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Spin-cluster resonance in the pseudo-one-dimensional canted Ising antiferromagnet $RbFeCl_3 \cdot 2H_2O$

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Spin-cluster resonance (SCR) is observed in the pseudo-one-dimensional canted Ising antiferromagnet $RbFeCl_3 \cdot 2H_2O$. Transitions between clusters up to 9 spins ($|m> \Rightarrow |m+9>$) could be detected. Since the moments in the chain are canted with respect to each other, SCR were observed which show characteristics of a ferromagnetic chain and an antiferromagnetic chain for the external magnetic field parallel to the c and a axis, respectively. The experimental data for $\vec{H} \parallel \vec{c}$ could excellently be described by a pure Ising model, with $J_b/k = 0.76$ K, $J_c/k = -0.21$ K, $J_{bc}/k = -0.13$ K, $\vec{\mu} \cdot \vec{H}/|\vec{H}| = 1.50\,\mu_B$, and a correction for a demagnetizing field. In order to describe the SCR for $\vec{H} \parallel \vec{a}$ the influence of the crystal-field splitting of the pseudo-ground-doublet of the Fe^{2+} ion had to be taken into account.

I. INTRODUCTION

The elementary excitations in an $S = \frac{1}{2}$ Ising system are not collective spin waves like in a Heisenberg system, but localized spin reversals called spin clusters or magnon bound states. An m-fold spin cluster $|m\rangle$ is defined as a cluster of m neighboring spins which are reversed with respect to their position in the ground state.

Although spin clusters are expected to exist in all Ising systems, they have been observed in only a few compounds. Direct observations of spin clusters by far-infrared experiments have been reported for the well-known Ising compounds $CoCl_2 \cdot 2H_2O$ (Ref. 1) and $CoBr_2 \cdot 2H_2O$ (Ref. 2). Recently spin clusters were observed in $CsCoCl_3$ by both Raman scattering and far-infrared experiments.[3]

Transitions between spin clusters, called spin-cluster resonance (SCR), were reported for $CoCl_2 \cdot 2H_2O$,[4] $NiCl_2 \cdot 2H_2O$,[5] $FeCl_2$,[6] and $FeCl_2 \cdot 4H_2O$.[7] In all these cases changes in cluster size by one spin, ($|m\rangle \quad |m+1\rangle$) were observed. These excitations can give detailed information about the magnetic moment and the exchange interactions, as was shown in the case of $CoCl_2 \cdot 2H_2O$.[1]

In one-dimensional systems the excitation of a spin cluster involves an energy determined by both the intrachain and interchain exchange interactions and Zeeman energy. In such a system, the spin-cluster-resonance (SCR) energies are much smaller, since only the interchain interactions and Zeeman energy are involved. In this paper we want to report SCR experiments in the pseudo-one-dimensional Ising antiferromagnet $RbFeCl_3 \cdot 2H_2O$,[8] in which we have observed changes in cluster size up to 9 spins ($|m\rangle \Rightarrow |m+9\rangle$). Although we have also observed SCR in $CsFeCl_3 \cdot 2H_2O$, we will confine ourselves in this paper to the SCR experiments on $RbFeCl_3 \cdot 2H_2O$.

$RbFeCl_3 \cdot 2H_2O$ belongs to the series of isomorphic transition-metal halides $AMB_3 \cdot 2H_2O$ (A = Cs, Rb; M = Mn, Co, Fe; B = Cl, Br). All members of this series show pronounced linear chain ($d = 1$) characteristics.[9,10] In $RbFeCl_3 \cdot 2H_2O$ the interchain interactions give rise to an ordered phase below $T_N = 11.96$ K.[10] The magnetic specific heat of $RbFeCl_3 \cdot 2H_2O$ could be described both above and below T_N with Onsagers rectangular $S = \frac{1}{2}$ Ising model with $|J/k| = 39$ K and $|J'/k| = 0.7$ K. The Ising character of $RbFeCl_3 \cdot 2H_2O$ was confirmed by magnetization measurements in the ordered state. Application of a magnetic field along the c axis resulted in two metamagnetic transitions at 8.1 and 12.4 kOe, respectively. The increase of the magnetization at both transitions appeared to be equal. A possible explanation of the metamagnetic transitions is given in Sec. II, in which we will describe the preparation of the crystals and the crystallographic and magnetic structure of $RbFeCl_3 \cdot 2H_2O$.

A simple SCR theory for a pure Ising system will be given in Sec. III. Experimental equipment and results are presented in Sec. IV. In Sec. V the influence of deviations from the pure Ising case will be considered. In Sec. VI we discuss the results.

II. CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE

Single crystals of $RbFeCl_3 \cdot 2H_2O$ were grown by slow evaporation at 37 °C from a solution of $FeCl_2 \cdot 4H_2O$ and RbCl in a molar ratio of 3.2 : 1. A 0.03N solution of HCl was used to prevent oxidation of the crystals. The single crystals obtained by this procedure had typical dimensions up to $2 \times 2 \times 0.5$ cm^3. The very pale violet-brown crystals may be easily cleaved parallel to the largest crystal face, which corresponds to the a-b plane.

X-ray and neutron diffraction experiments[11] showed that the crystallographic structure of $RbFeCl_3 \cdot 2H_2O$ is orthorhombic and may be described by space group *Pcca* with $a = 8.876$ Å, $b = 6.872$ Å, and $c = 11.181$ Å. Like the cobalt and maganese isomorphs 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 ions. In the c direction the chains are weakly coupled by hydrogen bonds.

The magnetic space group was determined as $P_{2_b}c'ca$ by nuclear magnetic resonance and neutron diffraction experiments at $T = 4.2$ K.[11] This space group allows a canting of the magnetic moments in the a-c plane with a net magnetization of each chain along the c direction. The resulting array of the moments is sketched in Fig. 1. From dipole-field calculations the direction of the moment in a cluster was found to be close to the direction pointing to the shared chlorine ion.

Preliminary measurements yielded a phase diagram schematically given in Fig. 2. This phase diagram resembles that of $CoCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot 2H_2O$,[12] with the notable difference that the magnetization in the ferrimagnetic (FI) phase is one half of the magnetization in the ferromagnetic (F) phase. The two metamagnetic transitions in $RbFeCl_3 \cdot 2H_2O$ are associated with a reorientation of the ferromagnetic component of the chains. In order to explain these two transitions and the values of the magnetization, we applied the method developed by Kudo and Katsura[13] to determine ground-state spin configurations, i.e., the spin configurations having the lowest energy, at zero temperature in a magnetic field.

Since the ordering within a chain does not change when an external magnetic field is applied, we may use a two-dimensional model in which a chain is represented by a single moment. Since the method is rather straightforward we will only present the results.

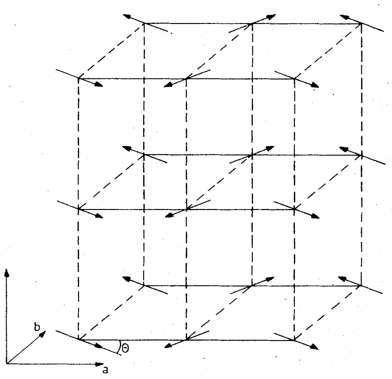

FIG. 1. Array of the magnetic moments in the ordered state. All the moments are located in the a-c plane at an angle θ from the a axis.

