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Electron paramagnetic resonance governed by the Dzyaloshinsky–Moriya antisymmetric exchange interaction in CuGeO_3

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Abstract. Several reports of electron paramagnetic resonance experiments performed on the spin–Peierls compound CuGeO_3 have appeared so far, but none of them have precisely explained the origin of the line broadening and the temperature dependence of both the linewidth and the resonance field, all of which differ from those of conventional one-dimensional Heisenberg antiferromagnets in which the dipolar or anisotropic exchange interaction brings about line broadening. In the present report, it is clarified that the antisymmetric exchange interaction, $\sum_i \mathbf{d}_{i+1} \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1})$ with $\mathbf{d}_{i+1} \perp c$ -axis (magnetic chain), between nearest-neighbour Cu spins on the c -axis governs all factors which characterize the EPR line of CuGeO_3 , i.e., the value and the angular dependence of the linewidth at high temperatures where the short-range order is completely absent, the temperature dependence of the linewidth, and the resonance field, as well as the high-temperature lineshape. The present conclusion indicates that the crystal symmetry of this compound is lower than that given by the space group $Pbmm$ which was reported by Völlenkle *et al* in 1967, because the symmetry $Pbmm$ does not allow the antisymmetric exchange interaction mentioned above.

1. Introduction

The spin–Peierls compound CuGeO_3 has recently attracted much attention. This compound was found to form linear Heisenberg antiferromagnetic chains along the c -axis, and to turn into the spin–Peierls state below $T_{\text{sp}} = 14$ K [1]. Many studies on this compound have been reported so far. Among them, several electron paramagnetic resonance (EPR) investigations are included [2–6]. The experimental results given in them are summarized as follows. The linewidth ΔH which reaches approximately 1–2 kOe at room temperature decreases very rapidly with decreasing temperature, but it does not increase over the short-range ordering region. In contrast to ΔH versus temperature T , the resonance field H_{res} does not change with T above T_{sp} . Although these results are common to all reports except one [3], precise explanations for the respective results were not given.

The EPR experimental results summarized above are not similar to those of conventional one-dimensional Heisenberg antiferromagnets (1DHAF) such as TMMC [7–9] and $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$ [9–11]; the characteristics of the EPR line of these well investigated 1DHAFs are summarized as follows.

- (i) The lineshape at high T departs from the Lorentzian shape; high T means the temperature region where the short-range order is completely absent.
- (ii) The angular dependence of ΔH at high T obeys a relation such as $(3 \cos^2 \theta - 1)^{4/3}$, where θ is an angle between the chain axis and an external field.
- (iii) Over the short-range ordering region, ΔH increases with decreasing T .
- (iv) Over the short-range ordering region, H_{res} for external fields parallel and perpendicular to the chain axis shift from those observed at high T to directions opposite to each other.

Phenomena (i) and (ii) are due to the long-time diffusive relaxation process [7]. That is, only long-wavelength ($\mathbf{q} \sim \mathbf{0}$) spin fluctuations survive over the $\tau^{-1/2}$ part of the relaxation process. As a result, contribution from the $\mathbf{q} \sim \mathbf{0}$ components of the secular parts of the perturbation terms to line broadening is enhanced, which brings about the $(3 \cos^2 \theta - 1)^{4/3}$ -like angular change in the linewidth, as well as a non-Lorentzian lineshape. When T is decreased, the $|\mathbf{q}| \sim \pi/a$ spin fluctuations take the place of $\mathbf{q} \sim \mathbf{0}$ over the short-range ordering region (where a is the spin–spin distance in the chain), which then causes the phenomenon (iii). The crossover from $\mathbf{q} \sim \mathbf{0}$ to $|\mathbf{q}| \sim \pi/a$ appears in $\Delta H(T)$ more clearly in 1DHAFs with Cu^{2+} compounds such as $\text{CuCl}_2 \cdot 2\text{NC}_5\text{H}_5$ [12] and $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$ [13] than in the Mn^{2+} compounds introduced above. That is, $\Delta H(T)$ in the Cu^{2+} compounds first decreases gradually with decreasing T and then begins to increase rapidly over the short-range ordering region, while $\Delta H(T)$ in the Mn^{2+} compounds is first almost constant and begins to increase with decreasing T . Furthermore, the increase of the two-spin correlations over the short-range ordering region affects H_{res} , which results in (iv), as was proven in [9].

Considering that ΔH and H_{res} of the EPR line depend on the perturbation terms, one must remember that the phenomena given by (i)–(iv) are due to spin-symmetric perturbation terms such as the dipole–dipole (DD) and the anisotropic exchange (AE) interactions, i.e., the perturbation terms in which the coefficients of two-spin interactions are not related to exchanging relevant spins with each other.

When the perturbation consists of a spin-antisymmetric interaction such as the Dzyaloshinsky–Moriya (DM) exchange interaction, the dependence of ΔH and H_{res} on T is quite different from that of spin-symmetric ones, as will be explained later. Therefore, one must first clarify what kinds of perturbation are the leading term for the line broadening in an analysis of EPR data. The EPR studies [2–6] on CuGeO_3 mentioned above did not address this indispensable process.

In the present study, attention is solely given to the paramagnetic region, and it is made clear from our EPR data that the DM interaction $\sum_i \mathbf{d}_{i+1} \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1})$ between nearest-neighbour Cu spins on the c -axis governs the EPR absorption line of CuGeO_3 . That is, $\Delta H(T)$ and $H_{\text{res}}(T)$, as well as the value of ΔH and the lineshape at high T , are well explained when the DM interaction is considered as a main perturbation term. From the analysis of the angular dependence of ΔH at high T , the direction of \mathbf{d}_{i+1} is determined to be perpendicular to the c -axis. Based on the fact that CuGeO_3 should have DM interaction between the spins along the c -axis, it is concluded that the crystal symmetry of this compound proposed by Völlenkle *et al* [14] about three decades ago that has been accepted so far is not correct, because this symmetry has an inversion centre at the midpoint between nearest-neighbour Cu^{2+} sites on the c -axis, which does not allow the DM interaction.

The outline of this paper is as follows. The experimental results and theoretical background which is necessary to analyse them are given in sections 2 and 3, successively.

Analysis and discussion are developed in section 4. In section 5, it is pointed out that the crystal symmetry of this compound must be lower than that given in [14].

2. Experimental results

EPR measurements for single crystals of CuGeO_3 were made using a 100 kHz field-modulated K-band spectrometer operated at 24.48 GHz. For the measurements below room temperature, a resonance cavity was inserted in a liquid-He cryostat. Above room temperature, a water-cooled cavity was employed, using a platinum-strip-coated quartz tube inserted in the cavity as a resistive heater. Each cavity had a sample rotation mechanism around a vertical axis, and T was electronically controlled. Resonance absorption was recorded as a derivative line.

