Resonance fields of the electron paramagnetic resonance lines in KCuF: the effect of the Dzyaloshinsky-Moriya exchange interaction and the inequivalent g-tensors

1990 J. Phys.: Condens. Matter 2 5771

(http://iopscience.iop.org/0953-8984/2/26/014)

J. Phys.: Condens. Matter 2 (1990) 5771–5776. Printed in the UK

Resonance fields of the electron paramagnetic resonance lines in $KCuF_3$: the effect of the Dzyaloshinsky–Moriya exchange interaction and the inequivalent g-tensors

T Ishii and I Yamada

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

Received 1 February 1990

Abstract. We report that the electron paramagnetic resonance field H_{res} measured at a fixed microwave frequency in $KCuF_3$, a compound having one-dimensional Heisenberg antiferromagnetic properties in spite of its pseudocubic crystal structure, is temperature independent for the external field $\boldsymbol{H}$ parallel to the chain axis, while H_{res} for $\boldsymbol{H}$ perpendicular to the chain axis shows a very weak decreasing tendency with decreasing temperature to $T_N = 39$ K over the wide region of short-range order. Considering the recent discovery that this compound has a Dzyaloshinsky–Moriya (DM) antisymmetric exchange interaction which overwhelms other perturbation terms such as the dipolar and the anisotropic exchange interactions, we suggest that H_{res} is governed by the DM interaction; the alternate change in the direction of the DM vectors and also the antisymmetric spin-correlation functions $\langle S_n^\alpha S_{n+1}^\beta - S_n^\beta S_{n+1}^\alpha \rangle$ with $\alpha \neq \beta$ ($\alpha, \beta = x, y, z$) result in the temperature independence of H_{res}. We also point out that the two inequivalent **g**-tensors in this compound can be the origin of the very weak decreasing tendency of H_{res} observed for $\boldsymbol{H}$ perpendicular to the chain axis.

1. Introduction

The resonance field H_{res} of electron paramagnetic resonance (EPR) lines in conventional one-dimensional Heisenberg antiferromagnets (1DHAFs) shows a characteristic temperature dependence. That is, with decreasing temperature to T_N, H_{res} measured at a fixed microwave frequency for the external field $\boldsymbol{H}$ parallel to the chain axis, denoted $H_{res}^{\parallel}$, decreases, while that for $\boldsymbol{H}$ perpendicular to the chain axis, denoted $H_{res}^{\perp}$, increases and these two fields obey the relation $[H_{res}^{\parallel}(H_{res}^{\perp})^2]^{1/3} =$ constant. These phenomena were pointed out theoretically by Nagata and Tazuke [1] for a 1DHAF with the dipolar interaction as a perturbation term. They used Fisher's [2] classical spin model in an equation for the resonance frequency that is justified in a spin-wave region and derived a formula for the shift of the resonance frequency with decreasing temperature over the short-range order region; the formula explained well the experimental results observed for a representative 1DHAF such as TMMC and $CsMnCl_3 \cdot 2H_2O$ [1]. In their calculation, the quantum axis is always assumed to be parallel to the external field, i.e. the magnitude of the external field is larger than the anisotropy field.

On the other hand, Okamoto and Karasudani [3] and Karasudani and Okamoto [4] discussed the temperature dependence of the resonance frequency of a 1DHAF based on Mori's [5] theory of generalised Brownian motions and showed a more general formula

that can be applicable for a 1DHAF having an anisotropy field larger than the external field. When the formula given in [3, 4] is expanded in powers of the anisotropy field, the lowest-order term results in the expression given in [1]. Even when we take account of the higher-order terms, i.e. the condition that the external field is larger than the anisotropy field is relaxed, the substantial qualitative feature brought about by the lowest-order term is maintained.

As the theories [1, 3, 4] indicate, other symmetric perturbation terms such as the anisotropic exchange interaction and the single-ion anisotropy also cause a shift of H_{res} over the short-range order region similar to the dipolar interaction. Then the question arises of how H_{res} will behave with temperature over the region of short-range order in a 1DHAF when an antisymmetric interaction is the main perturbation term.

