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1979 J. Phys. C: Solid State Phys. 12 L739

(http://iopscience.iop.org/0022-3719/12/18/008)

J. Phys. C: Solid State Phys., Vol. 12, 1979. Printed in Great Britain. © 1979

LETTER TO THE EDITOR

Spin wave energy dispersion in $KCuF_3$: a nearly one-dimensional spin-$\frac{1}{2}$ antiferromagnet

M T Hutchings†, H Ikeda‡ and J M Milne†

† Materials Physics Division, AERE Harwell, Didcot, Oxon OX11 0RA, UK

‡ Department of Physics, Faculty of Science, Ochanomizu University, Tokyo 112, Japan

Received 3 July 1979

Abstract. Using inelastic neutron scattering techniques, the spin wave energy dispersion in the (010) plane of the distorted perovskite $KCuF_3$, which exhibits many magnetic properties of the spin-$\frac{1}{2}$ one-dimensional antiferromagnet, has been investigated at 4·7 K ($T_N = 39$ K). The measurements confirm the very strong exchange interaction between the spins in the [001] direction, and show that in this direction the expression for the excitation energies of the spin-$\frac{1}{2}$ antiferromagnetic chain given by J des Cloizeaux and J J Pearson is obeyed. The exchange interaction between these chains is found to be only 1·6% of that within the chains.

Potassium copper fluoride ($KCuF_3$) exhibits remarkable magnetic properties for a compound with a tetragonal structure closely related to the cubic perovskite. Much of its magnetic behaviour is characteristic of a one-dimensional (1-D) spin $S = \frac{1}{2}$ Heisenberg system, and indeed it was one of the first compounds to be investigated which showed such behaviour. In order to obtain direct measurements of the exchange interactions in this unique material, we have investigated the spin wave energy dispersion in two directions in the (010) plane at 4·7 K, well below the Néel temperature $T_N = 39$ K (indexing, as throughout this Letter, on the pseudo-perovskite tetragonal unit cell of sides a_0, a_0, c_0).

The origin of the observed one-dimensional magnetic behaviour has been explained by Kadota *et al* (1967) to result from the distortion of the lattice from the ideal perovskite structure (Okazaki and Suemune 1961). The cooperative Jahn–Teller effect causes the fluorines to move off their mid-positions in the (001) plane and leads to an ordering of the Cu^{2+} ion orbitals in an Ising-like pattern; this in turn gives rise to overlap integrals which give strong exchange coupling between the Cu^{2+} ions along the tetragonal [001] axis, but relatively much weaker coupling between ions in the (001) plane. There thus exist chains of strongly coupled ions along the [001] direction which interact only weakly with each other. The magnetic susceptibility (Kadota *et al* 1967) shows a broad peak at ~ 243 K, which is fitted very well by the theory of Bonner and Fisher (1964), and yields a value for the intrachain exchange constant $J_c = 32{\cdot}8$ meV (where J is defined such that the pair interaction is $\mathscr{H}^{12} = J\boldsymbol{S}_1.\boldsymbol{S}_2$). A similar value has recently been obtained from optical birefringence measurements (Iio *et al* 1978). A truly 1-D chain of spins with a finite range of interactions cannot show long-range magnetic order (e.g. see Mermin and Wagner 1966 and references therein), but weaker interchain

interaction will cause a system to order in three dimensions (3-D) at a finite temperature T_N (Oguchi 1964). $KCuF_3$ is found to order antiferromagnetically in 3-D at $\sim 39 \pm 1$ K or $\sim 22 \pm 4$ K, depending on the structure type (Hutchings *et al* 1969). The early work on $KCuF_3$ has been reviewed by Hirakawa and Kurogi (1970). More recently Ikeda and Hirakawa (1973) have investigated the static critical scattering in the region of T_N and have deduced a value for the ratio of the inter- to intrachain exchange constants of $|J_a/J_c| = 0{\cdot}027 \pm 0{\cdot}005$. Other estimates of this ratio range between 0·001 and 0·1. Electron spin resonance measurements (Ikebe and Date 1971) have shown that the major anisotropy is an '*XY*-type' contribution to the interaction along the chain, and that the anisotropy in the (001) plane is very weak.

The dynamics of 1-D spin systems have recently been the subject of a great deal of theoretical and experimental interest (see e.g. Steiner *et al* 1976). des Cloizeaux and Pearson (1962) have given an exact result for the excitation energy dispersion in the 1-D $S = \frac{1}{2}$ Heisenberg chain with antiferromagnetic interactions. This result has recently been shown to account very well for the measured excitation spectrum in $CuCl_2.2N(C_5D_5)$ just above T_N (Endoh *et al* 1974). Although the present measurements were made in the antiferromagnetic state, the same dispersion relation might be expected to hold for spin waves in the ordered state of very weakly coupled chains of spins.

