Experimental evidence of the Dzyaloshinsky-Moriya antisymmetric exchange interaction in the one-dimensional Heisenberg antiferromagnet $KCuF_3$: EPR measurements

1989 J. Phys.: Condens. Matter 1 3397

(http://iopscience.iop.org/0953-8984/1/22/002)

J. Phys.: Condens. Matter 1 (1989) 3397–3408. Printed in the UK

Experimental evidence of the Dzyaloshinsky–Moriya antisymmetric exchange interaction in the one-dimensional Heisenberg antiferromagnet $KCuF_3$: EPR measurements

I Yamada†, H Fujii‡ and M Hidaka‡

† Department of Physics, Faculty of Science, Chiba University, Yayoi-cho, Chiba-260, Japan

‡ Department of Physics, Faculty of Science, Kyushu University, Hakozaki, Fukuoka-812, Japan

Received 23 August 1988, in final form 2 November 1988

Abstract. Based on our results of EPR experiments, we point out that $KCuF_3$, a one-dimensional Heisenberg antiferromagnet in spite of its pseudo-cubic crystal structure, has a Dzyaloshinsky–Moriya (DM) antisymmetric exchange interaction $\Sigma d_{ij} S_i \times S_j$ between spins on the c-axis; the direction of d_{ij} is perpendicular to the c-axis. The observed EPR linewidth shows $(2 + \sin^2\theta)$-like angular behaviour (θ is the angle between the c-axis and the external field), which coincides well with the theory of line broadening due to the DM interaction with $d_{ij} \perp c$-axis. The linewidth shows a rapid decrease with lowering temperature and its value extrapolated to $T = 0$ K from the paramagnetic region is zero. As the theory by Soos *et al* shows, this temperature dependence also indicates that the EPR line is governed by the DM interaction; i.e., it arises from the four-spin correlation functions $\langle (S_i^\alpha S_j^\beta - S_i^\beta S_j^\alpha)^2 \rangle$ (where α and $\beta = x, y$ and z) in the second moment due to the DM interaction which is different from $\langle (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)^2 \rangle$ of the perturbation terms of both the dipole–dipole and the anisotropic exchange interactions.

1. Introduction

Among the many compounds of KMF_3 (M is a 3d metal ion) studied to date, $KCuF_3$ is unique. In spite of its pseudo-perovskite crystal structure (the distances between magnetic atoms are essentially the same along the principal axes), it has one-dimensional magnetic properties. Hirakawa and co-workers have successfully grown single crystals of $KCuF_3$ large enough for precise experiments by employing their own method of precipitation, and have clearly explained the origin of the magnetic one-dimensionality (Kadota *et al* 1967, Hirakawa and Kadota 1967). The latter arises from the cooperative Jahn–Teller distortion of F^- octahedra. Due to the cooperative Jahn–Teller effect, each F^- ion is slightly displaced from the centre of adjacent Cu^{2+} sites in the c-plane. Then the hole orbital of Cu^{2+}, i.e., $d_{z^2-x^2}$ or $d_{z^2-y^2}$, shows an alternate ordering in the c-plane. The overlap of orbitals along the c-axis results in a strong superexchange interaction J_c, whereas the superexchange interaction J_a perpendicular to the c-axis is very weak because of the poor overlap of orbitals. J_c is estimated as -190 K in $-2J_c\Sigma S_i S_j$ with fitting the susceptibility, which shows a broad peak at about 243 K (Kadota *et al* 1967)

0953-8984/89/223397 + 12 $02.50

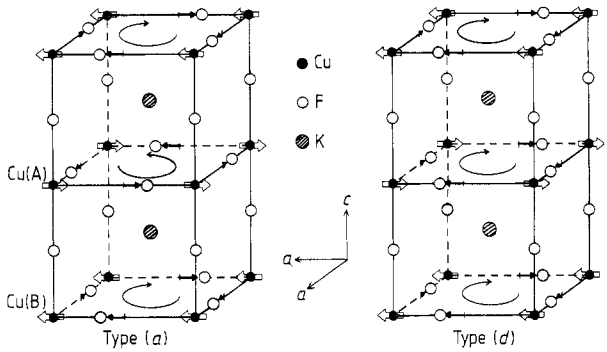

Figure 1. Crystal structure of $KCuF_3$ types (*a*) and (*d*) reported by Okazaki *et al*. The accepted magnetic structure is also shown; the larger arrow on each Cu site indicates the spin direction. Since the magnetic anisotropy in the *c*-plane is very weak, the spin direction in the *c*-plane is tentatively shown as parallel to that of the *a*-axis. The smaller arrows show the F^- ion displacement from the midpoint between adjacent Cu sites and circles with arrows show the F^- ion displacement in the respective *c*-plane.

using the theory of Bonner and Fisher (1964). The magnetic specific heat obtained by measuring the linear birefringence also shows a broad peak around 180 K and is well reproduced by the Bonner–Fisher theory with almost the same value of J_c (Iio *et al* 1978). More direct evidence of magnetic one-dimensionality was found in inelastic neutron scattering experiments (Ikeda and Hirakawa 1973, Hutchings *et al* 1979, Satija *et al* 1980) from which $J_c = -230$ K and $|J_a/J_c| \simeq 0.01$ were determined.