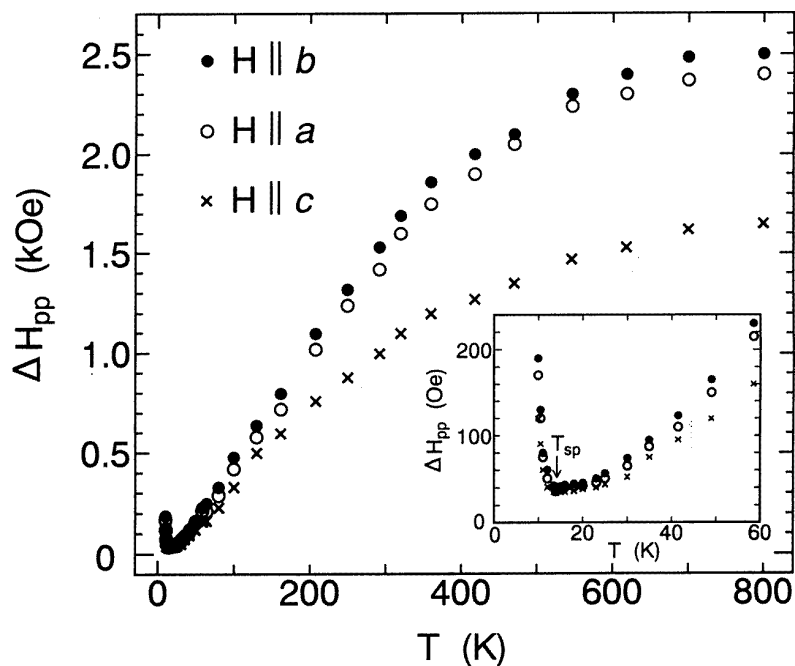


Figure 1. The dependence of derivative peak-to-peak linewidth on temperature observed at 24.48 GHz for $\mathbf{H} \parallel a$ -, b -, and c -axes. The lower-temperature part is enlarged in the inset, where the extrapolation of $\Delta H(T)$ from the paramagnetic region seems to go down to zero with $T \rightarrow 0$.

Figure 1 shows the T dependence of the derivative peak-to-peak linewidth ΔH_{pp}^a , ΔH_{pp}^b , and ΔH_{pp}^c obtained for an external field \mathbf{H} applied along the a -, b -, and c -axis, respectively. As can be seen in this figure, they nearly saturate above approximately 600 K, which indicate that the theory for high T developed in subsection 3.1 below can be applied to the data obtained above this temperature. Furthermore, one finds the relation $\Delta H_{pp}^c < \Delta H_{pp}^a \simeq \Delta H_{pp}^b$. The angular dependence of ΔH_{pp} observed on rotating the direction of \mathbf{H} in the bc - and ac -planes is shown in figure 2.

From the results shown in figures 1 and 2, several striking features can be pointed out. First, the values of ΔH_{pp} at high T for all directions of \mathbf{H} are extremely large, in spite of

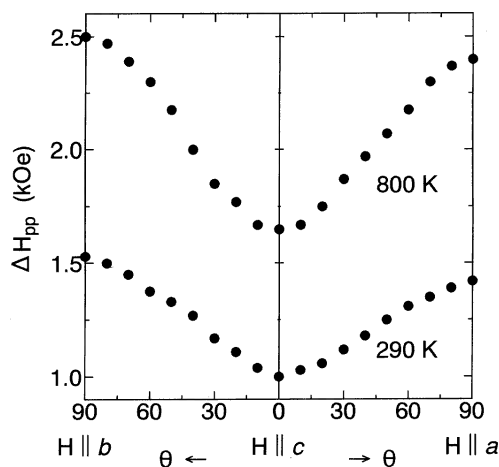


Figure 2. The angular dependence of linewidth at 800 K where the theory for high T developed in subsection 3.1 can be applied, as well as that observed at 290 K. For both temperatures, the ratio $\Delta H_{pp}^b/\Delta H_{pp}^c \simeq \Delta H_{pp}^a/\Delta H_{pp}^c \simeq 1.5$ is found.

the fact that the absorption line is strongly exchange narrowed. Second, $\Delta H_{pp}^c < \Delta H_{pp}^a$ or (ΔH_{pp}^b), i.e., ΔH_{pp} for \mathbf{H} applied along the chain axis is narrower than that for \mathbf{H} applied perpendicular to the chain axis, and it seems as if $\Delta H_{pp}(\theta) \propto (2 + \sin^2 \theta)$ for the direction of \mathbf{H} rotated in both the ac - and bc -planes. This angular dependence is in contrast to that of conventional 1DHAFs in which the DD and AE interactions are the main origin of line broadening. Third, $\Delta H_{pp}(T)$ for all directions of \mathbf{H} decreases monotonically with decreasing T , and does not show any increase over the short-range ordering region.

To examine the lineshape at high T , the derivative absorption line for $\mathbf{H} \parallel c$ -axis is analysed. The result for the line observed at 495 K which is high enough for the analysis is shown in figure 3. The figure with an ordinate and an abscissa given as figure 3 is convenient, because a Lorentzian lineshape is reproduced as a straight line, as first introduced in [7]. The experimental data plotted in figure 3 coincide well with the straight line that is derived from the Lorentzian. Thus, the observed lineshape is defined to be a Lorentzian. For reference, the lineshape which arises from the spin-diffusion process is also given in figure 3.

Finally, the T dependence of the resonance field, H_{res} , is shown in figure 4. In the figure, the values of $H_{res} - H_{DPPH}$ are plotted as a function of T , where H_{DPPH} is the field that corresponds to $g = 2.00$. One finds that the distribution of $H_{res} - H_{DPPH}$ is within ± 10 Oe for $T > T_{sp}$, which indicates that H_{res} is not related to the change of T . This result is also different from that of conventional 1DHAFs with spin-symmetric perturbations, as will be clarified in subsection 3.4.

3. Theoretical background

Several years ago, one of the present authors (IY) and coworkers [15, 16] clarified that all factors of the EPR line observed in $KCuF_3$, which is known as one of the representative 1DHAFs, are wholly due to the DM interaction. However, the analysis given in [15] is insufficient. Therefore, a theory for the EPR line governed by the DM interaction is developed here.

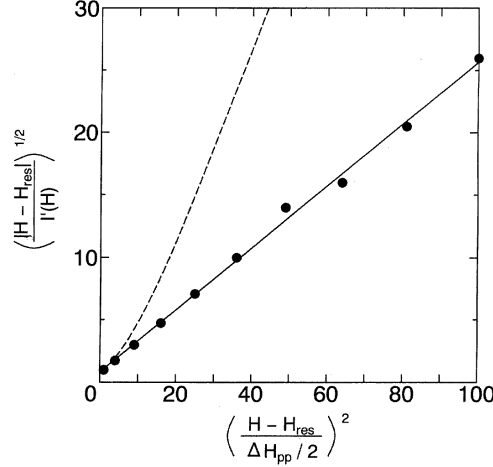


Figure 3. The lineshape observed at 495 K. The solid straight line corresponds to a Lorentzian, while the dotted line is derived from the Fourier transform of $\exp(-t^{3/2})$, which indicates a lineshape due to the spin-diffusion process. The factor $I'(H)$ is the height of the derivative line.

3.1. The linewidth at the high-temperature limit ($T \rightarrow \infty$)

In this subsection, formulae which are necessary to analyse the linewidth as well as its angular dependence at high T are derived. An EPR line of an exchange-coupled magnetic system can be analysed using the Kubo–Tomita theory [17]. In the following, the Hamiltonian defined as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad (1)$$

is used, where the main term \mathcal{H}_0 consists of the isotropic exchange between spins on the chain along the c -axis and Zeeman interactions, which is expressed as

$$\mathcal{H}_0 = \mathcal{H}_{\text{ex}} + \mathcal{H}_Z = -2J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} - \mu_B \sum_i \mathbf{S}_i \cdot \mathbf{g} \cdot \mathbf{H} \quad (2)$$

where \mathbf{g} is a g -tensor. The perturbation \mathcal{H}' contains all other terms that cause the line broadening such as the DD, AE, and DM interactions.