$KCuF_3$ is known to exist in two kinds of polytype structures, designated types (*a*) and (*d*): with space groups $I4/{}^*c^*$ including D_{4h}^{18}, and $P4/{}^*b^*$ including D_{4h}^{5} respectively (Okazaki 1969, Tsukuda and Okazaki 1972). The two structures are shown in figure 1. Both structures order antiferromagnetically in a 'type-A' ordering pattern, with layers of ferromagnetically aligned spins antiferromagnetically stacked along [001]. However,

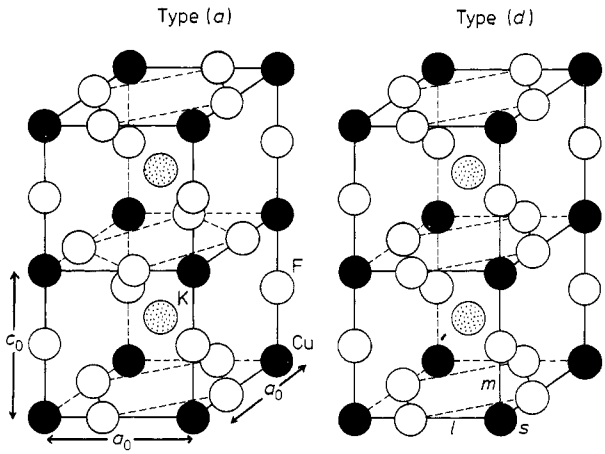

Figure 1. The two polytype structures of $KCuF_3$ (after Hirakawa and Kurogi 1970). (*a*) $c = 2c_0$; (*d*) $c = c_0$.

whereas the Néel temperature for type (*a*) is 39 ± 1 K, that for type (*d*) is $\sim 22 \pm 4$ K (Hutchings *et al* 1969, Ikebe and Date 1971). It should be noted that very similar ferromagnetic planes of spins are found in the compound K_2CuF_4 (see Funahashi *et al* 1976 and references therein).

The sample used for the present measurements consisted of a single crystal of volume $\sim 0{\cdot}2$ cm^3, with the type (*a*) D_{4h}^{18} structure. Measurement of the Néel temperature of

this sample from the temperature variation of the (001) M Bragg intensity confirmed $T_N = 39 \pm 1$ K. The sample was orientated with the [010] axis vertical and sealed in a helium-filled aluminium can attached to the cold finger of a CT14 Cryogenics Associates cryostat. It was maintained at 4·7 K for most of the measurements. The data were taken using the PLUTO triple-axis spectrometer at Harwell. The incident neutron wavelength λ_i between 1·0 Å and 2·351 Å was monochromatised using aluminium (111) or (220) planes. The analyser was a pyrolytic graphite (002) plane, and collimation angles of nominal values 120′, 30′, 40′ and 60′ were used before the monochromator, sample, analyser and counter respectively. A 'tuned' pyrolytic graphite filter was used at the longest wavelength to minimise higher-order contamination of the incident beam. Both constant-scattering vector ($\boldsymbol{Q}$), with constant λ_i, and constant-energy transfer scans were made to observe the spin waves via their excitation. The constant-$\boldsymbol{Q}$ scans were used to study the energy dispersion along [100], and at a few low energies in [001], but because of the very steep dispersion (~ 200 meV Å) along the [001] chains, constant-energy transfer scans were mainly employed in this direction. The excitations were measured mainly about the (0, 0, 1·5) magnetic reciprocal lattice point, at points (q_a, 0, 1·5), (0, 0, 1·5 + q_c) and ($\bar{0}\cdot\bar{2}$, 0, 1·5 + q_c), where we denote the spin wave wavevector in reciprocal lattice units as (q_a, q_b, q_c) along the pseudo-perovskite axes. At 4·7 K $a_0 = 4{\cdot}11 \pm 0{\cdot}01$ Å, and $c_0 = 3{\cdot}90 \pm 0{\cdot}01$ Å. The modes in the [100] direction were easily observable, but those along the chain axis were weak and lack of intensity precluded their observation above 25 meV (i.e. about 0·3 of the zone boundary wavevector of 0·403 Å^{-1}, corresponding to $q_c^{ZB} = 0{\cdot}25$). The modes were identifed as spin waves by their wavevector dependence and, in the case of the ($-0{\cdot}4$, 0, 0) mode, by the fact that it had broadened and become unobservable at 50 K. With the resolution available it was not possible to measure the energies of modes at $q = 0$ or very small wavevectors. There is evidence from extrapolation of higher-energy modes for a small energy gap at $q = 0$, but it was not possible to detect any splitting of the modes at low q. Before analysis all the data were corrected, using the Harwell program TXRES, for small shifts in the measured energy or wavevector arising from the finite resolution of the instrument. The corrected data points are shown in figure 2.