The magnetic structure so far accepted is as follows. Below $T_N = 39$ K, spins lie in the *c*-plane due to the small *XY*-like anisotropy and couple ferromagnetically with each other in the *c*-plane, which was proposed on the basis of antiferromagnetic resonance (Ikebe and Date 1971) and of neutron diffraction experiments (Hutchings *et al* 1969). The relationship between the ordering of hole–orbital and the exchange interaction has been explained by Khomskii and Kugel (1973), who showed theoretically that the ferromagnetic superexchange interaction in the *c*-plane arises from the orbital ordering of $d_{z^2-x^2}$ or $d_{z^2-y^2}$.

The crystal structure of $KCuF_3$ has also been studied intensively. Okazaki and Suemune (1961) pointed out that the compound has two kinds of polytype structure (see also Okazaki 1969, Okazaki and Tsukuda 1969, Tsukuda and Okazaki 1972), referred to as types (*a*) and (*d*), as shown in figure 1. In a crystal of type (*a*), the direction of displacement of F^- ions from the mid-point between the nearest Cu^{2+} sites rotates oppositely in adjacent *c*-planes, whereas the rotation is always in the same sense in type (*d*). When we pay attention to type (*a*), we find that there is no inversion centre halfway between adjacent Cu^{2+} sites on the *c*-axis or in the *c*-plane. Thus it is possible that the Dzyaloshinsky–Moriya (DM) antisymmetric exchange interaction $\Sigma d_{ij} S_i \times S_j$ in $KCuF_3$ occurs in type (*a*) structure. If so, the accepted magnetic structure shown in figure 1 should be modified.

Further, spin dynamics should also be strongly affected by the DM interaction. An absorption line of electron paramagnetic resonance (EPR) is one of the representative quantities that reflect this interaction. In an early study of ESR on $KCuF_3$ (Ikebe and Date 1971), the temperature dependence of EPR linewidth was reported, and the effects of its one-dimensionality on the temperature behaviour of the linewidth was discussed

but without further detailed analysis. As is well known, perturbation terms such as dipole–dipole (DD), anisotropic exchange (AE), DM interactions, etc, cause absorption line broadening. When the DM interaction term is remarkably predominant in magnitude, an angular or a temperature behaviour of the absorption line is different from when it is absent as was shown theoretically by Soos *et al* (1977a, b). After summarising their theory, we show the experimental EPR results and verify the existence of the DM interaction in $KCuF_3$.

2. Theoretical background

Based on the conventional theory of exchange narrowing, Soos *et al* treated the effect of the DM interaction on EPR lines focusing on the effect of spin correlations on local fields due to perturbations such as DM, AE, and DD interactions, etc, and considered the temperature dependence of the second moment. One of their results was that spin diffusion does not enhance the secular part of the DM interaction when each spin site is at an inversion centre (see Appendix 2). This suggestion is important in EPR studies of $KCuF_3$ because this compound is one-dimensional, even though its one-dimensionality is not so pronounced ($|J_a/J_c| \fallingdotseq 0.01$). When the secular part is not enhanced, the half linewidth is estimated as M_2/ω_e, where M_2 is the second moment including both secular and nonsecular parts, and ω_e is the corresponding exchange interaction frequency.

Here we summarise the theory of exchange narrowing taking account of the proposal by Soos *et al*. Exchange narrowing is treated by a Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \tag{1}$$

where the main term $\mathcal{H}_0$ consists of the isotropic exchange $-2J\Sigma S_i S_j$ and Zeeman interactions, and $\mathcal{H}'$ contains all other terms that cause the line broadening. The EPR absorption line $I(\omega - \omega_0)$ at ω_0 can be written as

$$I(\omega - \omega_0) = \int_{-\infty}^{\infty} \varphi(t) \exp[\mathrm{i}(\omega - \omega_0)t]\, \mathrm{d}t \tag{2}$$

in which the relaxation function $\varphi(t)$ is given by

$$\varphi(t) = \langle \tilde{M}_+(t) M_-(0) \rangle / \langle M_+ M_- \rangle \tag{3}$$

where M_+ and M_- are the transverse magnetisations and $\tilde{M}(t)$ is the interaction representation. As is well known, $\varphi(t)$ is represented by the correlation function $\psi(\tau)$ which is expressed (Kubo and Tomita 1954) as

$$\varphi(t) = \exp\left(-\int_0^t (t - \tau)\psi(\tau)\, \mathrm{d}\tau \right) \tag{4}$$

and $\psi(\tau)$ is given by

$$\psi(\tau) = \frac{\langle [\tilde{\mathcal{H}}'(\tau), M_+(0)][M_-(0), \mathcal{H}'(0)] \rangle}{\hbar^2 \langle M_+ M_- \rangle} \tag{5}$$

where

$$\tilde{\mathcal{H}}'(\tau) = \exp(-\mathrm{i}\mathcal{H}_0\tau/\hbar)\mathcal{H}'(0) \exp(\mathrm{i}\mathcal{H}_0\tau/\hbar).$$

When the exchange interaction is very large and spin diffusion is not effective, $\varphi(t)$ is approximated as

$$\varphi(t) = \exp\left(-t \int_0^{\infty} \psi(\tau)\, \mathrm{d}\tau \right) = \exp[-t\psi(0)\tau_c] \tag{6}$$

with a characteristic time $\tau_c \simeq \hbar/J$. $\psi(0)$ corresponds to the second moment $M_2(J/kT)$

of the resonance line. The absorption line $I(\omega - \omega_0)$ then becomes Lorentzian with its derivative peak-to-peak linewidth ΔH_{pp} approximated as

$$\Delta H_{pp} = (2/\sqrt{3})\psi(0)\tau_c = (2/\sqrt{3})M_2(J/kT)\tau_c. \tag{7}$$