At the beginning of the analysis, the DM interaction will be clarified as being a leading perturbation in CuGeO_3 . Since $S = 1/2$ in this compound, a single-ion anisotropy is completely absent. The hyperfine interaction also contributes to the line broadening, but its effect is negligible. Thus, the DD and AE interactions, as well as the DM interaction, are candidates for line broadening, i.e.,

$$\mathcal{H}' = \mathcal{H}'_{\text{DD}} + \mathcal{H}'_{\text{AE}} + \mathcal{H}'_{\text{DM}}. \quad (3)$$

In the present compound, the intrachain Cu–Cu distance is fairly short as compared with those of the interchain ones. Thus, it is enough to count only the spins on the c -axis for \mathcal{H}'_{DD} . Furthermore, both \mathcal{H}'_{AE} and \mathcal{H}'_{DM} arise from the intrachain exchange interaction, because interchain exchange interactions are extremely weak. Explicit values of the lattice parameters, as well as the intrachain and interchain exchange interactions, will be given in section 4.

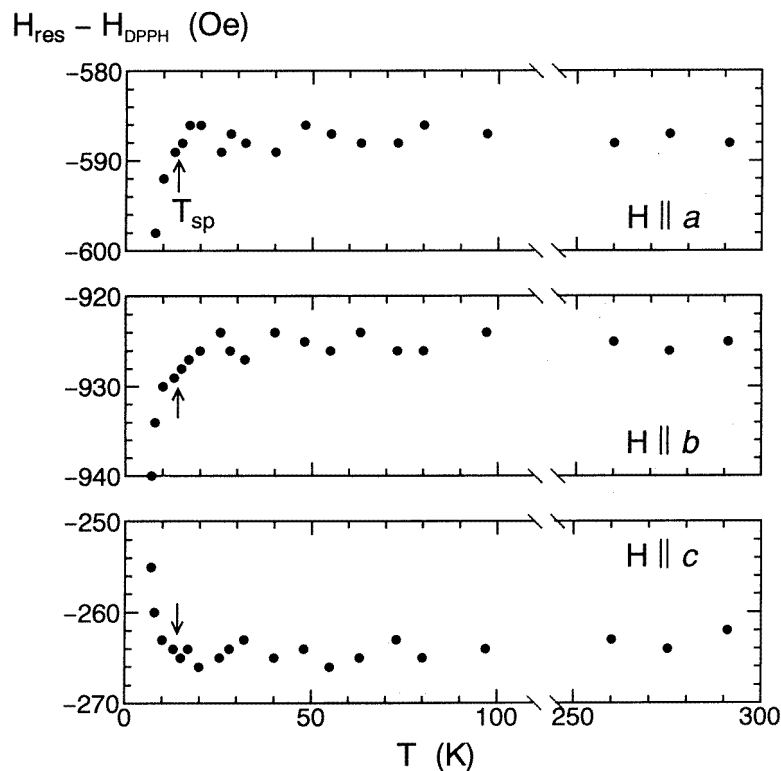


Figure 4. The dependence of resonance field on temperature observed at 24.48 GHz. The values of $H_{\text{res}} - H_{\text{DPPH}}$ are plotted, where H_{DPPH} is the resonance field that corresponds to the $g = 2$ line. The abscissa is common for $H \parallel a$ -, b -, and c -axes. From these data, $g_a = 2.15$, $g_b = 2.24$, and $g_c = 2.06$ are calculated.

The EPR absorption line $I(\omega - \omega_0)$ at a frequency ω is given by the Fourier transform of $\varphi(t)$ as

$$I(\omega - \omega_0) = \int_{-\infty}^{\infty} \varphi(t) \exp[i(\omega - \omega_0)t] dt \quad (4)$$

where ω_0 is the angular resonance frequency, and $\varphi(t)$ is a relaxation function expressed as

$$\varphi(t) = \frac{\langle \tilde{M}_+(t) M_-(0) \rangle}{\langle M_+ M_- \rangle}. \quad (5)$$

In the above, $\tilde{M}_+(t)$ is an interaction representation and $M_{\pm} = g\mu_B \sum_i S_i^{\pm}$. The relaxation function $\varphi(t)$ is expressed by the correlation function

$$\psi(\tau) = \frac{\langle [\tilde{\mathcal{H}}'(\tau), M_+(0)] [M_-(0), \mathcal{H}'(0)] \rangle}{\hbar^2 \langle M_+ M_- \rangle} \quad (6)$$

as

$$\varphi(t) = \exp \left[- \int_0^t (t - \tau) \psi(\tau) d\tau \right] \quad (7)$$

where

$$\tilde{\mathcal{H}}'(\tau) = \exp\left(\frac{-i\mathcal{H}_0\tau}{\hbar}\right) \mathcal{H}'(0) \exp\left(\frac{i\mathcal{H}_0\tau}{\hbar}\right). \quad (8)$$

When spin-diffusional relaxation is not effective, $\varphi(t)$ is approximated as

$$\varphi(t) = \exp\left(-t \int_0^\infty \psi(\tau) d\tau\right) = \exp[-t\psi(0)\tau_c] \quad (9)$$

with a characteristic time $\tau_c \simeq \hbar/|J|$. The function $\psi(0)$ corresponds to the second moment $M_2(J/kT)$. The absorption line observed by fixing a microwave frequency and sweeping an external field has ΔH which is approximated as

$$\Delta H \simeq \frac{\hbar^2}{g\mu_B|J|} M_2(J/kT) \text{ Oe}. \quad (10)$$

When the spin-diffusion process is effective, the approximate evaluation of ΔH given by equation (10) collapses, as intensively developed earlier [7, 18]. As will be clarified later in subsection 3.3, the spin-diffusion process has no effect on the EPR line governed by the DM interaction. Therefore, there is no problem with using equations (9) and (10) as long as \mathcal{H}'_{DM} is a leading term in \mathcal{H}' . Since the treatment of symmetric terms in 1DHAFs is established [7, 17, 18], only that of \mathcal{H}'_{DM} is presented here.

To see the value and angular dependence of ΔH at high T , $M_2(J/kT \rightarrow 0)$ is calculated. The process to derive $M_2(J/kT)$ is as follows. Two coordinate systems are employed. One is $[XYZ]$ which are fixed to the crystal axes $[abc]$ with $Z\parallel c$, while the other one is $[xyz]$ defined with $\mathbf{H}\parallel z$. The polar and azimuthal angles of \mathbf{H} with respect to the c -axis are θ and ϕ , respectively.

The term \mathcal{H}'_{DM} is decomposed into the secular and non-secular parts as

$$\begin{aligned} \mathcal{H}'_{\text{DM}}(\tau=0) &= \sum_i \mathbf{d}_{i+1} \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1}) \\ &= \sum_i \sum_{\alpha\beta} \lambda_{ii+1}^{\alpha\beta} (S_i^\alpha S_{i+1}^\beta - S_i^\beta S_{i+1}^\alpha) \equiv G_0^{\text{DM}}(0) + G_1^{\text{DM}}(0) + G_{-1}^{\text{DM}}(0) \end{aligned} \quad (11)$$

where $\mathbf{d}_{i+1} = (d_{ii+1}^X, d_{ii+1}^Y, d_{ii+1}^Z)$, and $\alpha, \beta = +, -, z$. Expressions of the secular part $G_0^{\text{DM}}(0)$ and the non-secular parts $G_{\pm 1}^{\text{DM}}(0)$ are

$$\begin{aligned} G_0^{\text{DM}}(0) &= \frac{1}{2} \sum_i \lambda_{ii+1}^{xy} (S_i^+ S_{i+1}^- - S_i^- S_{i+1}^+) \\ G_1^{\text{DM}}(0) &= \frac{1}{2} \sum_i (\lambda_{ii+1}^{xz} - i\lambda_{ii+1}^{yz}) (S_i^+ S_{i+1}^z - S_i^z S_{i+1}^+) \\ G_{-1}^{\text{DM}}(0) &= \frac{1}{2} \sum_i (\lambda_{ii+1}^{xz} + i\lambda_{ii+1}^{yz}) (S_i^- S_{i+1}^z - S_i^z S_{i+1}^-) \end{aligned} \quad (12)$$

in which

$$\begin{aligned} \lambda_{ii+1}^{xy} &= d_{ii+1}^X \sin\theta \cos\phi - d_{ii+1}^Y \sin\theta + d_{ii+1}^Z \cos\theta \\ \lambda_{ii+1}^{xz} &= d_{ii+1}^X \sin\phi - d_{ii+1}^Y \cos\phi \\ \lambda_{ii+1}^{yz} &= d_{ii+1}^X \cos\theta \cos\phi + d_{ii+1}^Y \cos\theta \sin\phi - d_{ii+1}^Z \sin\theta. \end{aligned} \quad (13)$$