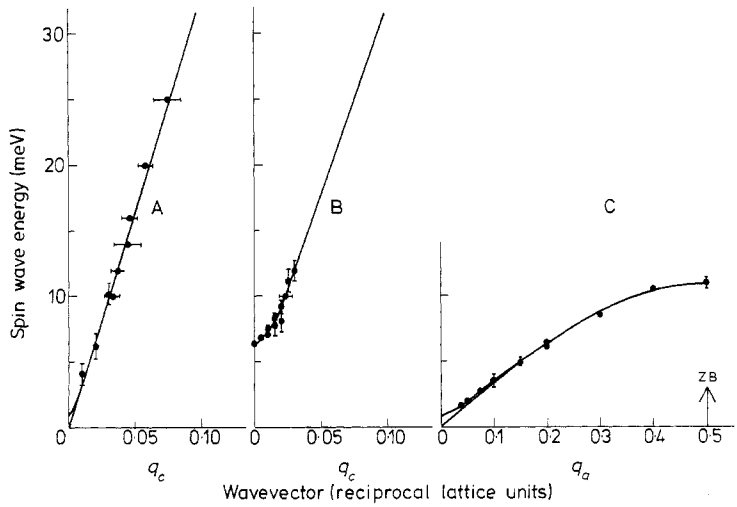

Figure 2. Spin wave energy dispersion in $KCuF_3$ at 4·7 K. The points are the present experimental values; the full curves are calculated from the parameters giving the best fit to the data: A $q = (0, 0, q_c)$; B $q = (-0{\cdot}2, 0, q_c)$; C $q = (-q_a, 0, 0)$.

The data were analysed in terms of the Hamiltonian

$$\mathcal{H} = +J_a \sum_{\langle i,\delta\rangle}^{\parallel \mathrm{NNN}} \boldsymbol{S}_i.\boldsymbol{S}_{i+\delta} + J_c \sum_{\langle i,\delta\rangle}^{a\parallel \mathrm{NNN}} \boldsymbol{S}_i.\boldsymbol{S}_{i+\delta} + D_c \sum_{\langle i,\delta\rangle}^{a\parallel \mathrm{NN}} S_i^x S_{i+\delta}^x$$

with $S = \frac{1}{2}$, where the z-axis is chosen along the spin direction in the (001) plane and the x-axis is along [001]. J_c couples the antiferromagnetically aligned nearest neighbours (NN) along the chain [001], and D_c is a small 'XY-like' anisotropic interaction. J_a couples the next-nearest neighbours (NNN) in the ferromagnetic planes. The sums are over all pairs of ions. The corresponding spin wave energies are given by

$$\hbar\omega_{1q} = RS[(\mu + \lambda)(\mu - \lambda - \rho)]^{1/2}$$

$$\hbar\omega_{2q} = RS[(\mu - \lambda)(\mu + \lambda + \rho)]^{1/2}$$

where

$$\lambda = 2J_c \cos(2\pi q_c)$$

$$\mu = 2J_c - 4J_a + 2J_a(\cos 2\pi q_a + \cos 2\pi q_b)$$

$$\rho = 2D_c \cos(2\pi q_c).$$

The lower mode goes to zero energy at $q = 0$ whilst the upper mode energy remains finite, and for small D_c the two modes rapidly converge with increasing wavevector. The factor R arises from higher-order corrections to the spin wave theory. It is unity for classical spin waves, but increases as S decreases and the dimensionality of the system decreases. Keffer (1966) has summarised estimated values of R in the form $R = (1 + \epsilon_0/2\eta S)$, where η = the number of NN ions, with ϵ_0 tabulated for a number of cases. However, there are no calculations of ϵ_0 for the magnetic structure of $KCuF_3$, with interactions of different magnitude and sign in different directions. Along the chains the dispersion is independent of J_a, and as the spins perpendicular to the chains are in ferromagnetic sheets one would expect the 1-D value to be appropriate. For the spin-$\frac{1}{2}$ 1-D 'ordered' antiferromagnet, spin wave theory gives $\epsilon_0 = 0{\cdot}726$ and $R = 1{\cdot}36$, whereas the exact result of des Cloizeaux and Pearson (1962) for the excitation spectrum from the ground state of the $S = \frac{1}{2}$ 1-D Heisenberg antiferromagnetic chain, showing no long-range order, is $R = \pi/2 = 1{\cdot}57$. This exact result should be the most accurate estimate for R along the chains at low temperatures where thermal renormalisation is small. Perpendicular to the chains the spins are coupled in ferromagnetic sheets, and although J_c influences the spin wave energies it seems reasonable to suppose that the correction term would be more appropriate to the ferromagnet, i.e. $R = 1$.