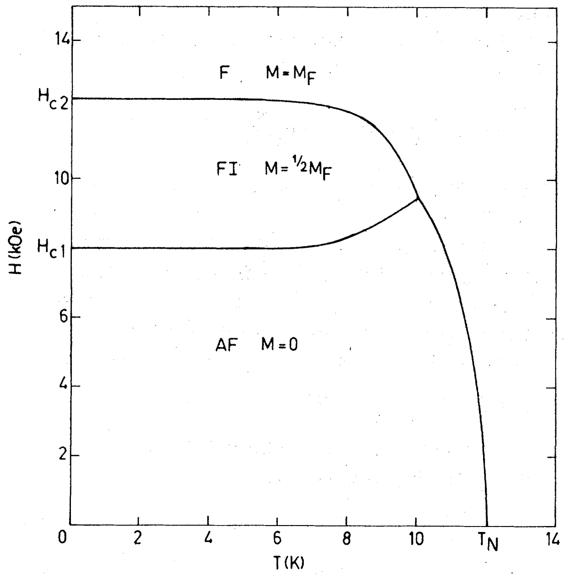

FIG. 2. Schematic phase diagram of $RbFeCl_3 \cdot 2H_2O$.

The suitable lattice for $RbFeCl_3 \cdot 2H_2O$ is a rectangular lattice (b-c plane). To explain two phase transitions, at least three exchange interactions have to be present, an interaction J_b along the b axis, an interaction J_c along the c axis and an interaction J_{bc} diagonally in the b-c plane. For $J_b, J_c, J_{bc} < 0$ and $|J_c| < |J_b|$, $|J_c| < |2J_{bc}|$ two phase transitions are obtained,[14] as well as the correct ground-state spin configuration in zero field.

The resulting arrays of the ferromagnetic components of the chains are given in Fig. 3. For the ferrimagnetic phase three different spin configurations with the same energy can be derived.

III. SIMPLE THEORY OF SCR IN A CANTED ANTIFERROMAGNETIC ISING CHAIN

In this section we will present a description of spin clusters and SCR in the case of pure Ising interactions. We will start with the treatment of an

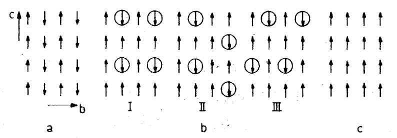

FIG. 3. Arrays of the ferromagnetic components of the chains. (a) Antiferromagnetic array of the chains. (b) Three possible ferrimagnetic arrays (the down moments are encircled). (c) Ferromagnetic array.

isolated chain.

The Hamiltonian describing such an Ising chain is given by

$$\mathcal{H} = -2J^{zz}\sum_j S_j^z S_{j+1}^z - \mu_B \sum_j g^{zz} S_j^z H^z . \tag{3.1}$$

For $S=\frac{1}{2}$, S_j^z is equal to $+\frac{1}{2}$ or $-\frac{1}{2}$, a spin may be "up" or "down."

We define a spin cluster $|m\rangle$ as a cluster of m adjacent spins in the chain which are reversed with respect to their ground state. The energy E_m needed to excite such a state in a ferromagnetic chain ($J^{zz} > 0$) is

$$E_m = 2J^{zz} + m\mu_B g^{zz} H^z, \quad m \geq 1 . \tag{3.2}$$

For an antiferromagnetic chain ($J^{zz} < 0$) the excitation energy E_m is given by

$$E_m = -2J^{zz} \quad (m \text{ even}), \tag{3.3}$$

$$E_m = -2J^{zz} \pm \mu_B g^{zz} H^z \quad (m \text{ odd}); \tag{3.4}$$

the plus and minus sign depend on the direction of the total magnetization of the cluster with respect to H. In $RbFeCl_3 \cdot 2H_2O$ the moments are nearly antiferromagnetically ordered along the a axis ($J^{zz} < 0$) and are tilted by an angle θ from the a axis towards the c axis as is shown in Fig. 1.

Assuming an Ising behavior, such a case has the interesting feature that application of a field along the ferromagnetic components in the c direction results in an excitation spectrum characteristic for a ferromagnetic chain, whereas application of a field along the antiferromagnetic components in the a direction results in an excitation spectrum characteristic for an antiferromagnetic chain.

So far only an isolated chain was considered. In a real crystal there exists a coupling between the chains. We have shown that for $RbFeCl_3 \cdot 2H_2O$ at least three different interchain interactions are necessary to explain the magnetization measurements. If these interchain interactions are described by an Ising Hamiltonian the excitation energies may be written generally as

$$E_m = -2J_a + m(\alpha J_b + \beta J_c + \gamma J_{bc}) \mp 2m\vec{\mu}\cdot\vec{H} \quad \text{for } \vec{H} \parallel \vec{c}, \tag{3.5}$$

$$E_m = -2J_a + m(\alpha J_b + \beta J_c + \gamma J_{bc}) \mp 2\delta_m \vec{\mu}\cdot\vec{H} \quad \text{for } \vec{H} \parallel \vec{a}, \tag{3.6}$$

with $\alpha = 2, 0$ or -2, $\beta = 2, 0$ or -2, $\gamma = 4, 2, 0, -2$ or -4, $\delta_m = 0$ for even m and $\delta_m = 1$ for odd m. The actual values of α, β, and γ in (3.5) and (3.6) depend on the local spin configuration. Due to the large value of the intrachain interaction J_a these energies are in the far-infrared region ($-2J_a/k \cong 80$ K). However, when a thermally excited cluster is present, an increase of the cluster size requires an energy determined only by the weak interchain interactions and the Zeeman energy. These transitions can be observed in the microwave region.

In Sec. II the ground-state spin configurations were given for the three phases: the antiferromagnetic (AF), ferrimagnetic (FI), and ferromagnetic (F) ordering of the total moments of the chains. Within these ground-state spin configurations, the energies needed to increase the cluster size within a chain by n spins ($|m\rangle \Rightarrow |m+n\rangle$) for $\vec{H} \parallel \vec{c}$ are given by the following: for the AF state,

$$E = n(-2J_b + 2J_c - 4J_{bc} \mp 2\vec{\mu}\cdot\vec{H}), \quad An, Bn;$$

for the FI state,

$$\begin{aligned}
&\text{I, II: } E = n(2J_b - 2J_c + 4J_{bc} + 2\vec{\mu}\cdot\vec{H}), \quad Cn\\
&\text{I: } E = n(2J_b + 2J_c - 4J_{bc} + 2\vec{\mu}\cdot\vec{H}), \quad Dn\\
&\text{II: } E = n(2J_c + 2\vec{\mu}\cdot\vec{H}), \quad En\\
&\text{I, II, III: } E = n(-2J_b - 2J_c - 4J_{bc} - 2\vec{\mu}\cdot\vec{H}), \quad Fn\\
&\text{I, III: } E = n(-2J_b + 2J_c + 4J_{bc} + 2\vec{\mu}\cdot\vec{H});\\
&\text{III: } E = n(2J_b + 2\vec{\mu}\cdot\vec{H});
\end{aligned} \tag{3.7}$$

for the F state,

$$E = n(2J_b + 2J_c + 4J_{bc} + 2\vec{\mu}\cdot\vec{H}), \quad Gn .$$

The labeling of the FI states refers to Fig. 3, while the labeling of the energies refers to the experimentally observed excitations (Fig. 4). If we use the expressions for the two critical fields H_{c1} and H_{c2},[14] the equations An, Cn, Fn, and Gn may be written

$$\begin{aligned}
E &= 2\mu_c n(H_{c1} - H_c), \quad An\\
E &= 2\mu_c n(H_c - H_{c1}), \quad Cn\\
E &= 2\mu_c n(H_{c2} - H_c), \quad Fn\\
E &= 2\mu_c n(H_c - H_{c2}), \quad Gn .
\end{aligned} \tag{3.8}$$

With an external magnetic field applied along the a axis, no phase transitions were detected in the experimental field region. The energy needed to increase the cluster size in the AF ground-state spin configuration by n spins is given by

$$E = n(-2J_b + 2J_c - 4J_{bc}) \mp 2\delta_n \vec{\mu}\cdot\vec{H} . \tag{3.9}$$

Since in our experiments $T \neq 0$ K, the ordering of the ferromagnetic components of the chains may locally differ from the ordering patterns determined by the method of Kudo and Katsura.[13] We call these arrays non-ground-state spin configurations. SCR which originate from such a non-ground-state spin configuration are contained in the more general Eqs. (3.5) and (3.6).