On the basis of the measurement of the EPR linewidth, we have recently reported that $KCuF_3$ with an (a)-type structure, a 1DHAF in spite of its pseudoperovskite crystal structure, has a Dzyaloshinsky–Moriya (DM) antisymmetric exchange interaction $\Sigma_n(-1)^n \boldsymbol{d}_{n,n+1} \cdot (\boldsymbol{S}_n \times \boldsymbol{S}_{n+1})$ between nearest-neighbour spins on the c axis (the chain axis) which dominates other perturbation terms such as the dipolar and anisotropic exchange interactions and governs the linewidth [6]. That is, the EPR linewidth at high temperatures shows a $(2 + \sin^2\theta)$-like angular behaviour (where θ is the angle between the c axis and $\boldsymbol{H}$) which coincides well with the linewidth theory owing to the DM perturbation term with $\boldsymbol{d}_{n,n+1} \perp \boldsymbol{c}$. We have pointed out that from its crystal symmetry the DM vector $\boldsymbol{d}_{n,n+1}$ changes its direction alternately, i.e. $\boldsymbol{d}_{n-1,n} = -\boldsymbol{d}_{n,n+1}$. Further the linewidth shows a gradual decrease with decreasing temperature to $T_N = 39$ K, reflecting the effect of antisymmetric correlation functions $\langle (S_n^\alpha S_{n+1}^\beta - S_n^\beta S_{n+1}^\alpha)^2 \rangle$ with $\alpha \neq \beta$ $(\alpha, \beta = x, y, z)$ which arise from the DM interaction as suggested theoretically by Soos *et al* [7].

The compound $KCuF_3$ with an (a)-type structure has one more factor that should be taken into account when we consider the temperature dependence of H_{res}, i.e. two inequivalent **g**-tensors. Owing to the cooperative Jahn–Teller effect, each F^- octahedron surrounding a Cu^{2+} ion is elongated along one of the principal axes in the c plane and the elongated axes are orthogonal to each other along the c axis. There then arises two inequivalent sites of Cu^{2+}, each accompanying a **g**-tensor different from each other as shown in figure 1. Such different **g**-tensors can be one of the origins of the shift of H_{res} as pointed out theoretically [8].

To investigate the effects of the DM interaction and the inequivalent **g**-tensors on the resonance frequency in $KCuF_3$, we have measured resonance fields at a fixed microwave frequency as a function of temperature. We shall show our experimental results in the next section and discuss it following the theories developed in [1, 8].

2. Experimental results and discussion

The sample employed in the present experiment was the same as used in the previous study [8]. That is, the sample has the (a)-type structure and hence the Cu^{2+} ions are located at two inequivalent sites. As is well known, this compound has a strong exchange interaction between the nearest-neighbour spins on the c axis owing to the orbital ordering of 3d holes. We thus carried out experiments for $\boldsymbol{H} \parallel \boldsymbol{c}$ and $\boldsymbol{H} \perp \boldsymbol{c}$.

Since the linewidth at high temperatures is broadened to 4 kOe, we used a K-band spectrometer rather than an X-band spectrometer to determine the resonance field more precisely. Owing to its strong exchange interaction $(J/k_B = -200$ K) between the

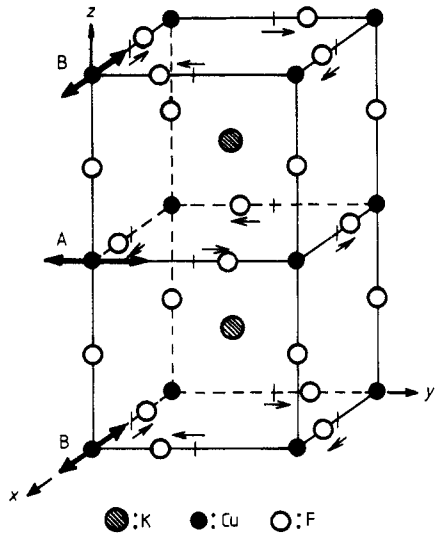

Figure 1. Crystal structure of (a)-type $KCuF_3$. The thin arrows indicate the direction of the shift of F sites from the centre between the adjacent Cu sites, while the bold arrows show elongated axes of F^- octahedra, the axes along which $g_\parallel$ is defined. Inequivalent Cu sites are indicated as A and B.

