Spin fluctuations in doped antiferromagnetic K_2FeF_5

1989 J. Phys.: Condens. Matter 1 147

(http://iopscience.iop.org/0953-8984/1/1/013)

J. Phys.: Condens. Matter 1 (1989) 147–152. Printed in the UK

Spin fluctuations in doped antiferromagnetic K_2FeF_5

D H Jones, J Chadwick and M F Thomas
Department of Physics, University of Liverpool, Liverpool L69 3BX, UK

Received 21 June 1988

Abstract. At 1.3 K the Mössbauer spectra of the typical quasi-1D antiferromagnet K_2FeF_5, which orders at 6.95 K, consist of a single narrow sextet with a hyperfine field significantly reduced from the free ion value by zero-point spin fluctuations. When some of the iron sites are substituted with small amounts of (non-magnetic) gallium, the lines become asymmetrically broadened and the mean hyperfine field is further reduced. It is shown that the spectra of the doped samples can be well simulated by a simple model of zero-point spin reduction for the finite chains produced by doping. It is suggested that, though the simulation would be more complicated, quantum fluctuations associated with surface or edge effects may also contribute to the line broadening at low temperatures in other finite systems, such as ferrimagnetic or antiferromagnetic superparamagnets.

1. Introduction

Quantum spin fluctuations are particularly important in quasi-1D antiferromagnets such as K_2FeF_5 [1, 2] which have a small ratio of inter-chain to intra-chain coupling ($J'/J \simeq 9 \times 10^{-4}$) and a small ratio of anisotropy field to exchange field ($\omega_A/\omega_E \simeq 4 \times 10^{-3}$). The weak anisotropy field allows spin reorientation transitions to be observed and these have been the subject of several studies by this laboratory [3].

In pure K_2FeF_5 the spin fluctuations lead to a zero-point spin reduction of about 30% compared with the free-ion value, yielding a reduced hyperfine field of 41 T. When the material is doped with a diamagnet the average zero-point spin reduction is expected to increase, since free chain ends are produced which experience a weaker exchange field. (The hyperfine field reduction for $T > 0$ also becomes steeper as the Néel temperature decreases but this effect is not of interest here.) Doping also changes the chemical environment of the atoms at the chain ends and this may affect the hyperfine field through covalency effects such as the supertransferred hyperfine interaction and the quadrupole interaction parameters through the change in local symmetry. In this paper we make the hypothesis that effects such as these are largely restricted to the extreme ends of chains (i.e. are short range) and for small amounts of doping will be negligible compared to quantum effects. We test the hypothesis against several spectra of K_2FeF_5 with different amounts of doping taken at 1.3 K.

2. Spin-wave theory of finite chains

The spin-wave theory of a 1D chain with periodic boundary conditions, i.e. a ring, is elementary [4] even if the system is anisotropic [4]. The Hamiltonian contains operators

0953-8984/89/010147 + 06 $02.50

such as $-2JS_i \cdot S_j$ and $-KS_{zi}^2$ since K_2FeF_5 is dominated by isotropic exchange and uniaxial anisotropy. This is first transformed using operators that create or annihilate spin deviations at each site and is then Fourier transformed into momentum space using the translational symmetry. Linear combinations of the basis states are then sought that satisfy harmonic oscillator commutation relations for the coupled system. This procedure results in the matrix equation

$$\begin{bmatrix} (\omega_E + \omega_A) & -\omega_E\gamma_k \\ -\omega_A\gamma_k & (\omega_E + \omega_A) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \lambda_k \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \tag{1}$$

where $\omega_E = 4JS$, $\omega_A = 2KS$, $\gamma_k = \cos(2\pi k/N)$, $k = 1, N$ and N is the number of atoms. If the column vector (c_1, c_2) is an eigenvector of (1), this means that $\alpha_k^* = (c_1 a_k^* + c_2 b_k)$ is the (unnormalised) creation operator for a spin wave of energy λ_k. To calculate the spin-wave reduction, ΔS_z, the relation $\Delta S_z = \langle a^* a \rangle$ is used, i.e. it is necessary to find a relation $a^* = u_1\alpha^* + u_2\beta$. This involves inverting the matrix of eigenvectors of (1) and gives the zero-point spin reduction u_2^2. There is no zero-point spin reduction in ferromagnets as the spin-wave operators do not combine creation and annihilation operators from different sites.