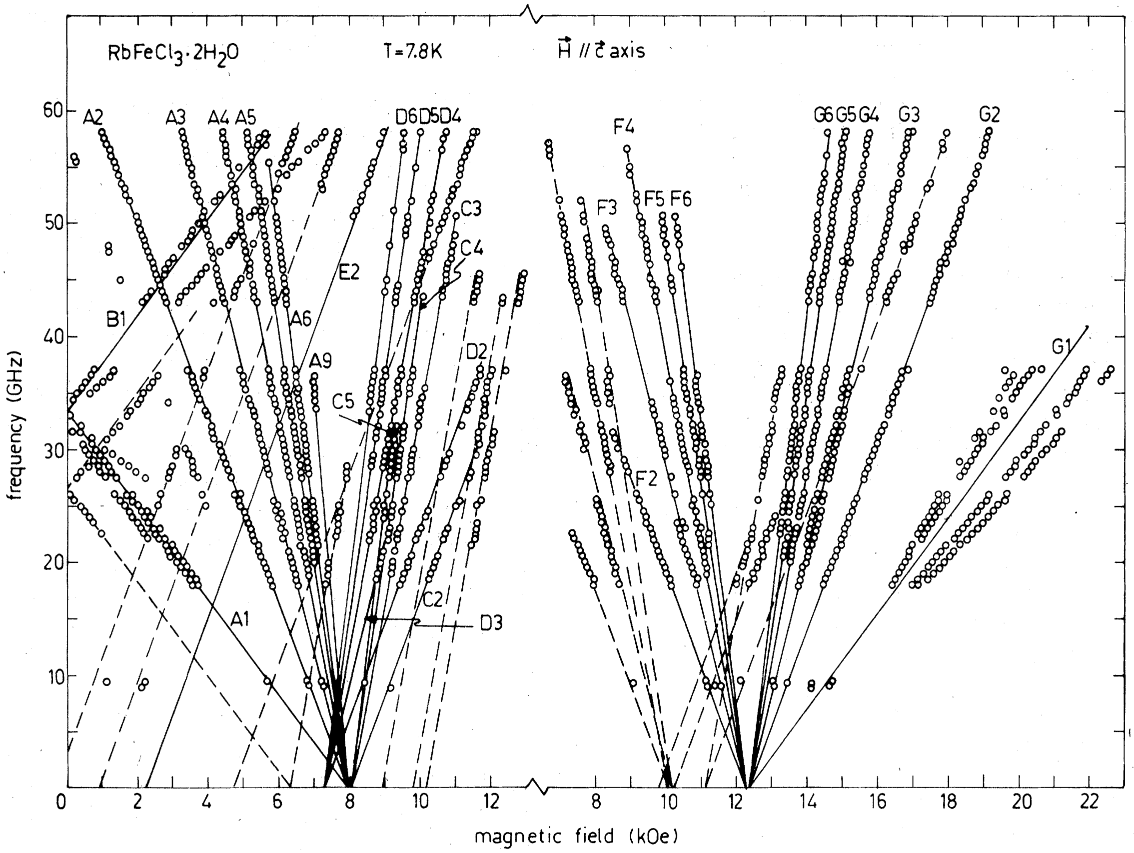

FIG. 4. Observed resonance frequencies plotted vs the magnetic field H, for H along c. The lines are the theoretical predictions for the pure Ising model, solid lines represent SCR in a ground-state spin configuration and broken lines represent SCR in a non-ground-state spin configuration. The labeling of the resonance lines corresponds to the labeling in Eq. (3.7).

IV. EXPERIMENTAL RESULTS

SCR experiments were performed with simple microwave spectrometers for the 9–12.4, 12.4–18, 18–26, 26–40, and 40–60 GHz frequency ranges. As microwave sources we used klystrons, except for the 12.4–18 GHz band where a solid-state oscillator was used.

The crystals were placed at the end of a closed waveguide without a cavity. The end of the waveguide was placed inside a temperature controlled cryostat in the center of a superconducting solenoid. The magnetic field was recorded by a Hall probe. The temperature could be established by a commercial temperature controller using a carbon resistor as sensor and was constant within 0.1 K for temperatures between 4.2 and 15 K and fields up to 25 kOe. The temperature was measured before every field sweep by a calibrated germanium thermometer.

At low temperatures the amount of thermally excited clusters and hence the intensity of the spin-cluster resonances will be very low. This is illustrated by the fact that at $T=4.2$ K no signals could be detected. The upper limit for the temperature at which the experiments are to be performed is in principle the Néel temperature where the long-range order between the chains is destroyed. One may expect (see Fig. 2) that below 7 K the spin configurations are basically those determined for $T=0$ K and hence the Eqs. (3.7) and (3.9) may be used in the analysis of the experimental results.

In Fig. 4 the observed resonance frequencies are plotted versus the magnetic field H, for $\vec{H}\parallel\vec{c}$. For the resonances $G1$ only data for $\nu<40$ GHz are shown. At higher fields no absorptions were detected. The drawn labeled lines in Fig. 4 represent Eqs. (3.7) with $J_b/k=-0.76$ K, $J_c/k=-0.21$ K, $J_{bc}/k=-0.13$ K, $\vec{\mu}\cdot\vec{H}/|\vec{H}|=1.50\mu_B$. The demagnetizing field was an adjustable parameter in the fitting procedure which yielded 100 Oe in FI phase and 200 Oe in the F phase. Given the rather cube-like shape of the sample and the magnetization in the FI phase (4.5×10^3 emu/mol) and in the F phase (9×10^3 emu/mol),[11] these demagnetizing fields seem somewhat too small. Not all sets of excitations predicted by Eqs. (3.7) were observed. The broken lines in Fig. 4 represent SCR in a non-ground-state spin configuration, contained in the more general equation (3.5) with the same set of parameters. The agreement between the theoretical prediction and the experiment is satisfying, and changes in cluster size up to nine spins can be observed. The splitting of some of the resonances ($A1, A3, G1, G3$) can be explained by a misorientation of the crystal in the a-c plane by about 1°. Only odd excitations split and the splitting decreases when more spins are involved in the excitation.

The amplitude of the signals increase with increasing temperature and reaches a maximum at about 9 K. When the temperature is increased further, the amplitude decreases. Excitations could be observed even above T_N at $T = 14$ K, indicating the existence of local $3d$ ordered regions. The resonance linewidth increases at higher temperatures, a typical value at 8 K is 100 Oe. As might be expected the intensity of excitations originating from non-ground-state spin configurations was found to be lower than the intensity of excitations from a ground-state spin configuration.

The resonance condition appeared to be temperature independent. The resonances could be detected with the direction of the microwave field along a and b (crystal mounted at the bottom of the waveguide) and along c (crystal mounted at the small side of the waveguide at $\frac{1}{4}\lambda$ above the bottom).