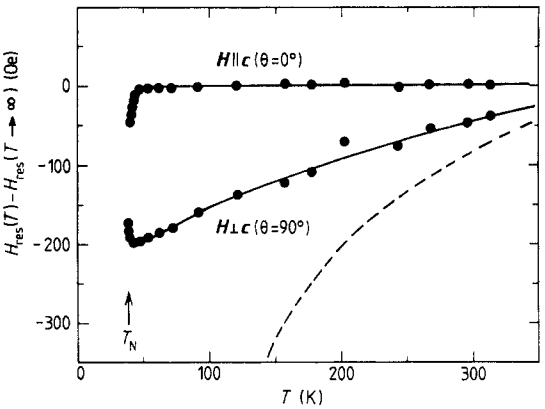

Figure 2. Temperature behaviour of the shift of resonance field $H_{res} - H_{res}$ $(T \to \infty)$ observed in $KCuF_3$ at 24.46 GHz. The broken curve is a calculation of the shift for $\boldsymbol{H} \perp \boldsymbol{c}$ caused by the inequivalent **g**-tensors, indicating a shift to lower values which is qualitatively consistent with the experiment. For $\boldsymbol{H} \| \boldsymbol{c}$ the inequivalent **g**-tensors are independent of the shift of resonance field as explained in the text. The abrupt change in the shift in the vicinity of $T_N = 39$ K indicates the development of three-dimensional long-range order. The full curves are simply to guide the eye.

nearest-neighbour spins on the c axis, the magnetic short-range order develops over a tremendously wide range of temperatures including even room temperature. The dependence of the shift of resonance field on temperature observed at 24.46 GHz is shown in figure 2 for $\theta = 0°$ and 90° where θ is the angle between the c axis and the external field $\boldsymbol{H}$. As can be seen in this figure, we find that the shift for $\theta = 0°$ is almost temperature independent, while that for $\theta = 90°$ shows a very weak decreasing tendency with decreasing temperature. These results are completely different from the theoretical prediction [1, 3] and the experimental results in several 1DHAFs introduced in section 1. As explained in the previous paper [6], the DM interaction dominates the dipolar and anisotropic exchange interactions, and hence the linewidth is governed by the DM interaction. A temperature dependence of the resonance field, if it exists, also arises from the spin-correlation functions coming from the perturbation terms. To interpret the present results, we employ the simple theory established earlier [1].

We now take the coordinates $[x, y, z]$ with $z \| c$ and the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_Z + \mathcal{H}' \tag{1}$$

where the terms are given by

$$\mathcal{H}_{ex} = -2J \sum_n \boldsymbol{S}_n \cdot \boldsymbol{S}_{n+1} \tag{2}$$

$$\mathcal{H}_Z = -\mu_B \sum_n \mathbf{g} \cdot \boldsymbol{S}_n \cdot \boldsymbol{H} \tag{3}$$

$$\mathcal{H}' = \sum_n (-1)^n \boldsymbol{d}_{n,n+1} \cdot (\boldsymbol{S}_n \times \boldsymbol{S}_{n+1}). \tag{4}$$

When the microwave frequency is larger than that corresponding to the perturbation term, the resonance frequency ω is given [1] as

$$\hbar\omega = \langle [S^-, [S^+, \mathcal{H}]] \rangle / 2\langle S^z \rangle \tag{5}$$

where $S^{\pm}$ are the transverse components of the total spin $\boldsymbol{S} = \Sigma_n \boldsymbol{S}_n$. Since $[S^+, \mathcal{H}_{ex}] = 0$ and the $\mathcal{H}_Z$ part in equation (5) results in $\mathbf{g}\mu_B \boldsymbol{H}$, the temperature-dependent part of $\hbar\omega$, given by $\hbar\,\Delta\omega(T)$, arises from the $\mathcal{H}'$ part in equation (5). When $\boldsymbol{d}_{n,n+1} \| x$, we obtain

$$\hbar\,\Delta\omega_{\parallel}(T) = \frac{1}{2\langle S^z \rangle} \sum_n (-1)^n d^x_{n,n+1} \langle (S^y_n S^z_{n+1} - S^z_n S^y_{n+1}) - \mathrm{i}(S^z_n S^x_{n+1} - S^x_n S^z_{n+1}) \rangle_{H \| z} \tag{6}$$

and

$$\hbar\,\Delta\omega_{\perp}(T) = -\frac{1}{\langle S^x \rangle} \sum_n (-1)^n d^x_{n,n+1} \langle (S^y_n S^z_{n+1} - S^z_n S^y_{n+1}) \rangle_{H \| x}. \tag{7}$$