When the periodic boundary conditions are removed, the Fourier transform becomes useless as ΔS_z becomes a function of position within the chains as well as the chain length. Nevertheless for long chains the centre of the chain must become equivalent to the ring and hence it is useful to speak of 'end effects'. Without the Fourier transform the equivalent of the matrix of (1) is an $N \times N$ matrix, labelled by site spin deviation operators

$$\begin{bmatrix} \omega_E/2 + \omega_A & -\omega_E/2 & \dots & \dots \\ \omega_E/2 & -(\omega_E + \omega_A) & \omega_E/2 & \dots \\ 0 & -\omega_E/2 & (\omega_A + \omega_E) & \dots \\ \dots & \dots & & \end{bmatrix}. \tag{2}$$

Since we are interested in end effects and ΔS_z is highly sensitive to the nature of the matrix (it diverges for $\omega_A = 0$), it is necessary to solve this finite matrix numerically, and invert the matrix of eigenvectors. This can be easily achieved for N of several hundred using standard library routines, in our case the NAG library. A typical plot of spin reduction against chain position is shown, for two typical chain lengths, in figure 1.

As expected, for large N the centre of the chain becomes equivalent to the closed ring, but as ω_A tends to zero the N necessary for this increases rapidly. Thus, defining N_c as the critical N, such that atoms further from a chain end than N_c have the infinite ring spin reduction, to an accuracy of 1%, $N_c(\omega_A/\omega_E = 0.01) = 28$, $N_c(\omega_A/\omega_E = 0.001) = 80$. In applications, errors of 1% in the spin reduction are insignificant and hence chains larger than N_c can be treated without calculating a larger matrix by inserting a ring segment into the centre of a smaller chain. In general ΔS_z increases towards the chain ends but there is a noticeable alternation. In particular, the end atom has the lowest spin reduction of any atom in the system (i.e. the largest hyperfine field). Physically, the end atom experiences only half the usual exchange field and hence has less spin reduction (if it was totally decoupled from the rest of the chain ΔS_z would be zero). As a result the penultimate atom 'sees' a large S on the end atom; hence it experiences an anomalously

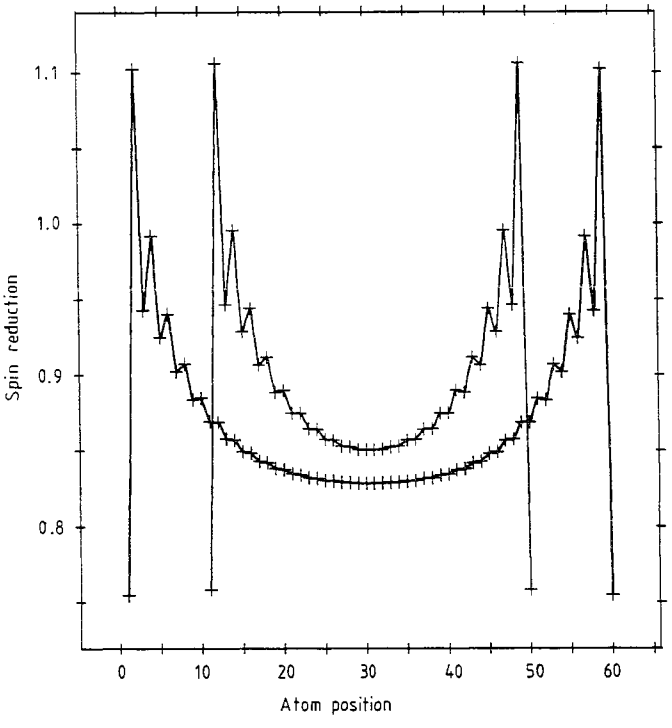

Figure 1. The spin reduction in units of $\hbar$ along chains of 40 and 60 spins for $\omega'_A/\omega_E = 0.002$.

large ω_E and thus it has more spin reduction. This effect continues into the chain and is gradually damped.

Some numerical calculations on two sublattice systems in two and three dimensions have shown us that this oscillation, with extremes of spin reduction for the surface layers, is also found in higher dimensions, though in less extreme form. This may be relevant to the question of whether surface hyperfine fields in superparamagnets are enhanced or suppressed, which has been much discussed [6]. For antiferromagnetic systems both answers may be correct.