The expressions for the spin wave energies given above were fitted to the data using the method of least-squares minimisation. The three lowest neutron groups were assigned to the upper spin wave mode and the rest to the average of the two modes. The best fit gave values of $RJ_a = -0{\cdot}54 \pm 0{\cdot}01$ meV, $RJ_c = 53{\cdot}5 \pm 1{\cdot}0$ meV and $RD_c = -0{\cdot}007 \pm 0{\cdot}003$ meV, and the solid curves in figure 2 are calculated from these values. The exact form of the anisotropic interaction is not determined uniquely by the data as no neutron groups associated with the lower mode were observed. The gap for the upper mode at $q = 0$ is calculated to be 0·86 meV.

The values obtained for the interaction constants are given in table 1, where they are compared with other estimates. The most remarkable result is that, in taking a value of $R = \pi/2$ for the dispersion along the chain, the value obtained for J_c is 34 ± 1 meV $= 395 \pm 12$ K, compared with 32·8 meV = 380 K deduced from the susceptibility. The factor of des Cloizeaux and Pearson (1962) thus indeed appears to be appropriate

Table 1. Values of exchange interaction parameters for $KCuF_3$ in meV (1 meV = 11·6 K).

Method	J_a	J_c	D_c	$\lvert J_a/J_c \rvert$
Present work	$-0{\cdot}54 \pm 0{\cdot}01$†	$+34{\cdot}0 \pm 1{\cdot}0$‡	$-0{\cdot}004 \pm 0{\cdot}002$‡	$0{\cdot}016 \pm 0{\cdot}001$
Susceptibility and T_N (a)	—	$+32{\cdot}8$		$0{\cdot}018 \pm 0{\cdot}004$
Critical scattering (b)	—	—		$0{\cdot}027 \pm 0{\cdot}005$
Ordered moment (c)	—	—		$\sim 0{\cdot}1$
K_2CuF_4 (d)	$-1{\cdot}9 \pm 0{\cdot}1$	—		—

† Taking $R = 1$.
‡ Taking $R = \pi/2$.
(a) Kadota *et al* (1967) and Oguchi (1964); (b) Ikeda and Hirakawa (1973); (c) Hutchings *et al* (1969); (d) Funahashi *et al* (1976).

for the ordered state. The value for $J_a = -0{\cdot}54 \pm 0{\cdot}01$ meV, using $R = 1{\cdot}0$ for the ferromagnetic layers, gives a ratio $|J_a/J_c| = 0{\cdot}016 \pm 0{\cdot}001$. This ratio is in fair agreement with the 0·018 deduced from the susceptibility maximum and the T_N using Oguchi's (1964) expression. The critical-scattering experiment gave a higher value ($0{\cdot}027 \pm 0{\cdot}005$), and an estimate from the spin wave deviation in the ordered moment gave 0·1, although the latter assumed a 10% reduction due to covalency, which may be an overestimate. It is interesting to compare the value for J_a with the much larger value of $-1{\cdot}9$ meV found in K_2CuF_4. Since the $Cu^{2+} - F^-$ bonds are very similar to the two compounds, this illustrates the great sensitivity of the exchange to their lengths. For $KCuF_3$ $l = 2{\cdot}25$ Å, $s = 1{\cdot}89$ Å (figure 1) compared with 2·18 Å and 1·94 Å respectively in K_2CuF_4 (Ito and Akimitsu 1976). The value of J_c is surprisingly large for a Cu^{2+} compound, and the dispersion slope (~ 200 meV Å) is among the steepest found in localised systems.

The nature of the spin wave dispersion in $KCuF_3$ suggests that very interesting renormalisation effects should be observed as the temperature is increased above T_N. It is anticipated that these will be very anisotropic, with usual renormalisation along [100] but very weak renormalisation and persistence of the spin waves well above T_N along the chain [001] direction, as has been found in other 1-D compounds (Steiner *et al* 1976). However, higher neutron beam intensities or a larger sample than used here will be necessary to make a detailed study of these effects.

We wish to thank Dr C Sayers for helpful discussions.

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