Similar results are obtained for $\boldsymbol{d}_{n,n+1} \| y$ with $\boldsymbol{H} \| x$. The alternate change in the direction of $\boldsymbol{d}_{n,n+1}$, i.e. $\boldsymbol{d}_{n-1,n} = -\boldsymbol{d}_{n,n+1}$, results in $\Sigma_n (-1)^n d^x_{n,n+1} \langle \ldots \rangle = 0$ in equations (6) and (7). Even if $\boldsymbol{d}_{n-1,n} = \boldsymbol{d}_{n,n+1}$, the average $\langle S^\alpha_n S^\beta_{n+1} - S^\beta_n S^\alpha_{n+1} \rangle$ with $\alpha \neq \beta$ ($\alpha, \beta = x, y, z$) is zero for the Hamiltonian $\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_Z$, contrary to the symmetric correlation function such as $\langle S^\alpha_n S^\alpha_{n+1} - S^\beta_n S^\beta_{n+1} \rangle$ which is produced when $\mathcal{H}'$ consists of symmetric terms. As a result, we can say that the DM perturbation term does not produce a change in the resonance frequency with temperature.

We next discuss the effect of the inequivalent **g**-tensors. Let us denote the two inequivalent sites as A and B, and hence the total spin at each site as $\boldsymbol{S}_A$ and $\boldsymbol{S}_B$, while the **g**-tensors are $\mathbf{g}_A$ and $\mathbf{g}_B$. The Hamiltonian for such a spin system is expressed as $\mathcal{H} = \mathcal{H}_{ex} - \mu_B \boldsymbol{H} \cdot (\mathbf{g}_A \boldsymbol{S}_A + \mathbf{g}_B \boldsymbol{S}_B)$. For this Hamiltonian, equation (5) gives the resonance frequency as

$$\hbar\omega(T) = \mu_B \mathbf{g} \boldsymbol{H} [1 + (\Delta\mathbf{g}\boldsymbol{H}/\mathbf{g}\boldsymbol{H})^2 (\langle s^z s^z \rangle / \langle S^z S^z \rangle)] \tag{8}$$

where S^z and s^z are the z components of $\boldsymbol{S} = \boldsymbol{S}_A + \boldsymbol{S}_B$ and $\boldsymbol{s} = \boldsymbol{S}_A - \boldsymbol{S}_B$, respectively, while $\Delta\mathbf{g} = (\mathbf{g}_A - \mathbf{g}_B)/2$ and $\mathbf{g} = (\mathbf{g}_A + \mathbf{g}_B)/2$ [8]. Since the thermal average $\langle S^z S^z \rangle$ decreases, while $\langle s^z s^z \rangle$ increases with decreasing temperature for the antiferromagnetic coupling between the nearest-neighbour spins located at the inequivalent sites, the resonance frequency increases with decreasing temperature. For the classical model of spins, the ratio of these correlation functions for zero field is given as

$$\langle s^z s^z \rangle / \langle S^z S^z \rangle = [(1 - u)/(1 + u)]^2 \tag{9}$$

where $u(x) = x - \coth(1/x)$ and $x = (k_B T/2)|J|S(S+1)$. At a fixed microwave frequency, H_{res} for both $\boldsymbol{H}$ parallel to the chain axis and $\boldsymbol{H}$ perpendicular to the chain axis decrease with decreasing temperature to T_N when $\Delta\mathbf{g}\,\boldsymbol{H}$ is not zero. The classical model is inadequate for $S = \frac{1}{2}$ as in the present case, but we think that the qualitative behaviour expected for $S = \frac{1}{2}$ should be similar to that obtained for the classical model. Indeed, several compounds with $S = \frac{1}{2}$ such as $Cu(C_6H_5COO)_2 \cdot 3H_2O$ and $Cu(NH_3)_4SO_4 \cdot H_2O$ have been found to show a decreasing tendency of H_{res} regardless of the direction of the external field with respect to the chain axis [9], indicating qualitative agreement with the theory.