In the present case, $\mathcal{H}'$ contains DD, AE, DM interactions, the g-tensor inequivalence, the hyperfine interactions, etc. We shall show later that the effect of both the inequivalent g-tensor and the hyperfine interaction is too small to broaden the line in the present case. Thus we consider the DD, AE and DM interactions, i.e.,

$$\mathcal{H}' = \mathcal{H}'_{DD} + \mathcal{H}'_{AE} + \mathcal{H}'_{DM} \tag{8}$$

and we can write the expressions

$$\mathcal{H}'_{AE} = \sum_{i>j} S_i A S_j \qquad \text{and} \qquad \mathcal{H}'_{DM} = \sum_{i>j} d_{ij} S_i \times S_j.$$

The respective second moment at the high-temperature limit ($J/kT = 0$), $M_2^{DD}(0)$, $M_2^{AE}(0)$ and $M_2^{DM}(0)$ are given as follows:

$$M_2^{DD}(0) = g^4\mu_B^4 \frac{3S(S+1)}{2\hbar^2} \sum_{i>j} \frac{(1 + \cos^2\theta_{ij})}{r_{ij}^6} \tag{9}$$

$$M_2^{AE}(0) = \tfrac{1}{4}A^2(1 + \cos^2\theta) \tag{10}$$

$$M_2^{DM}(0) = \begin{cases} \tfrac{1}{8}d_{ij}^2(2 + \sin^2\theta) & \text{for } d_{ij} \perp c\text{-axis} \quad (11a) \\ \tfrac{1}{4}d_{ij}^2(1 + \cos^2\theta) & \text{for } d_{ij} \parallel c\text{-axis} \quad (11b) \end{cases}$$

where θ_{ij} is the angle between r_{ij} and the external field H_0 (r_{ij} is the displacement between lattice sites i and j), and θ is the polar angle of H_0 with respect to the c-axis. We have counted only spins on the c-axis for $M_2^{AE}(0)$ and $M_2^{DM}(0)$. The parameters $A \simeq (\Delta g/g)^2 J$ and $d_{ij} \fallingdotseq (\Delta g/g)J$ can be used with $g = (g_\parallel + g_\perp)/2$ and $\Delta g = g - 2$, where $g_\parallel$ and $g_\perp$ are the g-values parallel and perpendicular to the principal crystal field axes.

To discuss linewidths at finite temperatures above the critical region, we must first determine the temperature dependence of $M_2(J/kT)$. From equation (5) we obtain

$$\psi(\tau = 0) = M_2(J/kT) = \frac{\langle [\mathcal{H}'(0), M_+(0)]^2 \rangle}{\hbar^2 \langle M_+ M_- \rangle} \tag{12}$$

where the numerator yields four-spin correlation functions. There appears to be a basic difference between the four-spin correlation functions in $M_2^{DM}(J/kT)$ and in $M_2^{AE}(J/kT)$ [or $M_2^{DD}(J/kT)$] (see Appendix 1), i.e.,

$$M_2^{DM}(J/kT) = \psi^{DM}(0) \propto \frac{\langle (S_i^\alpha S_j^\beta - S_i^\beta S_j^\alpha)^2 \rangle}{\langle M_+ M_- \rangle} \tag{13a}$$

whereas

$$M_2^{AE}(J/kT) = \psi^{AE}(0) \propto \frac{\langle (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)^2 \rangle}{\langle M_+ M_- \rangle} \tag{13b}$$

in which $\alpha, \beta = x, y, z$. The four-spin correlation function in $M_2^{DD}(J/kT)$ is similar to

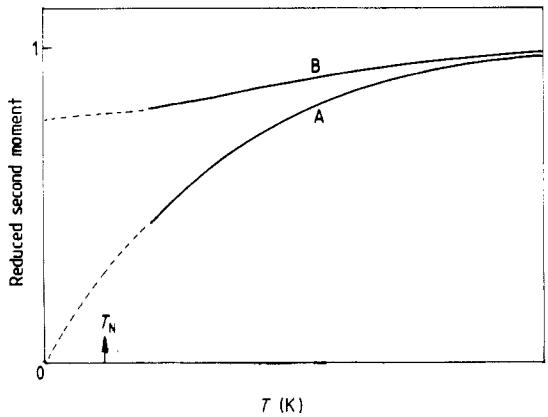

Figure 2. Schematic drawing of the temperature dependence of the reduced second moment $M_2^{DM}(J/kT)/M_2^{DM}(0)$ (line A) and $M_2^{AE}(J/kT)/M_2^{AE}(0)$ or $M_2^{DD}(J/kT)/M_2^{DD}(0)$ (line B). The line A tends to zero with $T \rightarrow 0$ K, whereas the line B keeps a non-zero value with $T \rightarrow 0$ K.