From equations (12), $g_m(0) \equiv [G_m^{\text{DM}}(0), M_+(0)]$ for $m = 0, 1$, and -1 are calculated as

$$\begin{aligned} g_0(0) &= \sum_i \Lambda_{ii+1}^{(0)} (S_i^+ S_{i+1}^z - S_i^z S_{i+1}^+) \\ g_1(0) &= 0 \\ g_{-1}(0) &= \sum_i \Lambda_{ii+1}^{(-1)} (S_i^- S_{i+1}^+ - S_i^+ S_{i+1}^-) \end{aligned} \quad (14)$$

where

$$\Lambda_{ii+1}^{(0)} \equiv ig\mu_B\lambda_{ii+1}^{xy} \quad \Lambda_{ii+1}^{(-1)} \equiv \frac{1}{2}g\mu_B(\lambda_{ii+1}^{xz} + i\lambda_{ii+1}^{yz}) \quad (15)$$

and $\Lambda_{ii+1}^{(m)}$ does not depend on i . From equation (6), the second moment $M_2^{\text{DM}}(J/kT)$ is given by

$$M_2^{\text{DM}}(J/kT) = \left(\sum_m \langle g_m(0)g_m(0)^\dagger \rangle \right) / \hbar^2 \langle M_+ M_- \rangle. \quad (16)$$

Applying equation (14) to $\langle g_m(0)g_m(0)^\dagger \rangle$, one finds that

$$\begin{aligned} \langle g_0(0)g_0(0)^\dagger \rangle &= \sum_{i,j} \Lambda_{ii+1}^{(0)} (\Lambda_{jj+1}^{(0)})^\dagger \langle (S_i^+ S_{i+1}^z - S_i^z S_{i+1}^+) (S_j^- S_{j+1}^z - S_j^z S_{j+1}^-) \rangle \\ \langle g_{-1}(0)g_{-1}(0)^\dagger \rangle &= \sum_{i,j} \Lambda_{ii+1}^{(-1)} (\Lambda_{jj+1}^{(-1)})^\dagger \langle (S_i^- S_{i+1}^+ - S_i^+ S_{i+1}^-) (S_j^+ S_{j+1}^- - S_j^- S_{j+1}^+) \rangle. \end{aligned} \quad (17)$$

Counting only $i = j$ terms in equations (17), and using a decoupling scheme for four-spin correlation functions, one can calculate $M_2^{\text{DM}}(0)$. In the calculation, the isotropy of correlations is assumed, and then relations $\hbar^2 \langle M_+ M_- \rangle = 2N\hbar^2 g^2 \mu_B^2 S(S+1)/3$ which is satisfied at high T and $\langle S_i^+ S_i^- \rangle = 2\langle (S_i^z)^2 \rangle = 2S(S+1)/3$ are used. The result is

$$M_2^{\text{DM}}(0) = (1/3\hbar^2) |\mathbf{d}_{ii+1}|^2 S(S+1)(1 + \cos^2 \theta) \quad \text{when } \mathbf{d}_{ii+1} \parallel \text{chain axis} \quad (18)$$

or

$$M_2^{\text{DM}}(0) = (1/6\hbar^2) |\mathbf{d}_{ii+1}|^2 S(S+1)(2 + \sin^2 \theta) \quad \text{when } \mathbf{d}_{ii+1} \perp \text{chain axis}. \quad (19)$$

The other two perturbations

$$\mathcal{H}'_{\text{DD}} = g^2 \mu_B^2 \sum_{i>j} \frac{1}{r_{ij}^3} \left[\mathbf{S}_i \cdot \mathbf{S}_j - \frac{3(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right] \quad (20)$$

and

$$\mathcal{H}'_{\text{AE}} = \sum_i \mathbf{S}_i \cdot \mathbf{A}_{ii+1} \cdot \mathbf{S}_{i+1} \quad (21)$$

with diagonal components of the tensor \mathbf{A}_{ii+1} as $(A_{ii+1}^X, A_{ii+1}^Y, A_{ii+1}^Z) \equiv (A, A, -2A)$, are familiar and have been intensively treated. Their respective second moments are

$$M_2^{\text{DD}}(0) = \frac{3g^4 \mu_B^4}{2\hbar^2} \left(\sum_{i>j} \frac{1}{r_{ij}^3} \right)^2 S(S+1)(1 + \cos^2 \theta) \quad (22)$$

$$M_2^{\text{AE}}(0) = \frac{3}{2\hbar^2} A^2 S(S+1)(1 + \cos^2 \theta). \quad (23)$$

Strictly speaking, the angular part in equation (23) is not exact for CuGeO_3 , because the principal axes of the CuO_6 octahedron do not coincide with the $[abc]$ -axes. However, estimation of the value of $M_2^{\text{AE}}(0)$ is possible without knowing the precise angular

dependence of $M_2^{\text{AE}}(0)$. In $M_2^{\text{DD}}(0)$ and $M_2^{\text{AE}}(0)$ given above, both the secular and non-secular parts are included. It can exactly be shown that a cross term between \mathcal{H}'_{DM} and \mathcal{H}'_{DD} (or \mathcal{H}'_{AE}) is absent, but the cross term between \mathcal{H}'_{DD} and \mathcal{H}'_{AE} yields an additional second moment

$$M_2^{\text{cross}}(0) = \frac{1}{4\hbar^2} A g^2 \mu_{\text{B}}^2 \left(\sum_{i>j} \frac{1}{r_{ij}^3} \right) S(S+1) \text{Ang}(\theta) \quad (24)$$

where $\text{Ang}(\theta)$ indicates an angular-dependent part. Using the formulae for $M_2^{\text{DM}}(0)$, $M_2^{\text{DD}}(0)$, and $M_2^{\text{AE}}(0)$ given above, one can estimate the contribution of respective second moments to the EPR linewidth observed at high T .

3.2. The temperature dependence of the linewidth

Based on equation (6), a theory which qualitatively explains the T dependence of ΔH observed in the present compound is developed. For convenience, T_{N} is used instead of T_{sp} in subsections 3.2 and 3.4. The T dependence of ΔH arises from that of $M_2(J/kT)$. When $\mathcal{H}' = \mathcal{H}'_{\text{DM}}$, $M_2(J/kT)$ is given by equation (16). The denominator $\langle M_+ M_- \rangle$ in equation (16) is approximated as

$$\langle M_+ M_- \rangle \propto \sum_{i,j} \langle S_i^z S_j^z \rangle \propto \chi(T) kT \quad (25)$$

where $\chi(T)$ is the static uniform susceptibility. Since $\chi(T)$ is approximated by the Bonner–Fisher curve [19], or by the Curie–Weiss curve, it is said that $\chi(T)kT$ over the short-range ordering region changes moderately and thus this factor does not bring about a drastic decrease in ΔH . Therefore, the T dependence of ΔH substantially arises from that of $\sum_m \langle g_m(0) g_m(0)^\dagger \rangle$. This factor, i.e., the numerator of equation (16), involves four-spin correlation functions. On the assumption of the classical spin defined as $s_i \equiv S_i / \sqrt{S(S+1)}$, and isotropic interactions, the four-spin correlation functions are calculated using Fisher's classical spin model [20]. Then, one obtains

$$\sum_m \langle g_m(0) g_m(0)^\dagger \rangle \propto \sum_{i,j} (\langle s_i^x s_{i+1}^y s_j^x s_{j+1}^y \rangle - \langle s_i^x s_{i+1}^y s_j^y s_{j+1}^x \rangle) \propto \frac{1}{3} K u(K) \quad (26)$$

where

$$K \equiv kT/2JS(S+1) \text{ and } u(K) \equiv \coth(1/K) - K. \quad (27)$$

Therefore, the qualitative T dependence of ΔH is given by $Ku(K)/3$, which is shown in figure 5(a): ΔH decreases monotonically with decreasing T and tends to zero.

