communication).
[3]A. I. Alekseev, Zh. Eksperim. i Teor. Fiz. 36, 1839 (1959) [Sov. Phys. JETP 9, 1312 (1959)].
[4]P. A. Fraser, Advan. At. Mol. Phys. 4, 63 (1968).
[5]C. J. Celitans and J. H. Green, Proc. Phys. Soc. (London) 83, 823 (1964).
[6]P. E. Osmon, Phys. Rev. 140, A8 (1965).
[7]L. O. Roellig and T. M. Kelly, Phys. Rev. Letters 18, 387 (1967).
[8]K. F. Canter, J. D. McNutt, and L. O. Roellig, Bull. Am. Phys. Soc. 14, 89 (1969).
[9]D. A. L. Paul and L. Saint-Pierre, Phys. Rev. Letters 11, 493 (1963).
[10]S. Cova and L. Zappa, J. Phys. B 1, 795 (1968).
[11]V. I. Goldanskii and Yu. S. Sayasov, Phys. Rev. Letters 13, 300 (1964).
[12]J. D. McNutt, V. B. Summerour, and D. A. Johnson (unpublished).
[13]L. O. Roellig, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 127.
[14]L. O. Roellig and J. D. McNutt, Bull. Am. Phys. Soc. 13, 634 (1968).
[15]D. A. L. Paul and C. Y. Leung, Can. J. Phys. 46, 2779 (1968).

PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

Antisymmetric Exchange and Exchange-Narrowed Electron-Paramagnetic-Resonance Linewidths*

T. G. Castner, Jr. and Mohindar S. Seehra†
Department of Physics and Astronomy,
University of Rochester, Rochester, New York 14627
(Received 10 March 1969; revised manuscript received 1 February 1971)

The Dzialoshinsky-Moriya (DM) antisymmetric exchange interaction between superexchange-coupled ions in antiferromagnetic salts is shown to contribute to the exchanged-narrowed electron-paramagnetic-resonance (EPR) linewidth in the paramagnetic state. The contribution of antisymmetric exchange to the second and fourth moments has been calculated and is analogous to that from symmetric anisotropic exchange and the dipole-dipole interaction. It is demonstrated that for $Cu(HCOO)_2 \cdot 4H_2O$, both the linear temperature dependence of the EPR linewidth and the temperature-independent exchange-narrowed linewidth (extrapolated to $T = 0\,°K$ from the paramagnetic region where $kT > J$) can be explained by the DM antisymmetric exchange interaction and are mutually consistent with one another. The analysis yields a value of the antisymmetric exchange $|\vec{\mathfrak{D}}_{jk}|/g\mu_B$ for $Cu(HCOO)_2 \cdot 4H_2O$ of order 2700 Oe and a second moment M_2 more than two orders of magnitude larger than the contribution to M_2 from the dipole-dipole interaction. Several other magnetic salts where the DM antisymmetric exchange interaction might contribute to the EPR linewidth are considered.

I. INTRODUCTION

In magnetic insulators with large exchange interactions, the electron-paramagnetic-resonance (EPR) linewidth is exchange narrowed. This phenomenon has been successfully described by the theories of Anderson and Weiss[1] and Kubo and Tomita.[2] These theories predict a frequency width of order ω_P^2/ω_e, where ω_e is the exchange frequency and ω_P^2 is the frequency second moment[3] of the EPR line shape due to various spin-spin interactions. Ordinarily it is the dipole-dipole interaction between spins which accounts for ω_P^2; however, it is also possible for symmetric anisotropic exchange terms[4] and crystal field fine-structure terms[5] to contribute to ω_P^2.

Crystals having large superexchange interactions (antiferromagnets) as well as sufficiently low symmetry[6] contain antisymmetric exchange terms resulting from the Dzialoshinsky-Moriya (DM) interaction.[7] The DM antisymmetric exchange interaction is known to account for the weak ferromagnetism of certain superexchange-coupled magnetic crystals and also to play an important role in the antiferromagnetic-resonance (AFMR) modes of such crystals. However, the role of antisymmetric exchange terms on the EPR linewidth has received little attention. Moriya has shown[7] that the magnitude (symmetry permitting) of the antisymmetric exchange should be of order $(\Delta g/g)J$, while the symmetric anisotropic exchange terms should be of order $(\Delta g/g)^2 J$, where g is the g shift and J the magnitude of the isotropic exchange interaction. Thus low-symmetry antiferromagnets with large exchange and sizable g shifts can produce a situation whereby the largest anisotropic exchange interaction is antisymmetric and can be larger than the dipole-dipole interaction. Because of their appreciable g shifts, copper salts which possess large exchange interactions are cases where antisym-

metric exchange may play a role in determining the EPR linewidth. One case, copper formate tetrahydrate [$Cu(HCOO)_2 \cdot 4H_2O$], seems to present an example where antisymmetric exchange makes the dominant contribution to the second moment.

