LETTER TO THE EDITOR

TEMPERATURE DEPENDENCE OF SPIN-CLUSTER RESONANCE INTENSITY IN $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$

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Received 28 September 1982

Revised 8 February 1983

The spin-cluster resonance intensity is observed as a function of temperature in the pseudo-one-dimensional canted Ising metamagnet $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$. For $T \ll 0.7T_N$ a pure one-dimensional Ising model gives a good description of the observed intensities. For $T \approx T_N$ the intensity decreases rapidly as a function of temperature due to the destruction of the local ordering around a spin-cluster. The measured value of the intrachain interaction J_a/k of -36 K is in good agreement with earlier measurements on spin-cluster excitations.

1. Introduction

In strongly anisotropic magnetic systems a localized excitation can exist as a spin-cluster, which is a group of adjacent spins with their orientation reversed relative to the ground state. If a thermally excited spin-cluster is present, a relatively small amount of energy might increase the length of the cluster. Such an absorption, which usually occurs in the microwave region, is called spin-cluster resonance.

$\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$ (RFC) is a pseudo-one-dimensional Ising metamagnet with chains of moments antiferromagnetically ordered along the a axis of the crystal. The moments are canted in the a - c plane and make an angle of about 20° with the a axis. Below the Néel temperature ($T_N = 11.96$ K) RFC orders antiferromagnetically in the absence of an external field [1].

With an external field applied parallel to the c axis, two phase transitions are observed. These can be explained in terms of three interchain interactions, J_b along the b axis, J_c along the c axis and J_{bc} diagonally in the b - c plane. Van Vlimmeren et al. [1] measured these interactions by spin-cluster resonance at different microwave frequencies and found $J_b/k = -0.76$ K, $J_c/k =$

-0.21 K and $J_{bc}/k = -0.13$ K. To measure the large intrachain interaction J_a they made use of a far-infrared spectrometer (1500 GHz) to create spin-clusters directly from the ground state and found $J_a/k = -35.0$ K [2].

This paper presents an alternative method to determine the intrachain interaction J_a by measuring the intensity of spin-cluster resonance as a function of temperature at one microwave frequency.

2. Theory

Van Vlimmeren et al. [1] concluded from their measurements that RFC can be described excellently by a pure Ising model if the external magnetic field is applied parallel to the c axis. Therefore we only take the pure Ising terms of the complete Hamiltonian of the antiferromagnetic chain with canted moments and obtain, in the fictitious spin $S = \frac{1}{2}$ formalism,

$$H_{AF} = -2J_a \sum_i S_i^z S_{i+1}^z - g_c \mu_B \mu_0 (H_c \pm H_c) \times \sum_i (-1)^{i+1} S_i^z, \quad (1)$$

with z the local canted spin axis, J_a the intrachain interaction, H_c the external field in the c direction and H_e the exchange field due to interchain interactions. We may include a dipole field and a demagnetizing field in the same form as H_e , but these do not influence the obtained results. The factor $(-1)^{i+1}$ takes care of the ferromagnetic character of the Zeeman interaction due to the spin canting. The minus sign before H_c is a consequence of possible antiferromagnetic ordering between the chains due to H_e .

H_e can be expressed in terms of the interchain constants by

$$H_e = (\alpha J_b + \beta J_c + \gamma J_{bc}) / g_c \mu_B \mu_0, \quad (2)$$

with $\alpha = 2, 0$ or -2 , $\beta = 2, 0$ or -2 and $\gamma = 4, 2, 0, -2$ or -4 depending on the local spin configuration.

Eq. (1) may be replaced by the Hamiltonian of a ferromagnetic chain:

$$H_F = -2|J_a| \sum_i S_i^z S_{i+1}^z - g_c \mu_B \mu_0 (H_e \pm H_c) \sum_i S_i^z, \quad (3)$$

if we take the absolute value of J_a .

To describe the observed intensities we will use the theory of Berim et al. [3], based on the general theory of Kubo and Tomita [4] and apply it to Hamiltonian (3). Berim et al. calculated the resonance frequencies and intensities of a one-dimensional Ising chain in the presence of a magnetic field. They found that, together with the usual resonance frequency ν_0 in the microwave region, two additional resonances should occur with frequencies $\nu_{\pm 1} = |\nu_0 \pm 2J_a/h|$, usually in the (far)-infrared region. The low frequency resonance ν_0 can be attributed to spin-clusters because it only occurs if the spins on sites $i-1$ and $i+1$ are antiparallel. The absorptions at the much higher frequencies $\nu_{\pm 1}$ require a parallel orientation of spins $i-1$ and $i+1$, which means an undisturbed chain and thus we call these spin-cluster excitations [2]. Our measurements were done in the microwave region, hence from now on we only consider ν_0 .