Although $\Delta H(T)$ for spin-symmetric 1DHAFs is already established, the formula of $\Delta H(T)$ for such systems is given here, and is compared with equation (26). For $\mathcal{H}'_{\text{DD}} + \mathcal{H}'_{\text{AE}}$, the calculation similar to the above yields [11]

$$\begin{aligned} \Delta H(T) &\propto M_2^{\text{DD}}(J/kT) + M_2^{\text{AE}}(J/kT) + M_2^{\text{cross}}(J/kT) \\ &\propto \sum_{i,j} \sum_{k,l} \langle S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha \rangle \langle S_k^{\alpha'} S_l^{\beta'} + S_k^{\beta'} S_l^{\alpha'} \rangle \\ &\propto \sum_{i,j} \sum_{k,l} (\langle s_i^\alpha s_j^\beta s_k^{\alpha'} s_l^{\beta'} \rangle + \langle s_i^\alpha s_j^\beta s_k^{\beta'} s_l^{\alpha'} \rangle + \dots) \propto \frac{12u^2}{5(1-v)} + 1 + \frac{v}{5} \end{aligned} \quad (28)$$

where

$$v(K) = 1 - 3Ku(K). \quad (29)$$

To obtain the final formula in equation (28), only nearest-neighbour spins are counted. The T dependence of ΔH given by the final expression in equation (28) is drawn in figure 5(b), which realizes the well known increase of ΔH over the short-range ordering region in spin-symmetric 1DHAFs.

It should be pointed out that equation (28) consists of a plus combination of four-spin correlation functions, which is in contrast to equation (26). As developed above, it is qualitatively clarified that the spin-antisymmetric and spin-symmetric perturbations result in completely different T dependence of ΔH from each other over the short-range ordering region.

Such contrasting T dependence of ΔH is also elucidated as follows. Converting a spin to q -space, i.e., $S_i = N^{-1/2} \sum_q S_q \exp(i\mathbf{q} \cdot \mathbf{r}_i)$, $\sum_m \langle g_m(0) g_m(0)^\dagger \rangle$ given by equations (17) can be expressed as a sum over the single wave vector \mathbf{q} . The decoupling scheme of four-spin correlation functions is also used and correlations are assumed to be isotropic, i.e., $\langle S_i^\pm(\tau) S_j^\mp \rangle = 2 \langle S_i^z(\tau) S_j^z \rangle$. Then, one obtains

$$\begin{aligned} \sum_m \langle g_m(\tau) g_m(0)^\dagger \rangle &= \sum_{i,j} [\Lambda_{ii+1}^{(0)} (\Lambda_{jj+1}^{(0)})^\dagger + 2\Lambda_{ii+1}^{(-1)} (\Lambda_{jj+1}^{(-1)})^\dagger] \langle S_i^z(\tau) S_j^z \rangle \langle S_{i+1}^z(\tau) S_{j+1}^z \rangle \\ &\quad - \langle S_i^z(\tau) S_{j+1}^z \rangle \langle S_{i+1}^z(\tau) S_j^z \rangle = \sum_q \{ [\Lambda_q^{(0)} (\Lambda_q^{(0)})^\dagger + 2\Lambda_q^{(1)} (\Lambda_q^{(-1)})^\dagger] \\ &\quad - [\Lambda_q^{(0)} (\Lambda_{-q}^{(0)})^\dagger + 2\Lambda_q^{(-1)} (\Lambda_{-q}^{(-1)})^\dagger] \} \langle S_q^z(\tau) S_{-q}^z \rangle^2 \end{aligned} \quad (30)$$

where

$$\Lambda_q^{(m)} = \sum_l \Lambda_{il}^{(m)} \exp(i\mathbf{q} \cdot \mathbf{r}_{il}) = \Lambda_{ii+1}^{(m)} e^{i\mathbf{q} \cdot (\mathbf{r}_{i+1} - \mathbf{r}_i)} + \Lambda_{ii-1}^{(m)} e^{i\mathbf{q} \cdot (\mathbf{r}_{i-1} - \mathbf{r}_i)} \quad (31)$$

because only the nearest-neighbour sites, $l = i \pm 1$, contribute to \sum_l in equation (31).

Since magnetic ions are located on each straight chain at the same interval $|a|$, then $\mathbf{d}_{ii+1} = -\mathbf{d}_{ii-1}$, and therefore $\Lambda_{ii+1}^{(m)} = -\Lambda_{ii-1}^{(m)}$. As a result, a relation

$$\Lambda_q^{(m)} = \Lambda_{ii+1}^{(m)} e^{i\mathbf{a} \cdot \mathbf{q}} - \Lambda_{ii+1}^{(m)} e^{-i\mathbf{a} \cdot \mathbf{q}} = 2i \Lambda_{ii+1}^{(m)} \sin \mathbf{a} \cdot \mathbf{q} \quad (32)$$

is obtained. The phase factor $\sin \mathbf{a} \cdot \mathbf{q}$ in equation (32) plays an important role, as will be explained later. Using equation (32), the expression given by equation (30) is simplified as

$$\sum_m \langle g_m(\tau) g_m(0)^\dagger \rangle = 8 [\Lambda_{ii+1}^{(0)} (\Lambda_{ii+1}^{(0)})^\dagger + 2\Lambda_{ii+1}^{(-1)} (\Lambda_{ii+1}^{(-1)})^\dagger] \sum_q \langle S_q^z(\tau) S_{-q}^z \rangle^2 \sin^2 \mathbf{a} \cdot \mathbf{q}. \quad (33)$$

Using $\langle S_q^z(\tau) S_{-q}^z \rangle = \langle S_q^z S_{-q}^z \rangle \exp(-\Gamma_q t)$ in which Γ_q is a damping factor and replacing \sum_q by $\int d\mathbf{q}$, one obtains a formula for $\Delta H(T)$ as

$$\begin{aligned} \Delta H(T) &\propto B \int_0^{\pi/a} q^{d-1} dq \frac{\langle S_q^z S_{-q}^z \rangle^2}{\Gamma_q} \sin^2 \mathbf{a} \cdot \mathbf{q} \\ &= B \int_0^{\pi/a} q^{d-1} dq \left(\frac{\langle S_q^z S_{-q}^z \rangle^2}{\Gamma_q} - \frac{\langle S_q^z S_{-q}^z \rangle^2}{\Gamma_q} \cos^2 \mathbf{a} \cdot \mathbf{q} \right) \end{aligned} \quad (34)$$

where $B \equiv 8 [\Lambda_{ii+1}^{(0)} (\Lambda_{ii+1}^{(0)})^\dagger + 2\Lambda_{ii+1}^{(-1)} (\Lambda_{ii+1}^{(-1)})^\dagger]$ and $d = 1$.