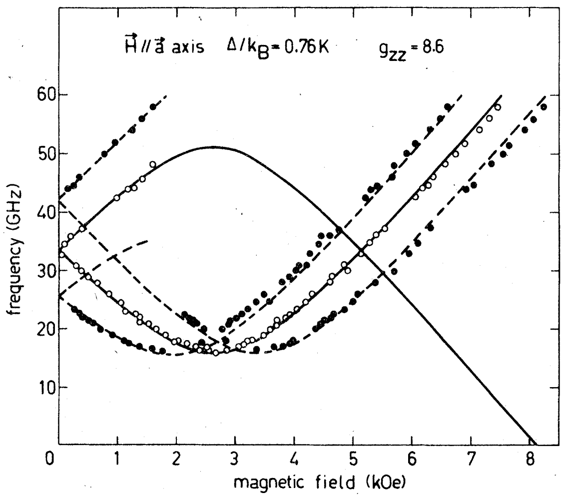

FIG. 5. Observed resonance frequencies plotted vs the magnetic field H, for H along the a axis. The open circles represent SCR in the AF ground-state spin configuration. The lines are the theoretical predictions for the field dependence of the SCR, in the presence of a crystal field splitting of the ground doublet Δ (Sec. V/D).

In Fig. 5 the observed resonance frequencies are plotted versus a magnetic field $\vec{H} \parallel \vec{a}$. Because of the high temperature (9.5 K) a large number of excitations originating from non-ground-state spin configurations are present. In Fig. 5 only a small number of these excitations is shown.

Since we used constant frequencies and varying magnetic field in the experiments no excitations involving an even number of spins are observed as these are field independent. When we compare the resonances having the highest intensity with the theoretical prediction of Eq. (3.9), it is obvious that the observed curvature of the resonance lines is not predicted by the simple Ising model. This is in contrast with the results for $\vec{H} \parallel \vec{c}$, which can be described by the simple Ising model. Therefore in Sec. V non-Ising terms and their influence on the SCR frequencies will be considered.

V. CANTED ANTIFERROMAGNETIC CHAIN

In this section we will present a more detailed treatment of the spin clusters in order to explain the observed deviations from the pure Ising prediction. First a survey of the deviations that might be expected in the case of $RbFeCl_3 \cdot 2H_2O$ will be given. Next, appropriate basis functions are defined and the effect of the non-Ising terms is calculated.

A. Deviations from the pure Ising behavior in $RbFeCl_3 \cdot 2H_2O$

In a crystal field of low enough symmetry, the ^5D ground state of the free Fe^{2+} ion will be split and an orbital singlet with fivefold spin degeneracy will have the lowest energy. Spin-orbit interactions will lift the spin degeneracy. So far we have assumed that this will result in a doublet ground state and we used the $s = \frac{1}{2}$ spin-Hamiltonian formalism. This assumption was based on crystal field calculations, comparison with $CsCoCl_3 \cdot 2H_2O$,[11] and specific-heat results. However, a small splitting of the doublet may not be excluded. Therefore we will now examine the splitting of the full spin quintet ($S = 2$). The splitting of this spin quintet, a second-order effect of the spin-orbit interaction, can be described by the Hamiltonian[15,16]

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) . \qquad (5.1)$$

The energy levels and eigenfunctions (in terms of $|m_s\rangle$) are given by

$$E_1 = 2D[1+3(E/D)^2]^{1/2}\,;$$

$$|\phi_1\rangle = \tfrac{1}{2}\sqrt{2}\,(\cos\alpha\,|2\rangle + \sqrt{2}\sin\alpha\,|0\rangle + \cos\alpha\,|-2\rangle);$$

$$E_2 = 2D,\quad |\phi_2\rangle = \tfrac{1}{2}\sqrt{2}\,(|2\rangle - |-2\rangle);$$

$$E_3 = -D + 3E,\quad |\phi_3\rangle = \tfrac{1}{2}\sqrt{2}\,(|1\rangle + |-1\rangle); \tag{5.2}$$

$$E_4 = -D - 3E,\quad |\phi_4\rangle = \tfrac{1}{2}\sqrt{2}\,(|1\rangle - |-1\rangle);$$

$$E_5 = -2D[1+3(E/D)^2]^{1/2},$$

$$|\phi_5\rangle = \tfrac{1}{2}\sqrt{2}\,(-\sin\alpha\,|2\rangle + \sqrt{2}\cos\alpha\,|0\rangle - \sin\alpha\,|-2\rangle);$$

with

$$\tan\alpha = \frac{E\sqrt{3}}{D + D[1+3(E/D)^2]^{1/2}}\,.$$

A pseudodoublet is lowest in energy when $D<0$ and $|E| \ll |D|$ or $D>0$ and $|E| \approx D$. These situations are basically identical but correspond to different sets of quantization axes. If we take $D<0$ the splitting of the two ground levels is $2D\{1-[1+3(E/D)^2]^{1/2}\}$. As was shown by Tinkham[15,17] this can be described by a $s=\frac{1}{2}$ spin Hamiltonian

$$H_\Delta = -\Delta S_x \tag{5.3}$$

with

$$\Delta = 2D\{1-[1+3(E/D)^2]^{1/2}\}\,.$$

When $\Delta=0$, the pure Ising case is obtained in which case the wave functions of the doublet are $|m_s=2\rangle$ and $|m_s=-2\rangle$. Hence a large anisotropy in the g tensor is expected when a $s=\frac{1}{2}$ spin Hamiltonian is used.

Additional non-Ising terms in the Hamiltonian (like J^{xx}, J^{yy}) may also be present. Below we will try to express these terms on a basis which also accounts for the canting of the moments. In principle we will follow the procedure given by Silvera *et al.* in their treatment of α-$CoSO_4$.[18]

In $RbFeCl_3 \cdot 2H_2O$ the clusters of adjacent Fe^{2+} ions in the chain are identical but canted with respect to each other. Hence the sets of principal axes of the crystal fields and, as a consequence, the sets of principal axes of the g tensors are also canted for adjacent positions in the chain. The exchange interaction is assumed to be isotropic in the real spin ($S=2$).

$$\mathcal{H} = -2J\vec{S}_1 \cdot \vec{S}_2\,. \tag{5.4}$$

To describe the effect of the exchange interaction on the ground doublet with a fictitious spin $s=\frac{1}{2}$, the different orientations of the g tensor of ion 1 and 2 with respect to the crystallographic axes must be taken into account. In Fig. 6 three different sets of axes are drawn: x''-y''-z'', the crystallographic system, the plane in which the canting occurs is the x''-z'' plane. For $RbFeCl_3 \cdot 2H_2O$ the axes correspond to the c, b, and a axes, respectively; x'_j-y'_j-z'_j, sets of principal axes of the g tensor of ion j, x_j-y_j-z_j, sets of axes for which $\langle\vec{s}_j\rangle$ is directed along z_j. The spin-only g factors g^s_l are defined by the following relation:

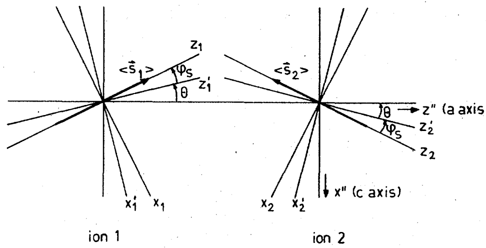

FIG. 6. Three different sets of axes of ion 1 and 2, which are used in the treatment of the canting mechanism. The plane of canting is shown, where x'', y'', z'' refers to crystallographic system ($x''=c$ axis, $y''=b$ axis and $z''=a$ axis), x', y', z' is the set of principal axes of the g tensor and x, y, z, is the set of axes for which $\langle\vec{s}\rangle$ is along the z axis.

$$S^l = \tfrac{1}{2} g^s_l s^l \tag{5.5}$$

with $l = x'_j, y'_j, z'_j$. Using an appropriate transformation from the double-primed to the single-primed axes, Eq. (5.5), and a transformation from the single-primed to the unprimed axes the Hamiltonian (5.4) may be written

$$\mathcal{H} = -2J^{xx}s^x_1 s^x_2 - 2J^{yy}s^y_1 s^y_2 - 2J^{zz}s^z_1 s^z_2 \tag{5.6}$$

with

$$J^{xx} = \tfrac{1}{4}J\{[(g^s_{x'})^2\cos^2\phi_s - (g^s_{z'})^2\sin^2\phi_s]\cos(2\theta) - g^s_{x'}g^s_{z'}\sin(2\phi_s)\sin(2\theta)\}\,,$$

$$J^{yy} = \tfrac{1}{4}J(g^s_{y'})^2\,,$$

$$J^{zz} = \tfrac{1}{4}J\{[(g^s_{z'})^2\cos^2\phi_s - (g^s_{x'})^2\sin^2\phi_s]\cos(2\theta) - g^s_{x'}g^s_{z'}\sin(2\phi_s)\sin(2\theta)\}\,,$$

where ϕ_s is the angle between $\langle\vec{s}_j\rangle$ and z'_j.