that of $M_2^{AE}(J/kT)$. In the usual manner, they are decoupled into products of two-spin correlation functions, expressed as

$$\langle S_i^\alpha S_j^\beta \rangle = \tfrac{1}{3}S(S+1)C(r_{ij}, T)\delta_{\alpha\beta} \tag{14}$$

where $C(r_{ij}, T)$ is the normalised static correlation function depending on the distance between spin sites i and j, which is zero at the high-temperature limit. $C(r_{ij}, T)$ is correlated to the static susceptibility $\chi(T)$ as $\chi(T) = \chi_C[1 + \Sigma C(r_{ij}, T)]$, where χ_C is the Curie law susceptibility, and can be determined from the high-temperature series expansion. Soos *et al* showed that the effect of $C(r_{ij}, T)$ on $M_2^{DM}(J/kT)$ is completely different from that on $M_2^{AE}(J/kT)$ or $M_2^{DD}(J/kT)$; even in the most simplified case where only the nearest-neighbour spin correlations are considered, there arises a difference as

$$\langle (S_i^\alpha S_j^\beta - S_i^\beta S_j^\alpha)^2 \rangle \propto [1 - C(1, T)] \tag{15a}$$

$$\langle (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)^2 \rangle \propto [1 + C(1, T)] \tag{15b}$$

where $C(1, T)$ represents the nearest-neighbour spin correlation defined in equation (14). Thus the following approximation is obtained,

$$[M_2^{DM}(J/kT)/M_2^{DM}(0)] \simeq (\chi_c/\chi(T))[1 - C(1, T)] \tag{16a}$$

$$[(M_2^{AE}(J/kT) + M_2^{DD}(J/kT)]/[M_2^{AE}(0) + M_2^{DD}(0)] \simeq (\chi_c/\chi(T))[1 + C(1, T)]. \tag{16b}$$

A relation $\langle M_+ M_- \rangle = \chi(T)kT$ is used to derive equations (16*a*) and (16*b*). In low-dimensional cases, $C(1, T)$ tends to one with decreasing temperature over a wide temperature range, and $M_2^{DM}(J/kT)$ gradually decreases to zero. On the contrary, $M_2^{AE}(J/kT)$ or $M_2^{DD}(J/kT)$ show moderate changes with the temperature due to both the decrease in $\chi_c/\chi(T)$ and the increase in $[1 + C(1, T)]$; these two second moments do not fall to zero with $T \rightarrow 0$ K (see figure 2). If the correlations between more distant neighbour spins are taken into account, the qualitative tendencies of the temperature behaviour of the second moments explained above are held unchanged.

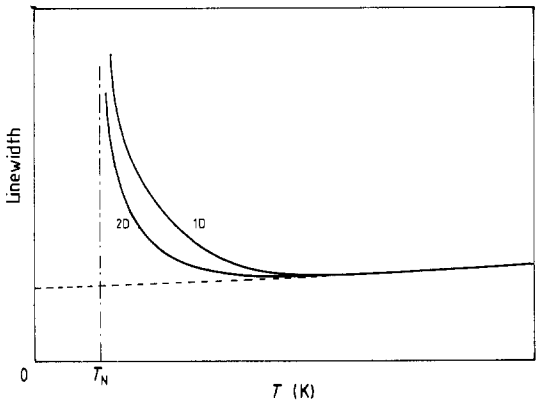

Figure 3. Schematic drawing of linewidth versus temperature for low-dimensional antiferromagnets without the DM interaction. The extrapolated line (dotted) does not go to zero. Near T_N, the linewidth increases over a wide temperature range.

Over the critical region, i.e. near T_N, where conventional low-dimensional antiferromagnets show rapid increases in linewidth (figure 3), on the other hand, a temperature behaviour of the linewidth should be treated as a special category of critical phenomena and the theory represented above should be modified. However, the variations in four-spin correlation functions $\langle(S_i^\alpha S_j^\beta - S_i^\beta S_j^\alpha)^2\rangle$ and $\langle(S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)^2\rangle$ with temperature near T_N should be different. Thus we can expect contrasting linewidth behaviours near T_N between systems with and without DM interactions.

3. Experimental procedure

As explained in § 1, $KCuF_3$ has two types of crystal structure designated (*a*) and (*d*). Single crystals of this compound used in early studies to clarify its magnetic one-dimensionality were grown from aqueous solution (the method is explained in Kadota *et al* 1967). It has been found, however, that growing crystals without a mixing of types (*a*) and (*d*) is almost impossible with this method; every crystal is more or less a mixed state of the two types so that the samples used in early work were not perfect. The quality of crystals obtained from the aqueous solution are examined in detail by Tsukuda and Okazaki (1972) and Hutchings *et al* (1969).

For several years the Bridgman method has been employed to obtain crystals. This was found to be an improvement on the former method of growing of crystals with single type (*a*) domains, but even so, crystals thus grown from melting still sometimes show mixtures of the two types. Further, twins appear easily because the crystal is pseudocubic with lattice parameter ratio of $c/a = 0.95$. One more disadvantage is a stacking disorder along the *c*-axis. Thus samples should be examined carefully. Among crystals precipitated from aqueous solution, on the other hand, there occasionally appears crystals rich in type (*d*). Of those we have so far examined, however, 90–95% single domains of type (*d*) are the best; a crystal with pure type (*d*) has not yet been produced.

A sample of size $2 \times 2 \times 2\ mm^3$ used in the present study was cut from a single crystal grown by the Bridgman method. By both x-ray diffraction and phonon–Raman scattering, the sample was confirmed as having pure type (*a*) structure with neither twins nor stacking disorders. The efficacy of phonon–Raman scattering for checking domain structures will be discussed elsewhere.