The intensity can be written as [3]

$$I = \frac{\pi^2}{h} g_c^2 \mu_B^2 \sinh L e^{-K} u^2 / (2 \cosh L + uv), \quad (4)$$

with

$$\begin{aligned} K &= 2J_a/kT, \\ L &= g_c \mu_B \mu_0 (H_e \pm H_c) / 2kT, \\ u &= (\sinh^2 L + e^{-K})^{-1/2}, \quad \text{and} \\ v &= \cosh 2L + e^{-K}. \end{aligned}$$

In the low temperature limit ($\sinh^2 L \gg e^{-K}$) eq. (4) can be approximated by

$$I = \frac{\pi^2}{h} g_c^2 \mu_B^2 \exp[-(K + 2L)], \quad (5)$$

which, in the same limit, can also be obtained from the theory of Date and Motokawa [5, 6]. At high temperatures ($\sinh^2 L \ll e^{-K}$)

$$I = \frac{\pi^2}{4h} g_c^2 \mu_B^2 \sinh L / \cosh^2(K/4), \quad (6)$$

which has a maximum at $T_{\max} = J_a/kx$, where x is the root of $p \coth(x/2) = \tanh(px)$ and $p = 2L/K$. If $px \ll 1$, which is fulfilled during the measurements, $x \approx 1.545$ and we obtain

$$T_{\max} \approx 0.65 J_a / k. \quad (7)$$

At very high temperatures ($L \ll 1$, $K \ll 1$) a simple Curie law (intensity $\propto 1/T$) is obtained.

To determine L we look more carefully to the resonance condition. The energy of a spin-cluster of length m is equal to

$$E_m = 2|J_a| + m(\alpha J_b + \beta J_c + \gamma J_{bc}) \pm m g_c \mu_B \mu_0 H_e.$$

In our experiments we changed the length of a thermally excited spin-cluster ($|m\rangle \rightarrow |m+n\rangle$) by applying an energy

$$\begin{aligned} E &= E_{m+n} - E_m \\ &= n(\alpha J_b + \beta J_c + \gamma J_{bc} \pm g_c \mu_B \mu_0 H_e) \end{aligned} \quad (8)$$

which is equal to $E = 2nLkT$. At resonance $E = h\nu$, with ν the microwave frequency, so that

$$L = h\nu / 2nkT. \quad (9)$$

We are now able to determine J_d/k at one microwave frequency by making a fit of eq. (4) through the datapoints.

3. Experimental set-up and results

We measured the microwave absorption of RFC in a spectrometer without a field modulation as a function of the external field. DPPH powder was used for the calibration of the magnetic field. During the experiments at a microwave frequency of 9.45 GHz the temperature was varied between 6.1 K and 12.5 K. The temperature was stabilized to within 0.05 K by using a heater and measured by a calibrated carbon glass resistor.

The spectra were digitized by a home-made 12-bits AD-converter and analysed by an LSI-11 minicomputer. First the computer determined the exact position of the top of the resonance peak. On each side of that top an equal number of datapoints were considered, corresponding to the approximate width of the line. Next the computer compensated for a shift in the baseline and finally a numerical integration gave the desired intensities.

Fig. 1 presents a typical spectrum at a temperature of 7.69 K. If we substitute the given values of the interchain interactions and the ap-

Fig. 1. Spin-cluster resonance absorption versus applied magnetic field ($B_c = \mu_0 H_c$) of $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$ at a temperature of 7.69 K. DPPH powder was used for the calibration of the magnetic field. The four main resonances are named after ref. [1].

Fig. 2. Intensity of the A2-line versus temperature. Curve (a) represents the calculated results of eq. (5) and curve (b) the results of eq. (4), with $KT = 74$ K and $LT = 0.11$ K. T_c denotes the 3D ordering temperature at $B_c = 0.69$ T.

propriate values of α , β , γ and g_c [1] we can calculate the resonance fields from eq. (8). These fields are in excellent agreement with the measured ones if we take $n = 2$. Other resonances with different values of n are present as well, but are of no interest here.

In fig. 2 we made a plot of the intensities of the A2-line as a function of temperature. Below 6.1 K and above 12.0 K no absorption could be observed. At the lowest temperatures an exponential dependence on the inverse temperature was found (curve (a)) in accordance with eq. (5). Curve (b) represents eq. (4) with $KT = 74.2$ K and $LT = 0.113$ K. It is obvious that the temperature of maximum intensity $T_{\text{max}} (\approx 24$ K) is not in agreement with eq. (7). This will be discussed below. Above 9.9 K the intensity decreases rapidly. The other three main resonances show a similar temperature dependence, except for the G2-line where some absorption above 12.0 K could be measured.