The value of $\langle s^z\rangle$ is $\frac{1}{2}$ for $T=0$ K. In the pure Ising case $g^s_{x'}$ and $g^s_{y'}$ are zero and hence J^{xx} and J^{yy} are zero, in which case s^z_1 and s^z_2 commute with the Hamiltonian (5.6). Equation (5.6) is mathematically equivalent with a Hamiltonian describing the exchange interaction of a noncanted system. For the Zeeman interaction the situation is quite different. If the external magnetic field is expressed by the components on the crystallographic axes, the Zeeman interaction for ion 1 is given by

$$H_{\text{Zeeman}} = -\mu_B(g_{xx}s^x_1 H_{x''} + g_{zx}s^z_1 H_{x''} + g_{xz}s^x_1 H_{z''} + g_{zz}s^z_1 H_{z''} + g_{y'}s^y_1 H_{y''}) \tag{5.7}$$

with

$$g_{xx} = g_{x'} \cos\theta \cos\phi_s - g_{z'} \sin\theta \sin\phi_s ,$$

$$g_{zx} = -g_{x'} \cos\theta \sin\phi_s - g_{z'} \sin\theta \cos\phi_s ,$$

$$g_{xz} = g_{x'} \sin\theta \cos\phi_s + g_{z'} \cos\theta \sin\phi_s ,$$

$$g_{zz} = -g_{x'} \sin\theta \sin\phi_s + g_{z'} \cos\theta \cos\phi_s .$$

For ion 2 the terms g_{zx} and g_{xz} should be reversed in sign, since θ and ϕ_s are negative for ion 2. If we identify the odd spins of a chain with spin 1 and the even spins of a chain with spin 2 (see Fig. 6), the Hamiltonian of a chain of N spins can be described by

$$\begin{aligned}\mathcal{H} = {} & -2J^{zz} \sum_{j=1}^{N} s_j^z s_{j+1}^z - J^- \sum_{j=1}^{N} (s_j^+ s_{j+1}^+ + s_j^- s_{j+1}^-) \\ & - J^+ \sum_{j=1}^{N} (s_j^+ s_{j+1}^- + s_j^- s_{j+1}^+) \\ & - \mu_B g_{xx} H_{x''} \sum_{j=1}^{N} \tfrac{1}{2}(s_j^+ + s_j^-) - \mu_B g_{zx} H_{x''} \sum_{j=1}^{N} (-1)^{j+1} s_j^z \\ & - \mu_B g_{xz} H_{z''} \sum_{j=1}^{N} (-1)^{j+1} \tfrac{1}{2}(s_j^+ + s_j^-) - \mu_B g_{zz} H_{z''} \sum_{j=1}^{N} s_j^z \\ & - \mu_B g_y H_{y''} \sum_{j=1}^{N} \frac{1}{2i} (s_j^+ - s_j^-) \end{aligned} \tag{5.8}$$

with

$$J^- = \tfrac{1}{2}(J^{xx} - J^{yy}), \quad J^+ = \tfrac{1}{2}(J^{xx} + J^{yy}), \quad g_y = g_{y'} .$$

The magnitude of the deviations, which may arise from exchange interactions, is almost completely determined by the intrachain interaction. The interchain exchange interactions will be described by only the Ising part of the interactions, and are taken into account by an exchange field

$$\mathcal{H} = -\sum_{j=1}^{N} (-1)^{j+1} H_e s_j^z \tag{5.9}$$

with $H_e = \alpha J_b + \beta J_c + \gamma J_{bc}$ and $\alpha = 2, 0$ or -2, $\beta = 2, 0$ or -2, $\gamma = 4, 2, 0, -2$ or -4. The influence of dipole fields is incorporated in the exchange interactions.

B. Ising basis functions of an antiferromagnetic chain

Before the energy levels of the combined Hamiltonian of Eq. (5.3), (5.8), and (5.9) can be calculated, proper wave functions have to be defined for the pure Ising case. In their treatment of the magnon bound states in $CoCl_2 \cdot 2H_2O$ Torrance and Tinkham[1] defined so-called Ising basis functions for a ferromagnetic chain. Similar basis functions can be defined for an antiferromagnetic chain.

In Sec. V A it was shown that also in a canted Ising system a good quantum number m_{sj} can be defined when the proper sets of axes are used. Hence Ising basis functions (IBF) may be defined for a canted chain.

An eigenstate of an Ising chain of N spins ($S = \frac{1}{2}$) can be described by the product of the single-spin states,

$$|\phi\rangle = \prod_{i=1}^{N} |m_{si}\rangle , \tag{5.10}$$

where m_{si} may have the values $+\frac{1}{2}$ or $-\frac{1}{2}$. The ground state of an Ising chain at $T = 0$ K is the Néel ground state, which is denoted by the eigenfunction $|0\rangle$. The first excited state above the ground state $|0\rangle$ is a state in which one spin is reversed, for instance the spin at position $j(R_j)$. If we use the operators S^+ and S^-, which reverse a "down" or an "up" spin, respectively, this state can be written

$$|+1, R_j\rangle = S_j^+ |0\rangle . \tag{5.11}$$

when a "down" spin is reversed,

$$|-1, R_j\rangle = S_j^- |0\rangle \tag{5.12}$$

when an "up" spin is reversed. The functions $|+1, R_j\rangle$ and $|-1, R_j\rangle$ have a $\frac{1}{2}N$-fold degeneracy as the spin reversal of a "down" or an "up" spin may occur at $\frac{1}{2}N$ sites. The spins at R_j with j odd are defined "up" and with j even are defined "down," in agreement with Eq. (5.8) and Fig. 6.

When we consider a closed chain of N spins (N is even) the Hamiltonian is periodic and the wave functions must have the Bloch form. We denote the distance between adjacent spins in the chain with d (for $RbFeCl_3 \cdot 2H_2O$ $a = 2d$). The periodicity of both the crystallographic and the canted magnetic chain amounts to $2d$. The IBF corresponding to a one-fold spin cluster is given by

$$|+1, k\rangle = \left(\frac{2}{N}\right)^{1/2} \sum_j e^{ikR_j} S_j^+ |0\rangle \quad (j \text{ even}) , \tag{5.13}$$

$$|-1, k\rangle = \left(\frac{2}{N}\right)^{1/2} \sum_j e^{ikR_j} S_j^- |0\rangle \quad (j \text{ odd}) . \tag{5.14}$$

Physically, Eqs. (5.13) and (5.14) represent normalized linear combinations of localized functions centered at all possible sites, with the familiar phase factor e^{ikR}. k is a good quantum number to label the $\frac{1}{2}N$ degenerate functions $|+1\rangle$ and $|-1\rangle$ and may have the values $-\pi/2d \leq k \leq \pi/2d$. The factor $(2/N)^{1/2}$ normalizes the wave function if $\langle 0 | 0 \rangle = 1$.