3. Application to K_2FeF_5

The doped K_2FeF_5 system, though it has accurately known hyperfine parameters and exchange and anisotropy fields, still cannot be exactly simulated on a 1D model because the precise behaviour of each chain segment will depend on the relative configuration of the atoms on the neighbouring chains that are weakly coupled to it by J'. Though J' is small, it is this term in the Hamiltonian that causes the magnetic ordering (impossible in 1D with finite range interactions), which makes spin-wave theory applicable. Rather than attempt a numerical simulation of all possible combinations of chain segments lying on adjacent chains, we have made the approximation that J', having caused the magnetic order, can be taken into an effective anisotropy field ω''_A. This approximation may well fail for very short chains, but as long as the doping is small such chains will not be important. Having made this approximation the lineshapes of the doped system can be

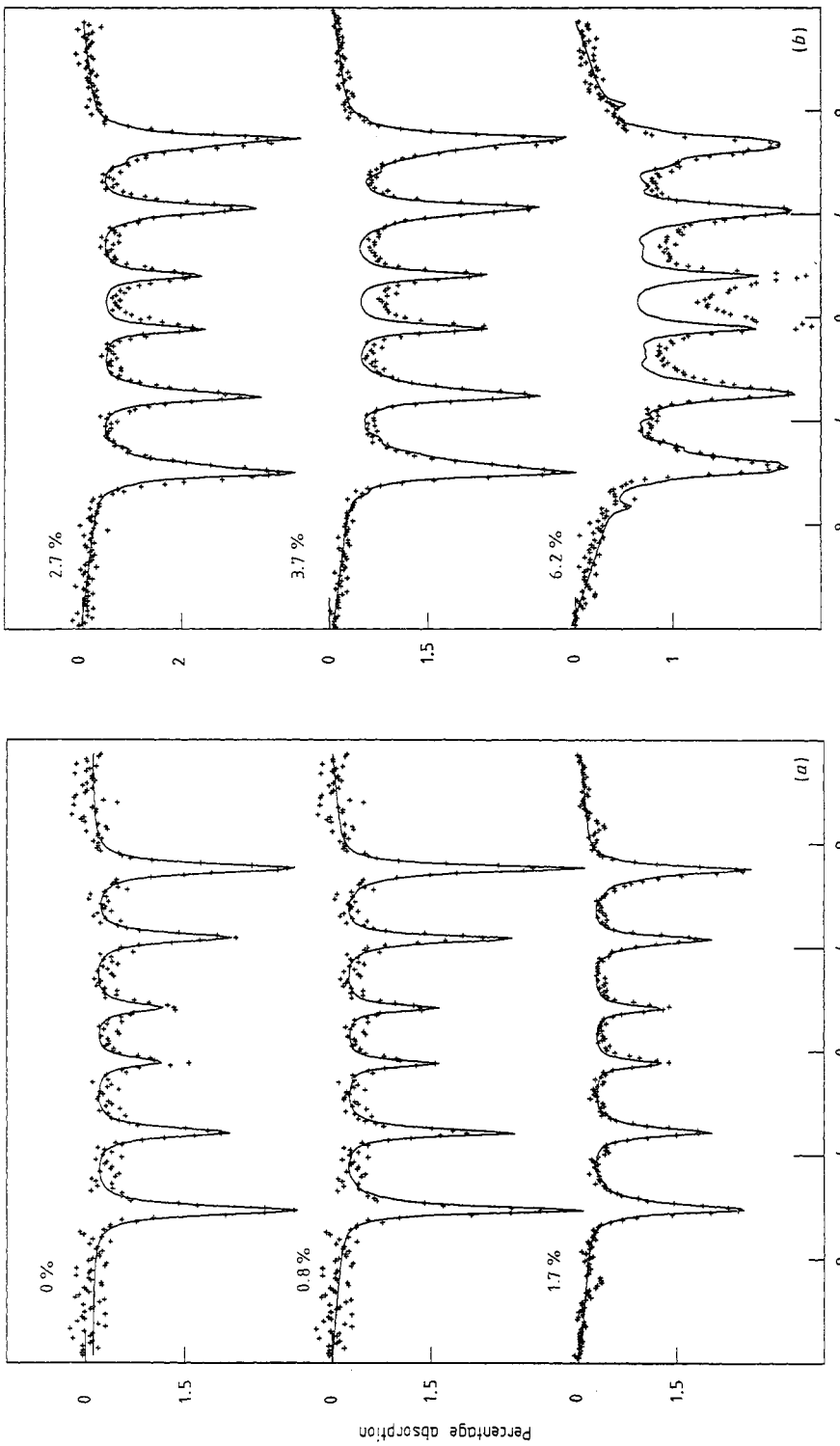

Figure 2. Simulated spectra for 0%, 0.8%, 1.7%, 2.7%, 3.7% and 6.2% doped K_2FeF_5 made using hyperfine parameters and linewidth defined by the 0% doped spectrum.

derived from the spectrum of the undoped system, without any free parameters, by obtaining the probability distribution of chain lengths and solving the matrix problem over this distribution. Each site on each chain contributes to an overall hyperfine field distribution.