We now apply equations (8) and (9) to $KCuF_3$. The **g**-tensors in this compound are given in $[x, y, z]$ coordinates as

$$\mathbf{g}_A = \begin{pmatrix} g_\perp & & \\ & g_\parallel & \\ & & g_\perp \end{pmatrix} \qquad \mathbf{g}_B = \begin{pmatrix} g_\parallel & & \\ & g_\perp & \\ & & g_\perp \end{pmatrix} \tag{10}$$

where $g_\parallel$ and $g_\perp$ are the g-values parallel and perpendicular to the elongated axis of the F^- octahedron and they were determined as $g_\parallel = 2.39$ and $g_\perp = 2.15$ from the experimental values $g_a = 2.27$ and $g_c = 2.15$ which have the relations $g_a = (g_\parallel + g_\perp)/2$ and $g_c = g_\perp$† [6]. We thus obtain

$$\Delta\mathbf{g} = \tfrac{1}{2}\begin{pmatrix} g_\perp - g_\parallel & & \\ & g_\parallel - g_\perp & \\ & & 0 \end{pmatrix} \qquad \mathbf{g} = \tfrac{1}{2}\begin{pmatrix} g_\parallel + g_\perp & & \\ & g_\parallel + g_\perp & \\ & & 2g_\perp \end{pmatrix}. \tag{11}$$

When $\boldsymbol{H} \| z$, i.e. $\boldsymbol{H} = (0, 0, H)$, we have $\Delta\mathbf{g}\,\boldsymbol{H} = 0$ and hence, from equation (8), $\hbar\omega(T) = \mu_B \mathbf{g} \boldsymbol{H}$ so that the resonance frequency is equal to the Zeeman frequency, independent of temperature. However, for $\boldsymbol{H} \perp z$, the expression for $\hbar\omega(T)$ is

$$\hbar\omega(T) = \tfrac{1}{2}(g_\perp + g_\parallel)\mu_B H + \tfrac{1}{2}(g_\perp + g_\parallel) \times \mu_B H[(g_\perp - g_\parallel)/(g_\parallel + g_\perp)]^2(\langle s^z s^z\rangle/\langle S^z S^z\rangle) \qquad \text{for } \boldsymbol{H} \perp z. \tag{12}$$

The second term in equation (12) causes a shift of ω to higher values, i.e. a downward shift of H_{res} at a fixed microwave frequency. It follows as a consequence that the inequivalent **g**-tensors in $KCuF_3$ have no effect for $\boldsymbol{H} \| \boldsymbol{c}$ because $\Delta\mathbf{g}\,\boldsymbol{H} = 0$, while they cause the shift to decrease as the temperature falls for $\boldsymbol{H} \perp \boldsymbol{c}$. Using equations (9) and (12) with the parameters $S = \frac{1}{2}$ and $J/k_B = -200$ K for $KCuF_3$ and $\omega = 24.46$ GHz, we have calculated the shift for $\theta = 90°$, the result of which is shown in figure 2. Of course, we cannot expect quantitative agreement between the present experimental results and the calculation based on the classical model, but we think that the decreasing tendency of the shift for $\theta = 90°$ observed in the present compound surely reflects the effect of the inequivalent **g**-tensors.

In conclusion, we can explain the temperature behaviour of the resonance field observed in $KCuF_3$ well by taking account of the DM interaction and the inequivalent **g**-tensors. That is, the DM interaction does not contribute to the shift of resonance field, while the inequivalent **g**-tensors can be the origin of a very weak downward shift of $\boldsymbol{H}_{res}$ for $\boldsymbol{H} \perp \boldsymbol{c}$.

Acknowledgment

We are grateful to Professor H Okamoto at Kyushu University for his kind and valuable advice.

References

[1] Nagata K and Tazake Y 1972 *J. Phys. Soc. Japan* **32** 337
[2] Fisher M E 1964 *Am. J. Phys.* **32** 343

† The expression $g_c = g_\parallel = 2.15$ given on p 3404 of [6] should be corrected to $g_c = g_\perp = 2.15$.

[3] Okamoto H and Karasudani T 1977 *J. Phys. Soc. Japan* **42** 717
[4] Karasudani T and Okamoto H 1977 *J. Phys. Soc. Japan* **43** 1131
[5] Mori H 1965 *Progr. Theor. Phys.* **33** 423
[6] Yamada I, Fujii H and Hidaka M 1989 *J. Phys.: Condens. Matter* **1** 3397
[7] Soos Z G, Mcgregor K T, Cheung T T P and Silverstein A J 1977 *Phys. Rev.* B **16** 3036
[8] Nagata K 1976 *J. Phys. Soc. Japan* **40** 1209
[9] Oshima K, Okuda K and Date M 1976 *J. Phys. Soc. Japan* **41** 475