On the other hand, \mathcal{H}'_{DD} (or \mathcal{H}'_{AE}) in 1DHAFs yields a formula of ΔH which is similar to equation (34). However, the formula involves a phase factor which is completely different from that for \mathcal{H}'_{DM} , as is explained below. For $\mathcal{H}' = \mathcal{H}'_{\text{DD}}$ (or $\mathcal{H}'_{\text{AE}} = \sum_m \sum_{i>j} F_{ij}^{(m)} S_i^\alpha S_j^\beta$ with $m = \pm 2, \pm 1, 0$) $\Delta H(T)$ is expressed as

$$\Delta H(T) \propto \sum_{m=-2}^2 \int_0^{\pi/a} q^{d-1} dq |F_q^{(m)}|^2 \frac{\langle S_q^z S_{-q}^z \rangle^2}{\Gamma_q} \quad (35)$$

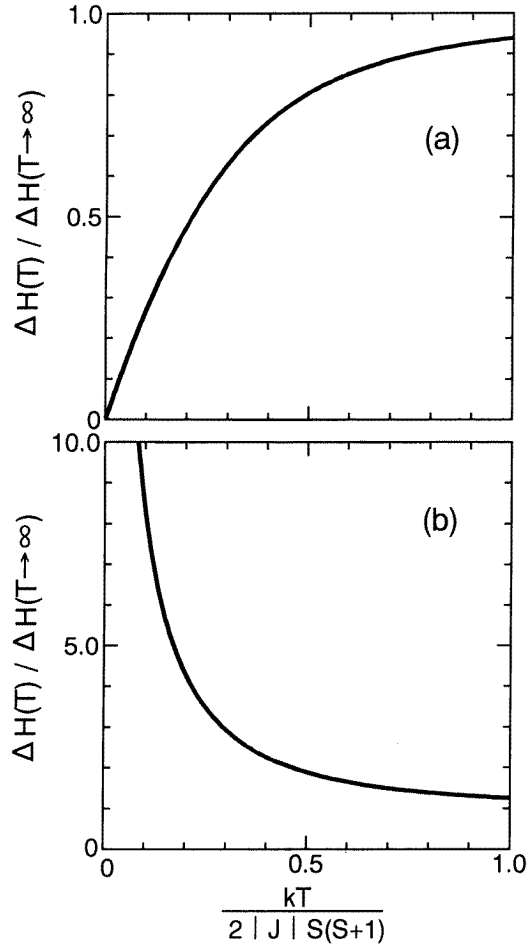


Figure 5. The theoretically suggested temperature dependence of the EPR linewidth normalized at high temperatures for 1DHAFs: (a) for the DM exchange interaction; (b) for the DD or AE interaction. Here, $T_N = 0$ K is assumed. The abscissa is common for (a) and (b).

where

$$\begin{aligned}
 F_q^{(m)} &= \sum_j F_{ij}^{(m)} \exp(i\mathbf{q} \cdot \mathbf{r}_{ij}) \\
 &= F_{ii+1}^{(m)} e^{i\mathbf{a} \cdot \mathbf{q}} + F_{ii-1}^{(m)} e^{-i\mathbf{a} \cdot \mathbf{q}} + F_{ii+2}^{(m)} e^{2i\mathbf{a} \cdot \mathbf{q}} + F_{ii-2}^{(m)} e^{-2i\mathbf{a} \cdot \mathbf{q}} + \dots
 \end{aligned}$$

Because the coefficients $F_{ij}^{(m)}$ are symmetric, i.e., $F_{ij}^{(m)} = F_{ik}^{(m)}$ for $\mathbf{r}_{ij} = -\mathbf{r}_{ik}$, then $F_q^{(m)}$ is given by

$$F_q^{(m)} = 2(F_1^{(m)} \cos \mathbf{a} \cdot \mathbf{q} + F_2^{(m)} \cos 2\mathbf{a} \cdot \mathbf{q} + \dots) \quad (36)$$

where $F_l^{(m)} \equiv F_{ii+l}^{(m)} = F_{ii-l}^{(m)}$ is the strength of l th-neighbour interactions. Consequently, the formula of ΔH for spin-symmetric perturbations, which should be compared with equation (34), is expressed as

$$\Delta H(T) \propto \sum_m \sum_l (F_l^{(m)})^2 \int_0^{\pi/a} q^{d-1} dq \frac{\langle S_q^z S_{-q}^z \rangle^2}{\Gamma_q} \cos^2 l\mathbf{a} \cdot \mathbf{q} \quad (37)$$

because $\int_0^{\pi/a} \cos l\mathbf{a} \cdot \mathbf{q} \cos k\mathbf{a} \cdot \mathbf{q} dq = 0$ for $l \neq k$.

Equations (34) and (37) contain the common factor $\langle S_q^z S_{-q}^z \rangle^2 / \Gamma_q$, which increases over the short-range ordering region. When T decreases toward T_N , spin fluctuations having $|\mathbf{q}| = \pi/a$ become dominant, and then $\cos^2 \mathbf{a} \cdot \mathbf{q} \simeq 1$ and $\cos^2 l\mathbf{a} \cdot \mathbf{q} \simeq 1$. Although quantitative estimation of the T dependence of the integrand in equation (34) is difficult, the two terms in parentheses in the integrand probably cancel each other with $T \rightarrow T_N$. This fact leads to the decrease of ΔH , as is observed in the present compound. In contrast, the integrand in equation (37) increases according to the T dependence of $\langle S_q^z S_{-q}^z \rangle^2 / \Gamma_q$, and then ΔH increases.

3.3. Lineshape

The Lorentzian lineshape observed at high T indicates that the effect of the spin-diffusion process is absent. In fact, it was proven [21] that the $\mathbf{q} \sim \mathbf{0}$ fluctuations do not enhance the secular part of \mathcal{H}'_{DM} as follows. The coefficient $\lambda_{ij}^{\alpha\beta}$ given by equations (13) is a component of a vector connecting sites i and j on the chain. Then, a relation $\lambda_{ij}^{\alpha\beta} = -\lambda_{ik}^{\alpha\beta}$ is held as long as each spin on the chain is located at regular intervals as in the present case, because there are sites j and k which satisfy $\mathbf{r}_{ij} = -\mathbf{r}_{ik}$. From equation (30), the Fourier-transformed secular part of $M_2^{\text{DM}}(J/kT)$ is found to be proportional to

$$\langle g_0(0)g_0(0)^\dagger \rangle = \sum_q [\Lambda_q^{(0)}(\Lambda_q^{(0)})^\dagger - \Lambda_q^{(0)}(\Lambda_{-q}^{(0)})^\dagger] \langle S_q^z S_{-q}^z \rangle^2. \quad (38)$$

Since $\Lambda_{\pm q}^{(0)} \propto \sin \mathbf{a} \cdot \mathbf{q}$, as given by equation (32), it is clear that $\Lambda_{\pm q}^{(0)} \rightarrow 0$ for $\mathbf{q} \rightarrow \mathbf{0}$. Thus, the enhancement of the $\mathbf{q} = \mathbf{0}$ components of the secular part cannot be expected for \mathcal{H}'_{DM} . This is why the lineshape does not depart from the Lorentzian in the spin-antisymmetric 1DHAFs. In contrast, the spin-symmetric perturbation terms result in $F_q^{(m)} \propto \cos l\mathbf{a} \cdot \mathbf{q}$, as explained before. Then the $\mathbf{q} \sim \mathbf{0}$ components of the respective secular parts which survive in the long-time part of $\psi(\tau)$ strongly contribute to the absorption line at high T . As a result, the lineshape becomes non-Lorentzian, as intensively discussed earlier [7].