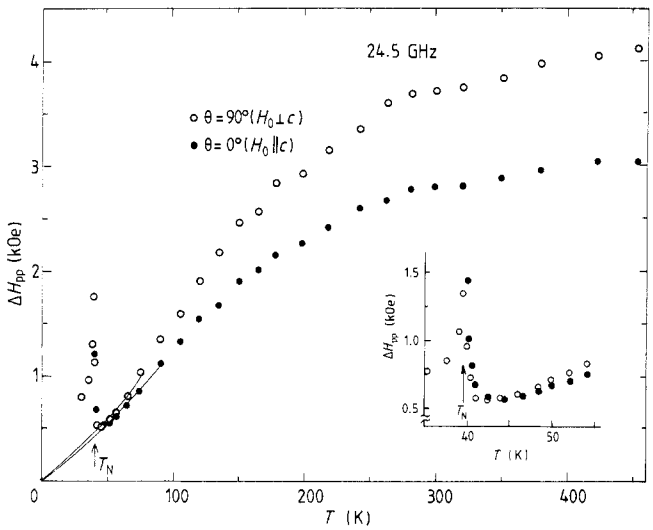

Figure 4. Temperature dependence of the peak-to-peak derivative linewidth ΔH_{pp} for the external field H_0 parallel ($\theta = 0°$) and perpendicular ($\theta = 90°$) to the c-axis, measured at 24.5 GHz. The solid lines indicate the extrapolation from the paramagnetic region; it goes down to zero. ΔH_{pp} near T_N is shown inset.

EPR measurements were done using a conventional K-band spectrometer. We used different cavities for the measurements below and above room temperature. Below room temperature, a TE_{011} cavity mode with a sample rotation mechanism around a vertical axis was inserted in a liquid-He cryostat with electronic temperature control. For the high-temperature measurements we employed a method proposed by Singer *et al* (1961); using a platinum-strip-coated quartz tube resistively heated in a water-cooled TE_{011} cavity.

4. Experimental results

As referred to above, both the static susceptibility and the magnetic specific heat of $KCuF_3$ show broad peaks around 200 K, suggesting the existence of the magnetic short-range order over a wide temperature range above 200 K; thus even room temperature is included in the region of short-range order. Above-room-temperature measurements are necessary to compare the experimental results with theories for $T \rightarrow \infty$.

Figure 4 shows the dependence of the derivative peak-to-peak linewidth ΔH_{pp} on temperature for the external field H_0 parallel and perpendicular to the c-axis measured at 24.5 GHz. The rapid increase in ΔH_{pp} below ~40 K indicates the development of long-range antiferromagnetic spin ordering, and will not be discussed here. Above 40 K we find that $\Delta H_{pp}(\theta = 0°) < \Delta H_{pp}(\theta = 90°)$, where θ is the angle between the external field and the c-axis. The lineshape observed at 50 K and 300 K has been confirmed as being Lorentzian. The θ dependence of ΔH_{pp} measured at 300 K is shown in figure 5. The curve of ΔH_{pp} versus temperature shows a plateau over the range 300–450 K, which indicates that the ΔH_{pp} from static spin correlations is approaching saturation. Thus $\Delta H_{pp}(T \rightarrow \infty)$ is estimated as ~5 kOe for $\theta = 90°$ and ~3.5 kOe for $\theta = 0°$ by extrapolating the observed ΔH_{pp} from the comparatively flat part below ~450 K. The ratio

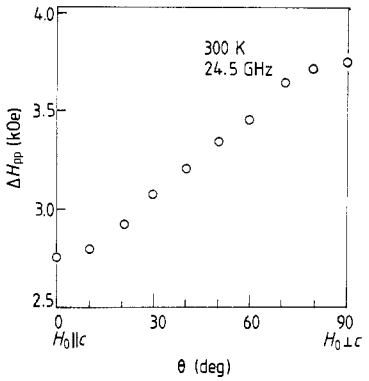

Figure 5. Angular dependence of ΔH_{pp} obtained at 300 K. θ is the angle between the external field and the c-axis.

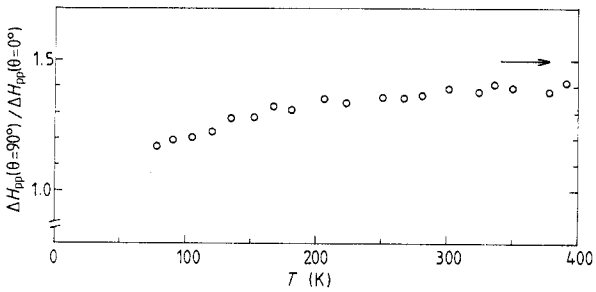

Figure 6. Ratio $\Delta H_{pp}(\theta = 90°)/\Delta H_{pp}(\theta = 0°)$ plotted as a function of temperature. The arrow indicates the position of 1.5, the theoretically expected value at high temperatures.

$\Delta H_{pp}(\theta = 90°)/\Delta H_{pp}(\theta = 0°)$ is plotted in figure 6 as a function of temperature; over the range of 300–400 K, this ratio is 1.4. In the c-plane, on the other hand, ΔH_{pp} does not show angular dependence within experimental accuracy.

5. Discussion and conclusions

Since $KCuF_3$ has magnetic one-dimensionality with Heisenberg-type exchange interactions, we must refer to whether there is a diffusive relaxation effect on the EPR line. If a one-dimensional diffusive relaxation governs the EPR line, ΔH_{pp} should have $(3\cos^2\theta - 1)^{4/3}$-like angular behaviour with a minimium at $\theta = 55°$ and the line-shape at $\theta = 0°$ should depart from Lorentzian. Contrary to this expectation, the experimental linewidth has no anomaly at $\theta = 55°$, as can be seen from figure 5, i.e., the observed ΔH_{pp} does not show $(3\cos^2\theta - 1)^{4/3}$-like behaviour. Furthermore, the observed lineshape is Lorentzian. From these results, we can say that it is not necessary to take acount of the one-dimensional diffusive effect on the spin relaxation. Or, even if the relaxation is diffusive, there should be perturbation terms that make spin diffusion ineffective.