In practice, the unreduced hyperfine field (in the paramagnetic state of K_2FeF_5) is not known precisely and this gives a small amount of freedom in the simulation. Thus a 41 T saturation field may result from either an ω'_A/ω_E of 0.001 and an unreduced field 65 T or an ω'_A/ω_E of 0.002 and an unreduced field of 61 T. We chose $\omega'_A/\omega_E = 0.0022$ (roughly equal to $\omega_A/\omega_E + J'/J$) and, therefore, an unreduced saturation field of 60.5 T for the simulations, but the results obtained are not qualitatively changed if this value is changed by 10% either way as long as the saturation field is scaled consistently.

For each doping the distribution of atoms between different chain lengths is calculated assuming that the gallium substitutes randomly on the iron sites, and the matrix problem is solved for representative chain lengths, appropriately weighted. The resulting hyperfine distribution was transformed to a simulated spectrum with a program that treated exactly all the hyperfine parameters. Only physically uninteresting parameters such as the parabolic background characteristic of our experiment and spectrum area were varied in most of the spectra. It was found for the two most doped samples that a reduction of 1% in the hyperfine field gave a better simulation, probably due to the reduction of the ordering temperature to a temperature closer to 1.3 K. The results of this procedure are compared with experimental data in figure 2.

It can be seen that the lineshapes of the lightly doped samples are well predicted, with most of any misfit observed being due to our modelling of a continuous hyperfine distribution by a discrete one (typically with 15 components). As the spin reduction becomes large the model breaks down, for two reasons. Spin-wave theory itself fails when $\Delta S_z \simeq S$, but also as the number of short chains increases relaxation associated with 'superparamagnetism' in these chains becomes possible, driven either by the small $k_B T$ available or quantum fluctuations reversing the magnetisation. The most significant misfit is at the centre of the spectrum—extra absorption in this region would be observed if relaxation were occurring.

One interesting feature of the spectra is the small extra sextet observed outside the major broad sextet in the 6.2% doped spectrum. This is clearly visible in the simulation and just about visible in the experimental data. This weak extra sextet is caused by the atoms at the ends of long chains. Its relative area goes through a maximum as the doping is increased since for small amounts of doping there are relatively few chains and for large amounts of doping there are few long chains. The small outer sextet in the 1.7% doped sample must have a different origin—it is probably due to impurity.

4. Conclusion

A simple model of zero-point spin fluctuations, which contains no free parameters, accurately predicts both the lineshape broadening and asymmetry, and the reduced hyperfine field observable in the Mössbauer spectra of gallium-doped K_2FeF_5 for small amounts of doping at low temperatures. Any other end effects, e.g. supertransferred hyperfine interactions, appear to be of relatively minor importance. At concentrations higher than about 5% a combination of a breakdown in spin-wave theory and possible relaxation effects increases the area at the centre of the spectrum in a way that is not modelled by the simple theory. We hope in future to model the hyperfine distribution

in antiferromagnetic superparamagnets at low temperatures (below the collective excitation region). As well as difficulties concerning the particle size distribution, there are problems associated with the possibility of non-collinear spin arrangements in these materials due to frustration or surface effects. However a fit to a size distribution and effective anisotropy of the low-temperature spectra might allow a check of the values of these parameters obtained by other techniques.

Acknowledgment

We would like to thank Dr H H A Smit of the University of Leiden for valuable suggestions concerning this work.

References

[1] Vlasse M, Matejka G, Tressaud A and Wanklyn B M 1977 *Acta Crystallogr.* **33** 3377
[2] Pankhurst Q A, Johnson C E and Thomas M F 1986 *Hyperfine Interact.* **29** 1361
[3] Pankhurst Q A, Johnson C E and Thomas M F 1985 *J. Phys. C: Solid State Phys.* **18** 3249
[4] Kittel C 1963 *Quantum Theory of Solids* (New York: Wiley)
[5] Jones D H, Pankhurst Q A and Johnson C E 1987 *J. Phys. C: Solid State Phys.* **20** 5149
[6] Morrish A H and Haneda K 1983 *J. Magn. Magn. Mater.* **35** 105