$Cu(HCOO)_2 \cdot 4H_2O$ is a layerlike crystal which closely approximates a two-dimensional antiferromagnet with strong superexchange between Cu^{++} ions in the same layer and very weak exchange between Cu^{++} ions in different layers. This salt has been the object of several magnetic studies.[8] More recently, an analysis[9] of the temperature dependence of the paramagnetic susceptibility and a detailed AFMR study[10] have yielded information on the exchange constants of this crystal. A previous EPR linewidth study[11] indicated an unusual linear temperature dependence of the linewidth from $T \sim 50\,^{\circ}K$ ($\sim 3T_N$, $T_N = 17\,^{\circ}K$) to $T \sim 273\,^{\circ}K$. This linear temperature dependence was qualitatively accounted for by the phonon modulation of the DM antisymmetric exchange interaction; however, the magnitudes of the exchange constants were not known at that time.

In this paper we calculate the contribution of the DM antisymmetric exchange interaction, in addition to that of anisotropic symmetric exchange, to the second and fourth moments of the line shape, and thereby to the exchange-narrowed EPR linewidth. The subsequent analysis shows that both the temperature-independent exchange-narrowed EPR linewidth and the linear temperature dependence of the EPR linewidth can be explained with reasonable values of the DM antisymmetric exchange constant. The possibility of antisymmetric exchange contributing to the EPR linewidth of other magnetic salts is also considered.

II. CALCULATION OF EPR LINEWIDTH

The spin Hamiltonian for the exchange-coupled paramagnetic ions, neglecting hyperfine interactions and fine-structure terms,[12] can be written as

$$H = \sum_{j<k} [J_{jk}\vec{S}_j \cdot \vec{S}_k + D_{jk}S_{jz}S_{kz} + E_{jk}(S_{jx}S_{kx} - S_{jy}S_{ky}) + \vec{\mathfrak{D}}_{jk} \cdot \vec{S}_j \times \vec{S}_k] + H_{dd} + H_{Zeeman} , \quad (1)$$

where H_{dd} is the dipole-dipole interaction term. Equation (1) represents the most general bilinear[13] exchange interaction between pairs of paramagnetic ions written in the principal axes of the symmetric exchange interaction. The symmetry rules of Moriya[7] for a pair of ions j and k may permit one to determine the allowed components of $\vec{\mathfrak{D}}_{jk}$ of the antisymmetric exchange term, which henceforth we shall designate H_{DM}. The dipole-dipole interaction H_{dd} has the usual form

$$H_{dd} = g^2\mu_B^2 \sum_{j<k} \left(\frac{\vec{S}_j \cdot \vec{S}_k}{r_{jk}^3} - \frac{3(\vec{S}_j \cdot \vec{r}_{jk})(\vec{S}_k \cdot \vec{r}_{jk})}{r_{jk}^5} \right) . \quad (2)$$

Although the hyperfine interaction can contribute to the second and higher moments, it will ordinarily be smaller than H_{dd} and the anisotropic exchange interactions and will be neglected in this work. The Zeeman interaction for low-symmetry crystals with two inequivalent ions per unit cell can be broken into two components—the first has a g tensor $\frac{1}{2}(\overleftrightarrow{g}_1 + \overleftrightarrow{g}_2)$ which is symmetric and determines the position of the exchange-coupled pair resonance, the second is $\frac{1}{2}(\overleftrightarrow{g}_1 - \overleftrightarrow{g}_2)$ (antisymmetric in the spin operators $\vec{S}_1 - \vec{S}_2$) and this term leads to a field-dependent contribution to the second moment which can produce exchange broadening.[14] This exchange broadening depends on the magnitude of certain off-diagonal components of the g tensor and was considered previously.[11] For small enough magnetic fields, the exchange-broadening terms can be neglected and will not be considered in this analysis.

A. Second Moment

The calculation of the second moment (measured with respect to EPR resonance frequency) of the EPR line-shape function is done with the expression

$$M_2 = -\frac{\mathrm{Tr}[S_x, H - H_{Zeeman}^{sym}]^2}{\mathrm{Tr}(S_x^2)} , \quad (3)$$

where we have subtracted from H that portion of the Zeeman interaction which determines the position of the resonance line. The individual contributions to the commutator take the form

$$[H_{sym\ ex}, S_x] = i \sum_{j<k} (D_{jk} + E_{jk})(S_{jy}S_{kz} + S_{jz}S_{ky}) , \quad (4a)$$

$$[H_{DM}, S_x] = i \sum_{j<k} \mathfrak{D}_{jk,y}(S_{jy}S_{kx} - S_{jx}S_{ky}) + \mathfrak{D}_{jk,z}(-S_{jx}S_{kz} + S_{jz}S_{kx}) , \quad (4b)$$

$$[H_{dd}, S_x] = -3ig_e^2\mu_B^2 \times \sum_{j<k} \frac{(\vec{S}_j \times \vec{r}_{jk})_x(\vec{S}_k \cdot \vec{r}_{jk}) + (\vec{S}_j \cdot \vec{r}_{jk})(\vec{S}_k \times \vec{r}_{jk})_x}{r_{jk}^5} . \quad (4c)$$