We now compare $M_2^{DM}(0)$, $M_2^{AE}(0)$ and $M_2^{DD}(0)$. Using the lattice parameters (a = 4.14 Å, c = 3.92 Å), g-values ($g_a = (g_\parallel + g_\perp)/2 = 2.27$ and $g_c = g_\parallel = 2.15$ determined in the present work) and $J = J_c = -203$ K, we obtain the second moments as

$$M_2^{dd}(0) \simeq 10^6 \text{ Oe}^2 \qquad M_2^{ae}(0) \simeq 10^8 \text{ Oe}^2 \qquad M_2^{DM}(0) \simeq 10^{10} \text{ Oe}^2.$$

It becomes clear that the effect of the DM interaction is overwhelmingly larger than the other two. Strictly speaking, there arises a cross term between the DD and AE interactions, but the second moment from the cross term does not exceed $M_2^{AE}(0)$. It can generally be shown, on the other hand, that there is no cross term between $M_2^{DM}(0)$ and $M_2^{AE}(0)$ (or $M_2^{DD}(0)$).

We note in passing the amount of the second moment of the inequivalent g-tensor and of the hyperfine interaction. The inequivalent g-tensor induces a perturbation $\mathcal{H}' = (g_\parallel - g_\perp)\mu_B H_0 \Sigma S_i^z$ (where $H_0 \| z$) and this term produces the second moment $(g_\parallel - g_\perp)^2 \mu_B^2 H_0^2/2g^2 \simeq 3 \times 10^5$ Oe^2 at 24.5 GHz ($H_0 \simeq 8$ kG). On the other hand, the hyperfine constant $\sim 10^2$ Oe results in the negligible second moment. Thus the con-

tribution to line broadening from both the inequivalent g-tensor and the hyperfine is negligible. The main origin of line broadening is therefore the DM interaction, so that the spin diffusion, even if it governs the spin relaxation process in $KCuF_3$, has no effect on the linewidth as introduced in § 2. Thus the angular behaviour of ΔH_{pp} at high temperatures should be reproduced by the angular part of $M_2^{DM}(0)$, namely by equations (11*a*, *b*). The experimental result shown in figure 5 is well reproduced by $(2 + \sin^2\theta)$; the ratio $\Delta H_{pp}(\theta = 90°)/\Delta H_{pp}(\theta = 0°) = 1.4$ obtained experimentally agrees well with the value 1.5 calculated from equation (11*a*). Thus we can identify that d_{ij} is perpendicular to the c-axis. Furthermore, the calculated ΔH_{pp} from equations (7) and (11*a*) is approximately 6 kOe, which is not far from the extrapolated value $\Delta H_{pp}(T \to \infty) \simeq 3.5$–5 kOe.

The dependence of ΔH_{pp} on temperature is well explained by equation (16*a*); i.e., ΔH_{pp} becomes narrower with decreasing temperature. Its value extrapolated to $T = 0$ K from the paramagnetic region goes to zero as indicated in figure 4. As far as we know, the linewidths of the magnetic compounds in which the DM interaction is absent, whether they are low-dimensional or not, do not tend to zero with extrapolating to $T = 0$ K as shown in figure 3. We can point out several cases such as TMMC (Cheung *et al* 1978, Tuchendler *et al* 1979), K_2MnF_4 (Richards and Salamon 1974, Yokozawa *et al* 1978), K_2CuF_4 (Yamada *et al* 1983), etc. The line broadening of TMMC and K_2MnF_4 comes from the DD interaction, whereas K_2CuF_4 has both AE and DD interactions. Then their linewidths change moderately with the temperature above their respective critical regions, as equation (16*b*) predicts.

In Heisenberg antiferromagnets in which the DM interaction is not the main origin of line broadening, ΔH_{pp} increases over the critical temperature region above T_N. In low-dimensional systems such a phenomenon can be seen over a wide temperature range above T_N, as shown in figure 3. In the present case, however, ΔH_{pp} begins to increase at 40–42 K, quite close to $T_N = 39$ K as can be seen in figure 4 (inset). Thus, we can say that the increase in ΔH_{pp} over the wide critical region which is expected from its one-dimensionality is substantially zero in $KCuF_3$. Over the critical region, a more precise treatment of the four-spin correlation functions should be necessary. However, a qualitative argument based on the theory by Soos *et al* as represented here is useful to point out the characteristic behaviours of ΔH_{pp} with T.

From the analysis of the observed EPR linewidth of $KCuF_3$, we have shown that the DM interaction exists in this system and that this is a major perturbation term for line broadening. The angular dependence of the linewidth indicates that $d_{ij} \perp c$-axis. Owing to this antisymmetric interaction, the spin ordering is no longer exactly antiparallel. With crystal symmetry of type (*a*), we can easily conclude that $d_{ij} = -d_{jk}$, i.e., the direction of d_{ij} reverses alternately along the c-axis. Since $d_{ij} \perp c$-axis, there should arise a c-component of spin, which is estimated as $\Delta g/g$ times the a-component. Taking account of J_c and the g-values given above, we estimate that the c-component is approximately 10% of the a-component. We therefore propose a new spin structure for $KCuF_3$ with type (*a*) structure, as shown in figure 7. A net weak ferromagnetic moment cannot be expected because the directions of the weak moments on each c-axis are opposite to each other.