In general any excited state of the Ising chain can be described by the effect of an appropriate excitation operator P acting on the ground state $|0\rangle$. In that case R_j has to be replaced by $\bar{R}_j$, the center of the m excited spins R_ν which is determined by

$$\bar{R}_j = \frac{1}{m} \sum_{\nu=1}^{m} R_\nu .$$

The wave functions of larger spin clusters are defined by

$$|+2m,k\rangle=\left(\frac{2}{N}\right)^{1/2}\sum_j e^{ik\bar{R}_j}S_j^+S_{j+1}^-\cdots S_{j+2m-1}^-|0\rangle \quad (j \text{ even}),$$

$$|-2m,k\rangle=\left(\frac{2}{N}\right)^{1/2}\sum_j e^{ik\bar{R}_j}S_j^-S_{j+1}^+\cdots S_{j+2m-1}^+|0\rangle \quad (j \text{ odd}), \tag{5.15}$$

$$|+(2m-1),k\rangle=\left(\frac{2}{N}\right)^{1/2}\sum_j e^{ik\bar{R}_j}S_j^+S_{j+1}^-\cdots S_{j+2m-2}^+|0\rangle \quad (j \text{ even}),$$

$$|-(2m-1),k\rangle=\left(\frac{2}{N}\right)^{1/2}\sum_j e^{ik\bar{R}_j}S_j^-S_{j+1}^+\cdots S_{j+2m-2}^-|0\rangle \quad (j \text{ odd}).$$

The wave functions of other excited states, for instance two onefold clusters separated by ρ spins can be obtained from the operators $S_j^+S_{j+\rho+1}^-$ (j even), $S_j^-S_{j+\rho+1}^+$ (j odd) for even ρ and $S_j^+S_{j+\rho+1}^+$ (j even), $S_j^-S_{j+\rho+1}^-$ (j odd) for odd ρ.

C. Computation of the energy levels of the spin clusters and SCR frequencies

The energy levels of the spin clusters ($\rho=0$) are calculated by diagonalization of the energy matrix of the Hamiltonian with the Ising basis functions of Eq. (5.15) as basis. The interactions of the cluster under consideration with the ground state and other spin clusters ($\rho\neq 0$) are neglected in the calculation of the energy levels (J^+/k_B, J^-/k_B, and Δ/k_B are expected to be much smaller than $-2J_a^{zz}/k_B\approx 80$ K). However, these interactions may be of primary importance if they relax the $\Delta m=1$ selection rule and enable the transition of m-fold spin clusters ($m>1$) from the ground state $|0\rangle$.

The non-Ising terms of the intrachain interaction J^- and J^+ give rise to a k dependence of the energy levels. The SCR frequencies of a $\Delta m=n$ excitation are given by the energy difference between the energy levels of $|\pm m,k\rangle$ and $|\pm(m+n),k\rangle$. The SCR frequencies may depend on m and in the case $J^-\neq 0$ or $J^+\neq 0$ they may also depend on k.[1] Unlike the experiments in which a spin cluster is excited from the ground state ($k=0$) we have to consider contributions of the entire Brillouin zone in SCR experiments.

D. Interpretation

As we saw before, the SCR results obtained for $\vec{H}\parallel\vec{c}$ could be satisfactorily explained with a simple Ising model. It seems, however, that this is not possible for $\vec{H}\parallel\vec{a}$. Our first task will thus be to understand what kind of deviations from the simple Ising model can explain the spectrum for $\vec{H}\parallel\vec{a}$ without affecting the results for $\vec{H}\parallel\vec{c}$ seriously.

The largest deviations from the pure Ising behavior of the SCR for $\vec{H}\parallel\vec{a}$ occur at low frequencies. Generally, the SCR frequency goes to zero when the energy levels of the spin clusters intersect. In the pure Ising case the energies of the spin clusters $|-(m-1)\rangle$, $|-m\rangle$, $|+m\rangle$, and $|+(m+1)\rangle$ (m even) are equal for $H_{z''}=H_e/\mu_B g_{zz}$, as can be deduced from Eqs. (3.9) and (5.9).

The experimentally observed deviations from the pure Ising behavior are apparently due to matrix elements between the four states mentioned above. Inserting the complete Hamiltonian, including all the non-Ising terms derived in Sec. V A, results [apart from common diagonal elements $-\frac{1}{2}(N-4)J^{zz}$ and $-\frac{1}{2}NH_e$] in a submatrix given by

$$\begin{array}{c|cccc} & |-(m-1)\rangle & |-m\rangle & |+m\rangle & |+(m+1)\rangle \\ \hline \langle-(m-1)| & (m-1)H_e+\mu_B g_{zz}H_{z''} & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & 0 \\ \langle-m| & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & mH_e & 0 & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} \\ \langle+m| & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & 0 & mH_e & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} \\ \langle+(m+1)| & 0 & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & -\frac{1}{2}\Delta+\frac{1}{2}\mu_B g_{xz}H_{z''} & (m+1)H_e-\mu_B g_{zz}H_{z''} \end{array} \tag{5.16}$$

It is clear that only the pseudodoublet splitting Δ combined with a field-dependent term—which is due to canting—enters this submatrix. Note that these four states are not mixed by J^+ and J^-. Therefore J^+ and J^- do not contribute to the repulsion of the energy levels. As a consequence the k dependence produced by these terms can be neglected in the current analysis. Inspection of the submatrix shows that because of the interaction between the states the intersection of the energy levels at the external field $H_{z''} = H_e/\mu_B g_{zz}$ is removed. The energies of the four states at this external field are

$$\begin{aligned} &E = mH_e + (-\Delta + \mu_B g_{xz} H_{z''}), \quad \text{“}|-(m-1)\rangle\text{”},\\ &E = mH_e, \quad \text{“}|-m\rangle\text{”},\\ &E = mH_e, \quad \text{“}|+m\rangle\text{”}\\ &E = mH_e - (-\Delta + \mu_B g_{xz} H_{z''}), \quad \text{“}|+(m+1)\rangle\text{”}, \end{aligned} \tag{5.17}$$

where the notation “$|m\rangle$” is used since $|m\rangle$ is not a proper eigenfunction.

In this model the energy separation between the clusters $|m\rangle$ and $|(m\pm 1)\rangle$ is at least $\Delta E = \Delta - \mu_B g_{xz} H_{z''}$. Comparing this with our experimental results (Fig. 5) we note that apparently the field dependence of the minimum splitting ΔE is rather small, as a number of resonance lines have approximately the same minimum frequency at different fields. Consequently $\Delta E \approx \Delta$. Equating ΔE with the observed minimum frequency yields $\Delta/k_B = 0.76$ K.

Our next step will be to calculate the expected overall field dependence of the SCR frequencies within this framework. Figure 7 shows the calculated energy levels for several clusters assuming $\Delta/k_B = 0.76$ K, all other non-Ising terms taken equal to zero, $H_e = 1.60$ K, and $g_{zz} = 8.6$.

