approx 2$ K the magnetic order or disorder, which will depend on the path followed through the (H, T) parameter space, is frozen in almost completely. Some relaxation towards the equilibrium state does occur after passing a phase boundary, but the relaxation time is in the order of hours. In the interval $2 \text{ K} \leq T \leq 3 \text{ K}$, changes in the magnetic array at varying H are realized more easily by reversal of single unstable chains at well-defined field values H_i . In general, the FI arrays formed either in a slow de-

creasing field sweep or after a rapid field change from $H > H_{c2}$, are partly disordered. It is found that the chain reversals are initiated by thermal excitation of a moment reversal at a chain end ($\Delta E/k \approx 30-40$ K), leading to relaxation times $\tau'(t=0)$ varying typically by a factor 300 within this interval of only 1 K. The next interval $3 \text{ K} \leq T \leq 6 \text{ K}$ may be considered as an intermediate region between the single-chain reversal regime and the fluctuation regime. The results obtained for RFC show that for increasing T the steps in the $M(H)$ curve at H_i disappear gradually, and that the magnetic correlation length increases. The phase transitions $H_{c1}(T)$ and $H_{c2}(T)$ in RFC are of second order for $T > 6.5 \pm 0.2$ K and $T > 9.0 \pm 0.5$ K, respectively, and changes in the magnetic ordering close to these boundaries will be governed by critical fluctuations, most probably in three dimensions.

Only two of the three proposed long-range-ordered FI structures, FI(I) and FI(II), are observed. The preference for one of these structures in separate regions of the (H, T) phase diagram indicates that they are energetically nonequivalent, which may be due to long-range dipole-dipole interactions¹⁴ or exchange interactions beyond nearest neighbors. Since the magnetization does not change in the FI(I)-FI(II) transition, this boundary will be unobservable in M or χ measurements. From the diffraction measurements on RFC no conclusion can be drawn with regard to the order of the transition.

In the low- T region, where the changes in the magnetic array are realized by single-chain reversals, the experimental results can be reproduced by computer simulations based on Tinkham's nucleation condition. The limited validity of this approach is most clearly demonstrated by the development of long-range correlations for $T \gtrsim 2$ K, corresponding to either the FI(I) or FI(II) structure. The amount of disorder in the FI array after passing H_{c2} gives a reliable indication for the applicability of Tinkham's model. The characteristic low- T features, e.g., steps in $M(H)$ and disorder in the FI phase, are still observable at $T = 4.2$ K in CFC, in contrast to RFC which at the same temperature is ordered over much larger distances. This difference cannot be explained by the relatively small difference in the intrachain interaction $|J_a|/k$ [42 K and 37(2) K], and may be related to the fact that CFC is a better approximation to a one-dimensional system than RFC. From Table I it is obvious that the ratios between the interchain and intrachain interactions are systematically smaller for CFC. On the other hand, the difference may arise from the fact that CFC has a more pronounced Ising character, as is indicated by the results of spin-cluster resonance and estimates of the crystal-field splitting between the electronic energy levels.¹²

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