Direct experimental evidence of this hidden weak moment should be obtained by neutron diffraction. Several neutron-scattering studies of $KCuF_3$ have been reported in § 1, but none of them referred to the DM interaction and no effort was made to identify the hidden weak moment along the c-axis. New magnetic reflections expected from the postulated c-component of spin should be very weak; we estimate their intensities to be two orders of magnitude smaller than the principal magnetic peaks. Because previous

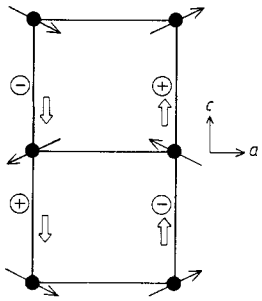

Figure 7. Proposed new spin structure expected from the effect of the Dzyaloshinsky–Moriya antisymmetric exchange interaction. + and − indicate that the direction of d_{ij} reverses alternately with $d_{ij} \perp c$-axis. White arrows represent the resultant c-component of spin.

neutron diffraction experiments were not precise enough to detect such small reflections (Hirakawa, personal communication), we plan to perform neutron diffraction experiments using a larger, higher-quality crystal to confirm directly the expected c-component of spin.

The present study has confirmed that $KCuF_3$ is a representative antisymmetric linear chain system. However, a serious problem arises when we take account of the simple rule to identify the direction of d_{ij} given by Moriya (1960) from symmetry considerations. For the coupling between two ions i and j located at points A and B, he obtained four rules.

(1) When a mirror plane perpendicular to AB bisects AB, $d_{ij} \parallel$ mirror plane.
(2) When there is a mirror plane including A and B, $d_{ij} \perp$ mirror plane.
(3) When a twofold rotation axis perpendicular to AB passes through the midpoint of AB, $d_{ij} \perp$ twofold axis.
(4) When there is an n-fold axis ($n \geqq 2$) along AB, $d_{ij} \parallel$ AB.

Let us apply this rule to $KCuF_3$. Two adjacent Cu^{2+} ions on the c-axis are denoted Cu(A) and Cu(B), as shown in figure 1. The results are as follows.

(1) There is no mirror plane perpendicular to AB that bisects AB. This rule is therefore out of the question.
(2) There are mirror planes including A and B, i.e., the (100) plane and equivalent planes. Thus $d \perp c$-axis.
(3) There are twofold axes perpendicular to AB which pass through the midpoint of AB; i.e., the [110] axis and equivalent directions satisfy this condition. Thus $d_{ij} \perp$ [110] and equivalent directions; i.e., $d_{ij} \perp c$-axis or $d_{ij} \parallel c$-axis.
(4) There is a twofold axis along AB, namely, the line of Cu(A)–Cu(B) bonding. Then $d_{ij} \parallel c$-axis.

We therefore get conflicting results in that $d_{ij} \perp c$-axis and $d_{ij} \parallel c$-axis, in which case one concludes that $d_{ij} = 0$. However, $d_{ij} \neq 0$ and $d_{ij} \perp c$-axis are clearly confirmed by our experiments, so we can question the crystal structure determined earlier (Tsukuda and Okazaki 1972).

We have recently re-examined the crystal structure of a type (*a*) sample by x-ray diffraction and have found new superlattice reflections that were not observed by Okazaki *et al*. In our opinion, these new reflections are due to the improved sample quality and suggest that the crystal symmetry should be lower than that reported so far. Then it is possible to get $d_{ij} \neq 0$ with $d_{ij} \perp c$-axis from the symmetry consideration. A detailed x-ray analysis of crystal symmetry is now in progress and the results will be reported elsewhere.

Appendix 1

We show three components of the DM interaction, secular and nonsecular parts. The coordinate system is as follows. $[XYZ]$ are fixed to the crystal axes $[aac]$ with $Z \| c$, and $[xyz]$ are defined with $H_0 \| z$. θ and φ are polar and azimuthal angles of H_0 with respect to the c-axis.

$$\mathcal{H}' = \sum_{i>j} d_{ij} S_i \times S_j = \sum_{i>j} \sum_{\alpha\beta} \lambda_{ij} S_i^\alpha S_j^\beta = \sum_{i>j} (G_0^{\mathrm{DM}} + G_1^{\mathrm{DM}} + G_{-1}^{\mathrm{DM}}) \tag{A1}$$

where $\alpha, \beta = x, y, z$, G_0^{DM} is the secular term and both G_1^{DM} and G_{-1}^{DM} are nonsecular terms. These three components are

$$\begin{aligned} G_0^{\mathrm{DM}} &= \tfrac{1}{2} \mathrm{i} \lambda_{ij}^{xy} (S_i^+ S_j^- - S_i^- S_j^+) \\ G_1^{\mathrm{DM}} &= \tfrac{1}{2} (\lambda_{ij}^{xz} - \mathrm{i}\lambda_{ij}^{yz})(S_i^+ S_j^z - S_i^z S_j^+) \\ G_{-1}^{\mathrm{DM}} &= \tfrac{1}{2} (\lambda_{ij}^{xz} + \mathrm{i}\lambda_{ij}^{yz})(S_i^- S_j^z - S_i^z S_j^-) \end{aligned} \tag{A2}$$

in which

$$\begin{aligned} \lambda_{ij}^{xy} &= \tfrac{1}{2} (d_{ij}^X \sin\theta \cos\varphi - d_{ij}^Y \sin\theta \sin\varphi + d_{ij}^Z \cos\theta) \\ \lambda_{ij}^{xz} &= d_{ij}^X \sin\varphi - d_{ij}^Y \cos\varphi \\ \lambda_{ij}^{yz} &= d_{ij}^X \cos\theta \cos\varphi - d_{ij}^Y \cos\theta \sin\varphi + d_{ij}^Z \sin\theta. \end{aligned} \tag{A3}$$