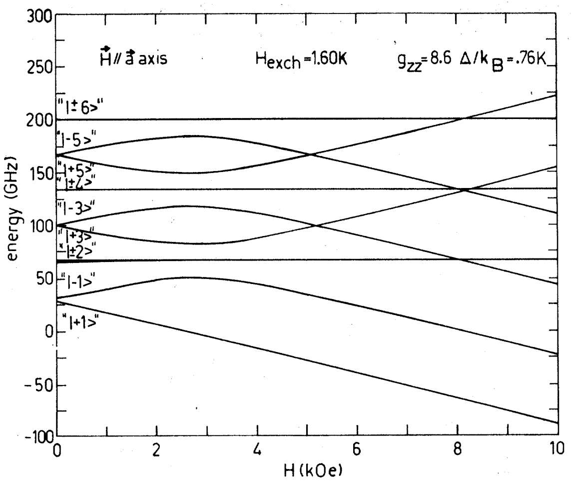

FIG. 7. Field dependence of the energy of the spin clusters for $\vec{H} \parallel \vec{a}$ in the presence of a crystal field splitting of the ground doublet Δ. The contribution of the intrachain exchange interaction $-2J_a^{zz}$ to the energy is not taken into account since it is equal for all spin clusters.

The deviations from the pure Ising behavior are obvious. From the energy levels, the SCR frequencies can be obtained. It appears that transitions between large clusters, $|m\rangle \Rightarrow |m+n\rangle$ where $m > 4$, are rather insensitive to the cluster size m. However, even transitions involving smaller clusters (except “$|+1\rangle$”) deviate only 1 GHz from transitions between larger clusters. In Fig. 5 the SCR frequencies (for large clusters) originating from the antiferromagnetic ground-state spin configuration ($\Delta/k_B = 0.76$ K, $H_e = 1.60$ K, and $g_{zz} = 8.6$) as well as from non-ground-state spin configurations ($H_e = 1.22$ K and $H_e = 2.02$ K) are shown together with the corresponding experimental data. The agreement is rather satisfying.

Concluding we state that the introduction of only the pseudodoublet splitting Δ is sufficient to explain the deviations from the pure Ising behavior of the spectrum of the antiferromagnetic chain ($\vec{H} \parallel \vec{a}$).

We will now have to investigate to which extent the introduction of Δ affects the spectrum for the ferromagnetic chain ($\vec{H} \parallel \vec{c}$), which—as we showed above—could be excellently explained without any non-Ising terms at all.

In the pure Ising case the energy levels of the functions $|+m\rangle$ and $|-m\rangle$ are degenerate when $\vec{H} \parallel \vec{c}$. In order to calculate the influence of the pseudodoublet splitting Δ, it is convenient to introduce the new basis functions, viz., “$|+m\rangle$” $= \frac{1}{2}\sqrt{2}(|+m\rangle + |-m\rangle)$ and “$|-m\rangle$” $= \frac{1}{2}\sqrt{2}(|+m\rangle - |-m\rangle)$. When we use these basis functions the matrix elements generated by the Hamiltonian H_Δ (5.3) are

$$\text{“}\langle +(m-1)|\text{”}\mathcal{H}_\Delta\text{“}|+m\rangle\text{”} = \text{“}\langle +(m+1)|\text{”}\mathcal{H}_\Delta\text{“}|+m\rangle\text{”} = -\Delta \tag{5.18}$$

while

$$\text{“}\langle -(m-1)|\text{”}\mathcal{H}_\Delta\text{“}|-m\rangle\text{”} = \text{“}\langle -(m+1)|\text{”}\mathcal{H}_\Delta\text{“}|-m\rangle\text{”} = 0\,.$$

Since there exist no matrix elements between the functions “$|+m\rangle$” and “$|-m\rangle$” in the current model we may treat the influence of Δ on both sets of functions separately.

The functions “$|-m\rangle$” are not influenced by the pseudodoublet splitting. Hence these states will have the energies of the pure Ising case. However, the functions “$|-m\rangle$” alone cannot explain the transitions $|m\rangle \Rightarrow |m+n\rangle$ with $n > 1$ (Fig. 4) since the $\Delta m = 1$ selection rule is not relaxed.

On the other hand the functions “$|+m\rangle$” mix when the influence of Δ is taken into account, giving rise to deviations of the energy levels from the pure Ising prediction. Moreover, in this case Δ relaxes the $\Delta m = 1$ selection rule for the functions "$|+m\rangle$", giving rise to transitions between spin clusters with $\Delta m > 1$ as observed in the experiment (Fig. 4). When we consider the influence of Δ on the energy levels of the functions "$|+m\rangle$" we can distinguish two major effects. Firstly, the deviations from the pure Ising case will be most clear when the energy levels of the clusters approach each other. This is the case in those SCR branches which approach zero frequency or for most of the branches near the critical fields. Secondly, the deviations decrease with increasing cluster size.[19]

However, unlike the AF case, the energy difference between cluster levels "$|m\rangle$" ⇒ "$|m+n\rangle$" (thus the SCR frequency) does not rapidly approach a constant value, but is also a continuous function of the cluster length m. Given some distribution of cluster lengths this would certainly lead to a broadening of the resonance lines when H approaches the critical fields. Inspection of the experimental results (Fig. 4) shows that this effect cannot be resolved in view of the limited number of data points at low frequencies and the additional collapsing of several SCR lines near the critical fields.

Nevertheless, calculations showed that insertion of Δ would result in rather pronounced deviations from the pure Ising behavior, also in the frequency regions where we have enough distinct data, provided that the clusters are of small size. The absence of these deviations in our experimental results thus indicates that either only excitations from large clusters are observed or only large clusters are present.

To investigate this problem we performed some calculations on the cluster distribution in a field for a ferromagnetic chain, which describes the chain of $RbFeCl_3 \cdot 2H_2O$ for $\vec{H} \parallel \vec{c}$. The field H_t is the sum of an external field and an exchange field arising from the interchain exchange interactions. For the ferromagnetic Ising chain the magnetization and energy are exactly known as a function of the temperature T, the field H_t and the intrachain exchange interaction J. The total number of reversed spins n_s is calculated from the magnetization and the total number of clusters n_c is calculated from the magnetization and the energy. Hence n_s and n_c may be expressed in T, H_t and J. Date and Motokawa[4] used a statistical distribution of the reversed spins over the clusters. The cluster distribution can also be obtained by the stochastic model of Alexandrowicz.[20]

Calculations showed that a small concentration of impurities (< 1%) does not change the cluster distribution, although the number of clusters may increase drastically.[21]

When $n_c, n_s \gg 1$ the number of clusters with l spins (n_l) is given by[4]

$$n_l = \frac{n_c^2}{n_s}\left(1 - \frac{n_c}{n_s}\right)^{l-1} . \tag{5.19}$$

The cluster distribution is shown in Fig. 8 for several fields and $kT/J = 0.2$, which matches the experimental conditions. Note that the total field H_t is zero at the critical fields and $\mu H_t/J = 0.02$ in zero external field. From Fig. 8 it can be seen that when the critical fields are approached the number of large clusters increases and subsequently the relative number of small clusters decreases drastically. This mechanism may very well be responsible for the experimental fact that no significant deviations from the pure Ising behavior of the SCR, originating from small cluster excitations near the critical fields, are observed.

So far we have not considered the effect of terms containing J^+ and J^- explicitly. Although we have shown that the introduction of the pseudodoublet splitting Δ was sufficient to obtain a consistent and satisfactory description of the experimental data, there is no argument why not also terms containing J^+ and J^- should enter the problem. Of course these terms would modify the energy levels of both "$|+m\rangle$" and "$|-m\rangle$". It can be shown that the modification decreases with increasing cluster size, as we noticed already in the case of Δ.