The calculated value of J_d/k from the best fit of eq. (4) through the datapoints yields 37 K for the A2-line, 38 K for the C2-line, 38 K for the F2-line and 32 K for the G2-line. The errors are about 8%. Averaging the four values we found $J_d/k = 36 \pm 3$ K, which is in very good agreement with the value found by Van Vlimmeren et al. [2].

4. Discussion

We will compare the observed intensities in RFC with those in $CoCl_2 \cdot 2NC_5H_5$ (=CoPC) [7] and $Co[(CH_3)_3NH]Cl_3 \cdot 2H_2O$ (=CoTAC) [8]. In all the three compounds there is a rise in the spin-cluster resonance intensity with increasing temperature up to a maximum and then a rapid decrease at higher temperatures (fig. 2).

The low-temperature behaviour can be explained as follows. We recall that the intensity is proportional to the number of thermally excited spin-clusters. This number is, to first order, proportional to $\exp(-E/kT)$ where E is the excitation energy of a spin-cluster (eq. (5)).

For RFC the temperature of maximum absorption should, according to eq. (7), be equal to $T_{max} \approx 24$ K, which is much higher than the observed value of 10 K. The same discrepancy is found in CoTAC and even in CoPC which is one of the best known quasi-one-dimensional Ising ferromagnets. A qualitative explanation can be given. At resonance eq. (8) is fulfilled and both frequency and external field are constant at a certain resonance line. Hence only those spin-clusters which have the right surroundings to yield the exchange field H_e contribute to the intensity. At the lowest temperatures almost all existing spin-clusters experience this field, but at higher temperatures, with a higher degree of disorder, the number of contributing clusters decreases. However, even above the transition temperature T_c there are some clusters with the right surroundings, which explains the occurrence of spin-cluster resonance above T_c . The pure one-dimensional theories [3, 5, 6, 8] do not take this decrease in the number of contributing spin-clusters into account and hence predict a too high T_{max} . Fig. 3 shows a graph of the ratio of the measured A2-intensities (I_m) and the calculated values after eq. (4) (I_b) versus temperature. According to the mentioned process this ratio should give the relative number of contributing spin-clusters. At the transition from the antiferromagnetic to the paramagnetic phase ($T_c = 10.7$ K) only about one-half of the existing clusters experience the exchange field H_e . For the other three resonances, the temperature where

Fig. 3. Ratio of the measured A2-intensities I_m and the calculated values I_b after eq. (4) versus temperature. The curve is drawn as a guide to the eye. T_c denotes the 3D ordering temperature at $B_c = 0.69$ T.

$I_m/I_b = 0.5$ are 9.9, 9.4 and 10.8 K. These temperatures indeed suggest that the rapid decrease in intensity should be related to the long-range ordering because the transition temperature to the paramagnetic state is 9.5 K for the C2-line and 8.2 K for the F2-line. A further indication may be found in the fact that the large absorption peak around the free electron value (0.3 T) strongly increases at T_c , indicating a large amount of spins which are not in an ordered environment.

We would like to note that interactions between two spin-clusters in neighbouring chains can be neglected, in the temperature region considered, because of the high excitation energy of a cluster (≈ 70 K).

The measurements on the G2-line and on CoPC and CoTAC, however, are done in the saturated paramagnetic state. For these resonances a relatively large external field is applied and therefore a higher temperature is necessary to destroy the local environment. Indeed for the G2-line absorption could be measured above 12 K. In CoPC and CoTAC only one resonance is observed so no comparison with other phases can be made.

It is worth mentioning that the very rapid decrease in intensity around T_c is also measured

in $\text{CsFeCl}_3 \cdot 2\text{H}_2\text{O}$, which is isostructural with RFC [9].

We may conclude that in the low-temperature region ($T \ll T_c/2$) a one-dimensional Ising model may be applied to explain the observed spin-cluster resonance intensities. For very low temperatures this model is consistent with the theory of Date and Motokawa. The high-temperature region ($T \approx T_c/2$) is not correctly predicted by the theory, because the decrease in the number of contributing spin-clusters due to the destruction of the local environment is not taken into account. The measured value of the intrachain exchange interaction is in good agreement with earlier measurements on direct spin-cluster excitations [2], specific heat [10] and Mössbauer linewidths [11].

Acknowledgement

We would like to thank Drs. A.C. Phaff of the

Eindhoven University of Technology for supplying the RFC crystals.

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