3.4. The temperature dependence of the resonance field

There are several theoretical treatments [9, 22, 23] for the T dependence of H_{res} in low-dimensional Heisenberg magnets. Their results are, of course, identical to each other. Readers should pay attention to the fact that perturbation terms treated in these theories are the spin-symmetric ones such as the DD or AE interactions. However, these theories can also be applied to spin-antisymmetric perturbations. Here, the theory given by Nagata and Tazuke (NT) [9] is employed. From now on, the coordinates $[X, Y, Z]$ with $Z \parallel$ chain axis are used. The resonance frequency ω is given by [9]

$$\hbar\omega = \langle [S_-, [S_+, \mathcal{H}]] \rangle / 2 \langle S^\zeta \rangle \quad (39)$$

where S_\pm are the transverse components of the total spin $\mathbf{S} = \sum_i \mathbf{S}_i$, and ζ indicates the direction of $\mathbf{g} \cdot \mathbf{H}$. When $\mathcal{H} = \mathcal{H}_{\text{ex}} + \mathcal{H}_Z + \mathcal{H}'$ is applied in equation (39), the T -dependent part arises from $[S_+, \mathcal{H}']$, because $[S_+, \mathcal{H}_{\text{ex}}] = 0$ and $\langle [S_-, [S_+, \mathcal{H}_Z]] \rangle$ results in $\mu_B \mathbf{g} \cdot \mathbf{H}$.

The NT result for \mathcal{H}'_{DD} is briefly reviewed before examining the effect of $\mathcal{H}' = \mathcal{H}'_{\text{DM}}$ on H_{res} . The resonance frequencies for $\mathbf{H} \parallel$ chain axis and $\mathbf{H} \perp$ chain axis are derived as

$$\begin{aligned} \hbar\omega_{\parallel}(T) &= g_{\parallel}\mu_{\text{B}}H - \left(C_1 \sum_i \langle S_i^Z S_{i+1}^Z - S_i^X S_{i+1}^X \rangle \right) / \langle S^Z \rangle & \text{for } \mathbf{H} \parallel Z \\ \hbar\omega_{\perp}(T) &= g_{\perp}\mu_{\text{B}}H + \left(C_2 \sum_i \langle S_i^X S_{i+1}^X - S_i^Z S_{i+1}^Z \rangle \right) / \langle S^X \rangle & \text{for } \mathbf{H} \parallel X \end{aligned} \quad (40)$$

where C_1 and C_2 are constant values related to both J and the value of the DD interaction. The thermal averages $\langle S_i^X S_{i+1}^X \rangle$ and $\langle S_i^Z S_{i+1}^Z \rangle$ were calculated using Fisher's classical spin model. As a result, ω_{\parallel} and ω_{\perp} were found to go up and to go down, respectively, as T decreases toward T_{N} . When H_{res} is measured at a fixed microwave frequency, H_{res} for $\mathbf{H} \parallel$ chain axis which is denoted as $H_{\text{res}}^{\parallel}$ decreases, while H_{res} for $\mathbf{H} \perp$ chain axis, denoted as H_{res}^{\perp} , increases, and these two fields obey the relation $\{H_{\text{res}}^{\parallel}(T) \cdot [H_{\text{res}}^{\perp}(T)]^2\}^{1/3} = \text{constant}$. This prediction well explains the experiments for TMMC [9] and CsMnCl₃·2H₂O [9], both of which have \mathcal{H}'_{DD} as a main perturbation term.

In the same way, the resonance frequency for $\mathcal{H}' = \mathcal{H}'_{\text{DM}} = \sum_i \mathbf{d}_{i+1} \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1})$ is derived as

$$\hbar\omega(T) = \mu_{\text{B}}\mathbf{g} \cdot \mathbf{H} + \frac{i}{2\langle S^z \rangle} \sum_i [d_{i+1}^Z \langle S_i^+ S_{i+1}^- - S_i^- S_{i+1}^+ \rangle - d_{i+1}^+ \langle S_i^Z S_{i+1}^- - S_i^- S_{i+1}^Z \rangle] \quad (41)$$

where $d_{i+1}^+ \equiv d_{i+1}^X + id_{i+1}^Y$.

Since $\langle S_i^Z S_{i+1}^- \rangle$ and $\langle S_i^- S_{i+1}^Z \rangle$ are zero, the DM interaction with $\mathbf{d}_{i+1} \perp Z$ has no effect on the resonance frequency. In contrast, the DM interaction with $\mathbf{d}_{i+1} \parallel Z$ contributes to the resonance frequency, because $\langle S_i^+ S_{i+1}^- - S_i^- S_{i+1}^+ \rangle$ does not generally vanish. However, even this correlation function becomes zero for isotropic spins. Therefore, H_{res} at a fixed microwave frequency holds constant above T_{N} for any direction of \mathbf{H} , as long as the DM interaction is a main perturbation term.

4. Discussion

Parameters of CuGeO₃ which are necessary for an analysis of the EPR line are as follows. The intrachain Cu–Cu distance 2.94 Å, is fairly short as compared with the interchain ones, 4.81 Å and 4.24 Å along the a - and b -axis, respectively [14]. The intrachain antiferromagnetic exchange interaction J defined by the Hamiltonian $\mathcal{H} = -2J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$ has been determined by several experimental methods. From neutron scattering, $J \simeq -60$ K was obtained [24], while the experiment on the high-field magnetization process yielded -91.5 K [25]. The interchain exchanges along the a - and b -axes were reported to be $-0.01J$ and $0.1J$, respectively [24]. The curve of the susceptibility χ versus T [1] shows a broad peak around 50 K, indicating the development of a short-range order over the wide range of T above T_{sp} . Although $\chi(T)$ given in [1] can not be fitted by the Bonner–Fisher curve [19], it is reasonable to treat this compound as a 1DHAF. Since the experimentally determined value of J is distributed as introduced above, the mean value, $J = -76$ K, is used in the calculation presented below, though no contradiction arises if $J = -60$ or -91.5 K is used. The g -factors which were determined from H_{res} at high T for $\mathbf{H} \parallel a$, b , and c are $g_a = 2.15$, $g_b = 2.24$, and $g_c = 2.06$, respectively. These values coincide well with those reported in [6].

Let us first estimate $M_2^{\text{DM}}(0)$, $M_2^{\text{DD}}(0)$, and $M_2^{\text{AE}}(0)$, and clarify the main origin of line broadening. To evaluate the values of A and $|\mathbf{d}_{i+1}|$, approximate relations

$|A| \simeq (\Delta g/g)^2 |J|$ and $|d_{ii+1}| \simeq (\Delta g/g) |J|$ are used, where $\Delta g = g - 2$. Using the mean value of g_a , g_b , and g_c for g , the respective second moments of the present compound are approximately calculated as

$$\begin{aligned} M_2^{\text{DM}}(0) &\simeq 5 \times 10^8 \text{ Oe}^2 \\ M_2^{\text{DD}}(0) &\simeq 2 \times 10^6 \text{ Oe}^2 \\ M_2^{\text{AE}}(0) &\simeq 10^7 \text{ Oe}^2. \end{aligned}$$

The value of $M_2^{\text{cross}}(0)$ is found to be comparable to $M_2^{\text{DD}}(0)$.