The fact that we did not observe deviations of

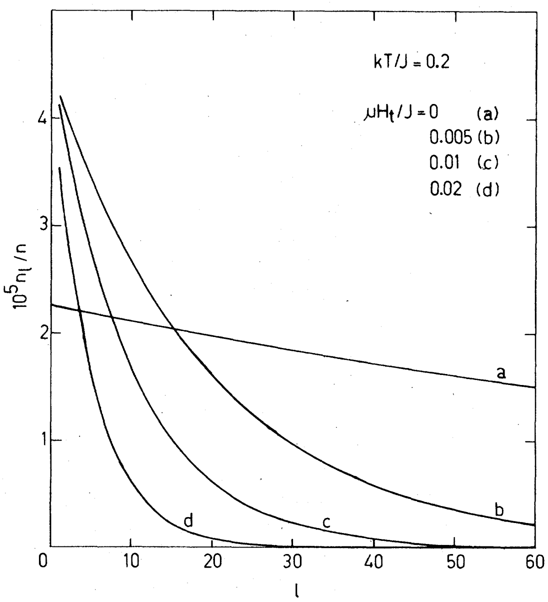

FIG. 8. Number of clusters n_l of a ferromagnetic chain of n spins, as a function of the cluster size l. The field H_t is the sum of an external field and an exchange field arising from the interchain-exchange interactions. J is the intrachain interaction.

the experimental results, which had to be ascribed to J^+ or J^-, may indicate that J^+ and J^- are small or indicates once again that only excitations from large spin clusters are observed. Quite generally one has to add that introduction of the anisotropy terms J^+ and J^- gives rise to a k dependence of the energy levels, causing rather wide resonance lines (several kOe) for excitations from small clusters, which could easily escape detection in a spectrum of many sharp resonances.

So far little attention has been given to the question whether the observed resonances are allowed. In the case of the ferromagnetic chain of $CoCl_2 \cdot 2H_2O$, the term J^- coupled all odd-spin clusters and separately all even-spin clusters. Excitations of even-spin clusters could only be observed with the microwave field parallel to the moments and excitations of odd-spin clusters with the microwave field perpendicular to the moments. However, in the case of a canted chain or in the case of a compound with a pseudodoublet ground state, like $RbFeCl_3 \cdot 2H_2O$, the odd-spin cluster functions and the even-spin cluster functions are mixed. Therefore, it is possible to observe all SCR with an arbitrary orientation of the microwave field.

VI. DISCUSSION AND CONCLUSIONS

In this paper we have presented the experimental SCR data on $RbFeCl_3 \cdot 2H_2O$. The data for $\vec{H} \parallel \vec{c}$ could be explained satisfactorily by the simple Ising model. The SCR for $\vec{H} \parallel \vec{a}$ could be explained with an extension of the Ising basis function method for the antiferromagnetic chain taking into account the crystal field splitting of the ground doublet.

Fitting the theoretical parameters to the experimental data yielded a set of detailed exchange and crystal field parameters, which for the sake of completeness are tabulated in Table I.

TABLE I. Parameters obtained from the SCR experiments compared with the results of magnetization measurements[10, 11] (MM), nuclear magnetic resonance[11] (NMR), and neutron diffraction[11] (ND). θ_m is the angle between the magnetic moment μ and the a axis.

Parameter	SCR	MM	NMR	ND
J_b/k	-0.76 K			
J_c/k	-0.21 K	-0.22 K		
J_{bc}/k	-0.13 K			
$(J_b + 2J_{bc})/k$	-1.02 K	-1.07 K		
Δ/k	0.76 K			
μ_c	$1.5\mu_B$	$1.6\mu_B$		
μ	$4.5\mu_B$		$4.6\mu_B$	$3.9\mu_B$
θ_m	19°		19°	16°

From this table it appears that in the ordered state the effective magnetic coupling between the a-b plane is very weak since the coupling by J_c is nearly compensated by J_{bc}. This may indicate why the specific-heat data[10] could be fitted surprisingly well by the two-dimensional Onsager model both above and below T_N. Moreover, the agreement between the largest interchain interaction $|J'/k| = 0.7$ K determined from the specific heat and the corresponding exchange interaction in our model $J_b/k = -0.76$ K is striking. The two critical fields found in the SCR spectrum for $\vec{H} \parallel \vec{c}$ agree very well with the critical fields obtained from magnetization measurements[10, 11] (SCR: 8.0, 12.3 kOe; magnetization: 8.1, 12.4 kOe). The magnetization measurements yielded $\mu_c = 1.6\ \mu_B$ for the component of the moment along the c direction, while SCR gave $\mu_c = 1.50\mu_B$. The direction and magnitude of the magnetic moment (angle with the a axis $\theta_m = 19°$ and $\mu = 4.5\mu_B$) may be compared to the results of nuclear magnetic resonance ($\theta_m = 19°$ and $\mu = 4.6\mu_B$) and neutron diffraction results ($\theta_m = 16°$, $\mu = 3.9\mu_B$).[11] The agreement is satisfying, although the neutron diffraction results seem somewhat too low. One should bear in mind, however, that these last results are rather sensitive to small changes in θ_m.

We have shown that in an antiferromagnetic chain the deviations from the Ising prediction are mostly directly visible in the SCR if matrix elements are present between intersecting energy levels of spin clusters.

Other deviations from Ising may be masked by the fact that the excitations from large spin clusters will always show the Ising behavior, while the linewidth of the excitations from small spin clusters may be large due to dispersion.

However, when the spin clusters are directly excited from the ground state, $k = 0$, the deviations from Ising will be observed. The small spin clusters have the highest intensities[1] and show the largest deviations. Therefore it would be worthwhile to study the far-infrared spectra of $RbFeCl_3 \cdot 2H_2O$ in order to determine the spin-cluster energies for both $\vec{H} \parallel \vec{a}$ and $\vec{H} \parallel \vec{c}$. From these excitations one may likely obtain more information about the non-Ising terms in the Hamiltonian (5.8). Information about these terms may also be obtained from a study of the high-temperature susceptibility from which the energy-level scheme and g tensor may be deduced.

The theoretical description given here may also be applied to other pseudo-one-dimensional canted Ising systems. However, the energies associated with deviations from the pure Ising model have to be small with respect to the intrachain exchange interaction. If this condition is not satisfied the interaction of spin clusters with the ground state and with other spin clusters in the chain must be taken into account. The method can be applied directly to $CsFeCl_3 \cdot 2H_2O$. Just like in $RbFeCl_3 \cdot 2H_2O$, in $CsFeCl_3 \cdot 2H_2O$ the repulsion of the energy levels was observed when $\vec{H} \parallel \vec{a}$, and a minimum frequency of 12.5 GHz was found. Apart from $CsFeCl_3 \cdot 2H_2O$ we have observed SCR in the one-dimensional Ising systems $CoBr_2 \cdot 2H_2O$, $CoCl_2 \cdot (C_5H_5N)_2$, and $CoCl_3[(CH_3)_3NH] \cdot 2H_2O$. The existence of thermally excited spin clusters in the latter compound was inferred from nuclear spin relaxation experiments by Goto *et al.*[22] We have stated in the introduction that spin clusters should exist in all Ising compounds. However, in order to observe SCR in the ordered state there have to be enough thermally excited clusters below T_N. This may be not the case in low-dimensional systems, where the ratio $k_B T_N/|J|$ is very small.[23,24]

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[24] In view of this and the results on $RbFeCl_3 \cdot 2H_2O$ and $CsFeCl_3 \cdot 2H_2O$, the interpretation of the earlier reported resonances in $CsCoCl_3 \cdot 2H_2O$ (Ref. 23), below $T_N = 3.38$ K (Ref. 10), as SCR must be mistrusted. Since the intrachain exchange interaction in $CsCoCl_3 \cdot 2H_2O$ ($|J/k| = 38$ K) (Ref. 10) is nearly equal to the interachain interaction in $RbFeCl_3 \cdot 2H_2O$, no SCR are expected to be observable below $T = 5$ K.