We define $g_m \equiv [G_m^{\mathrm{DM}}, M_+]$; each g_m is given as

$$\begin{aligned} g_0 &= -g\mu_{\mathrm{B}} \sum_{i>j} \lambda_{ij}^{xy} (S_i^+ S_j^z - S_i^z S_j^+) \\ g_1 &= 0 \\ g_{-1} &= \tfrac{1}{2} g \mu_{\mathrm{B}} \sum_{i>j} (\lambda_{ij}^{xz} + \mathrm{i}\lambda_{ij}^{yz})(S_i^- S_j^+ - S_i^+ S_j^-). \end{aligned} \tag{A4}$$

The second moment $M_2^{\mathrm{DM}}(J/kT)$ is

$$M_2^{\mathrm{DM}}(J/kT) = \frac{\Sigma_m \langle g_m g_m^\dagger \rangle}{\hbar^2 \langle M_+ M_- \rangle}.$$

Thus, $M_2^{\mathrm{DM}}(J/kT) \propto \langle (S_i^\alpha S_j^\beta - S_i^\beta S_j^\alpha)^2 \rangle$.

In the same way,

$$M_2^{\mathrm{AE}}(J/kT) \qquad \text{or} \qquad M_2^{\mathrm{DD}}(J/kT) \propto \langle (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)^2 \rangle$$

is derived.

Appendix 2

When each spin is at a centre of inversion, $\lambda_{ij} = -\lambda_{ik}$ because there are sites j and k which satisfy $r_{ij} = -r_{ik}$. After Fourier transformation, the secular part of the DM interaction yields

$$\langle g_0 g_0^\dagger \rangle = \sum_q |\lambda_q^{xy}|^2 \langle (S_q^+ S_{-q}^z - S_q^z S_{-q}^+)^2 \rangle$$

where $\lambda_q^{xy} = \Sigma_j \lambda_{ij}^{xy} \exp(\mathrm{i}qr_{ij})$.

When we consider spins on the c-axis,

$$\lambda_q^{xy} = \lambda_{ij}^{xy} \exp(iqr_{ij}) + \lambda_{ik}^{xy} \exp(iqr_{ik}) + \ldots$$
$$= \lambda_{ij}^{xy} \exp(iqr_{ij}) - \lambda_{ij}^{xy} \exp(-iqr_{ij}) + \ldots$$
$$\simeq \sin qc + \sin 2qc + \ldots.$$

Then λ_q^{xy} becomes zero for $q = 0$. Since the diffusional relaxation enhances the $q \simeq 0$ components of the secular part, $\lambda_q^{xy} \to 0$ with $q \to 0$ means that $\langle g_0 g_0^\dagger \rangle$ vanishes with $q \to 0$. Thus we cannot expect an enhancement of the secular part of the DM interaction.

Acknowledgments

This work was partly supported by a grant-in-aid for scientific research from the Japanese Ministry of Education, Science and Culture.

References

Bonner J C and Fisher M E 1964 *Phys. Rev.* **135** A640
Cheung T T P, Soos Z G, Dietz R E and Merritt F R 1978 *Phys. Rev.* B **17** 1266
Hirakawa K 1988 private communication
Hirakawa K and Kadota S 1967 *J. Phys. Soc. Japan* **23** 756
Hutchings M T, Ikeda H and Milne J M 1979 *J. Phys. C: Solid State Phys.* **12** L739
Hutchings M T, Samuelsen E J, Shirane G and Hirakawa K 1969 *Phys. Rev.* **188** 919
Iio K, Hyodo H, Nagata K and Yamada I 1978 *J. Phys. Soc. Japan* **44** 1393
Ikebe M and Date M 1971 *J. Phys. Soc. Japan* **30** 93
Ikeda H and Hirakawa K 1973 *J. Phys. Soc. Japan* **35** 722
Kadota S, Yamada I, Yoneyama S and Hirakawa K 1967 *J. Phys. Soc. Japan* **23** 751
Khomskii D I and Kugel K I 1973 *Solid State Commun.* **13** 763
Kubo R and Tomita K 1954 *J. Phys. Soc. Japan* **9** 91
Moriya T 1960 *Phys. Rev.* **120** 91
Okazaki A 1969 *J. Phys. Soc. Japan* **26** 870
Okazaki A and Suemune Y 1961 *J. Phys. Soc. Japan* **16** 176, 671
Okazaki A and Tsukuda N 1969 *J. Phys. Soc. Japan* **27** 267
Richards P M and Salamon M B 1974 *Phys. Rev.* B **9** 32
Satija S K, Axe J D, Shirane G, Yoshizawa H and Hirakawa K 1980 *Phys. Rev.* B **21** 2001
Singer L S, Smith W H and Wagoner G 1961 *Rev. Sci. Instrum.* **32** 213
Soos Z G, Cheung T T P and McGregor K T 1977b *Chem. Phys. Lett.* **46** 600
Soos Z G, McGregor K T, Cheung T T P and Silverstein A J 1977a *Phys. Rev.* B **16** 3036
Tsukuda N and Okazaki A 1972 *J. Phys. Soc. Japan* **33** 1088
Tuchendler J, Magarino J and Renard J P 1979 *Phys. Rev.* B **20** 2637
Yamada I, Morishita I and Tokuyama T 1983 *Physica* **115B** 179
Yokozawa Y, Tanimoto M and Takano H 1978 *J. Phys. Soc. Japan* **45** 67