It is clear from the above that $M_2^{\text{DM}}(0)$ is extremely larger than the other two. From equations (10), (22)–(24), ΔH is roughly estimated to be ~ 10 Oe, as long as only the perturbation $\mathcal{H}' = \mathcal{H}'_{\text{DD}} + \mathcal{H}'_{\text{AE}}$ is considered. Therefore, it can be said that the DD and AE interactions are not the main origin of line broadening in CuGeO_3 . In contrast, $\mathcal{H}' = \mathcal{H}'_{\text{DM}}$ well explains the value of ΔH_{pp} and its angular dependence observed at high T ; from equations (10) and (18) (or (19)), $\Delta H_{\text{pp}} \simeq 1$ kOe is estimated, the order of which approximately agrees with the observation in spite of the rough estimation of the value of $|d_{ii+1}|$. Moreover, the experimental result for the angular dependence of ΔH_{pp} coincides well with $(2 + \sin^2 \theta)$, as shown in figure 2. That is, the ratio $\Delta H_{\text{pp}}^b / \Delta H_{\text{pp}}^c \simeq \Delta H_{\text{pp}}^a / \Delta H_{\text{pp}}^c \simeq 1.5$ obtained experimentally agrees with the value 1.5 calculated from equation (19). This agreement indicates that d_{ii+1} is perpendicular to the c -axis. As a result, the value of ΔH_{pp} at high T and its angular dependence are well explained by the DM interaction with $d_{ii+1} \perp$ chain axis.

Furthermore, the lineshape at high T is well fitted by the straight line shown in figure 3, which indicates the Lorentzian of the observed absorption line. If the relaxation of spins obeyed the diffusion process, the plot should be on or near the dotted line figure 3. The Lorentzian lineshape thus confirmed also indicates that \mathcal{H}'_{DM} is the main perturbation in the present magnetic system.

Next, $\Delta H_{\text{pp}}(T)$ shown in figure 1 is discussed. In conventional 1DHAFs with spin-symmetric perturbations, $\Delta H(T)$ increases with decreasing T over the short-range ordering region. However, such an increase is not seen in the present data. With decreasing T , $\Delta H_{\text{pp}}(T)$ decreases monotonically for all directions of \mathbf{H} , and reaches the minimum at $T \simeq T_{\text{sp}}$. The extrapolation of the observed $\Delta H_{\text{pp}}(T)$ from the paramagnetic region seems to tend to zero. The experimental result is rather like the theoretical curve for \mathcal{H}'_{DM} given in figure 5(a). This agreement is another evidence that the EPR line of CuGeO_3 is due to the DM interaction.

Since $M_2^{\text{DM}}(0)$ is very much larger than $M_2^{\text{DD}}(0)$ or $M_2^{\text{AE}}(0)$ in the present compound, the experimental results are typical of the DM interaction. However, the 1DHAFs which have \mathcal{H}'_{DM} and satisfy the condition $M_2^{\text{DM}}(0) \gg M_2^{\text{DD}}(0)$ (or $M_2^{\text{AE}}(0)$) are rare. Besides the present compound, only KCuF_3 [15] was established to meet this condition. In most of the 1DHAFs with \mathcal{H}'_{DM} , the value of $M_2^{\text{DD}}(0)$ (or $M_2^{\text{AE}}(0)$) is comparable to that of $M_2^{\text{DM}}(0)$. In such a case, the dependence of ΔH on T or θ is not simple. One must therefore remember that the magnetic dimensionality is not a unique factor to determine $\Delta H(T)$ or $\Delta H(\theta)$ †.

Finally, the T dependence of H_{res} is discussed. The experimental result that shows no change of H_{res} with T for $T > T_{\text{sp}}$ is consistent with the theory given in subsection 3.4. Thus,

† A typical example is seen in $\Delta H(T)$ reported in the organic spin-Peierls compounds $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ ($\text{M} = \text{Au}, \text{Cu}$) [26]. For $T > T_{\text{sp}}$, $\Delta H(T)$ in the Au compound rather resembles that of CuGeO_3 : $\Delta H(T)$ decreases monotonically with decreasing T toward T_{sp} . On the other hand, $\Delta H(T)$ in the Cu compound seems to be almost independent of T . To understand this difference, the perturbation terms which contribute to the line broadening in the respective compounds must be clarified.

the T independence of H_{res} also proves that the DM interaction is a leading perturbation in CuGeO_3 .

As a whole, all factors of the EPR line of CuGeO_3 , i.e., the value of ΔH and $\Delta H(\theta)$ as well as the lineshape at high T , $\Delta H(T)$, and $H_{\text{res}}(T)$ are found to be completely explained by the DM interaction with $\mathbf{d}_{ii+1} \perp$ chain axis, which is the conclusion of the present experiments and analysis.

5. The present result and crystal symmetry

Concerning the crystal structure of this compound for $T > T_{\text{sp}}$, the space group $Pbmm$ given by Völlenklee *et al* [14] has been accepted so far. However, the present EPR experiments and analysis strongly suggest the impropriety of this symmetry, because the crystal structure represented by $Pbmm$ does not allow the presence of the DM interaction. That is, the Moriya rule [27] which gives relations between crystal symmetry and the DM interaction indicates the absence of the DM interaction in this compound. More precisely, a crystal symmetry should have no inversion centre halfway between nearest-neighbour magnetic ion sites if the DM interaction exists. As long as the crystal symmetry given by Völlenklee *et al* is employed, the midpoint between nearest-neighbour Cu sites on the c -axis is an inversion centre, which means that $\mathbf{d}_{ii+1} = \mathbf{0}$.

However, there are reasons to doubt the crystal symmetry given in [14], which was reported about three decades ago. At that time, the power of x-ray sources was not so strong as it is these days. Consequently, the results, of x-ray investigations on various compounds reported at that time have been corrected subsequently, which is due to improvements in x-ray sources as well as quality of the respective compounds achieved during the last two or three decades. For instance, concerning the crystal structure of KCuF_3 , the space group D_{4h}^{18} was accepted for a long time. Several years ago, the EPR investigations [15, 16] suggested the existence of the DM interaction in this compound, but the crystal symmetry mentioned above did not allow this interaction. However, recent x-ray diffraction experiments revealed that the crystal structure of KCuF_3 has a symmetry lower than that of D_{4h}^{18} , and the newly found structure accounts for the DM interaction [28]. The present compound is probably not an exception.

According to the Moriya rule [27], the condition $\mathbf{d}_{ii+1} \perp c$ restricts the crystal symmetry allowed for CuGeO_3 . The crystal symmetry should satisfy at least one of the following rules for the nearest-neighbour Cu pairs on the c -axis.

- (i) There should be a mirror plane which is perpendicular to the Cu–Cu bonding line and which bisects this bonding line.
- (ii) There should be a mirror plane including the Cu–Cu bonding line.
- (iii) There should be a twofold rotation axis which is perpendicular to the Cu–Cu bonding line and which passes through the midpoint of the bonding line.

6. Conclusion

From the present EPR experiments and analysis, the $\sum_i \mathbf{d}_{ii+1} \cdot (\mathbf{S}_i \times \mathbf{S}_{i+1})$ interaction with $\mathbf{d}_{ii+1} \perp c$ -axis between nearest-neighbour Cu spins on the c -axis is clarified to be the main perturbation term that characterizes the EPR line in CuGeO_3 . This fact suggests that the crystal symmetry should be lower than that given by the space group $Pbmm$ which has been accepted so far.

The crystal symmetry [29, 30] for $T < T_{sp}$ derived from the dimerization of Cu–Cu pairs should also be reexamined. If the DM interaction between the dimerized spins exists, how does it affect the singlet ground state, as well as the triplet excited state? In response to the present study, critical reexaminations of the crystal structure of this compound using high-quality single crystals are now proceeding†.

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† Note added in proof: Hidaka *et al* recently found a new superlattice reflection which was not reported in the paper by Völlenkne *et al*; they performed x-ray diffraction experiments on single crystals which were improved in quality. The results will be reported elsewhere in the near future.