In Eq. (4c), the complete dipole-dipole interaction has been employed because we consider the isotropic exchange to be much larger than the Zeeman energy ($J_{jk} \gg \mu_B \vec{H} \cdot \overleftrightarrow{g}_{sym} \cdot \vec{S}$), and therefore the nonsecular terms of H_{dd} will not be averaged to zero. For the case $J_{jk} \ll \mu_B \vec{H} \cdot \overleftrightarrow{g}_{sym} \cdot \vec{S}$, the truncated form of H_{dd} should be used leading to the result

$$[H_{dd}^{trunc}, S_x] = i \sum_{j<k} B_{jk}(S_{jy}S_{kz} + S_{jz}S_{ky}) , \quad (5a)$$

$$B_{jk}=\frac{3g_e\mu_B^2}{2r_{jk}^3}(1-3\cos^2\theta_{jk})\ . \tag{5b}$$

If we add Eqs. (4a)–(4c), square the result, take the traces over the individual spins considering them as completely uncorrelated (high-temperature approximation), and finally employ the relationships

$$\mathrm{Tr}S_{j\alpha}^2=\tfrac{1}{3}S(S+1)(2S+1),\quad \alpha=x,y,\text{ or }z \tag{6a}$$

$$\mathrm{Tr}S_{j\alpha}S_{k\beta}=\delta_{jk}\delta_{\alpha\beta}\mathrm{Tr}S_{j\alpha}^2,\quad \alpha,\beta=x,y,z \tag{6b}$$

$$\mathrm{Tr}S_{j\alpha}S_{j\beta}S_{k\sigma}S_{k\epsilon}=\delta_{\alpha\beta}\delta_{\sigma\epsilon}(\mathrm{Tr}S_{j\alpha}^2)(\mathrm{Tr}S_{k\sigma}{}^2)\ , \tag{6c}$$

then we get for the second moment

$$M_2=\frac{S(S+1)}{N}\left\{\tfrac{2}{3}\sum_{j<k}[\mathfrak{D}_{jk,y}^2+\mathfrak{D}_{jk,z}^2+(D_{jk}+E_{jk})^2 +2B_{jk}(D_{jk}+E_{jk})]+6g_e^4\mu_B^4\sum_{j<k}\frac{(r_{jk}^2-x_{jk}^2)}{r_{jk}^6}\right\}. \tag{7}$$

The last term, designated hereafter $M_{2\mathrm{dd}}$, is just the contribution to M_2 from the complete dipole-dipole interaction found previously by Waller[3] and also given by Cooper and Keffer.[15] Because of the diagonal form of the symmetric anisotropic exchange, the only cross term between $H_{\mathrm{sym\ ex}}$ and H_{dd} is with the truncated part of H_{dd}. Furthermore no cross terms appear between the DM antisymmetric exchange terms and any of the symmetric spin-spin interaction terms. With a knowledge of the positions of the magnetic ions and the various anisotropic exchange parameters, the second moment is readily evaluated.

B. Fourth Moment

The fourth moment is found employing the expression

$$M_4=\frac{\mathrm{Tr}[H-H_{\mathrm{Zeeman}}^{\mathrm{sym}},[H-H_{\mathrm{Zeeman}}^{\mathrm{sym}},S_x]]^2}{\mathrm{Tr}(S_x^2)}\ . \tag{8}$$

The fourth moment represents a tedious calculation involving a large number of terms. In the situation where the DM antisymmetric exchange interaction is the largest anisotropic spin-spin interaction, namely, the regime $J_{jk}\gg|\vec{\mathfrak{D}}_{jk}|\gg D_{jk}$, E_{jk}, and $H_{\mathrm{dd},jk}$, then the largest contribution to the fourth moment will result from the term $[H_e,[H_{\mathrm{DM}},S_x]]^2$. This term will be of order $J^2|\vec{\mathfrak{D}}|^2$. Other terms in M_4 will be of order $J|\vec{\mathfrak{D}}|^3$, J^2D^2, J^2E^2, $J^2H_{\mathrm{dd}}{}^2$, $|\vec{\mathfrak{D}}|^4$, JD^3, etc.; however, all of these terms will be very much smaller than the leading term $[H_e,[H_{\mathrm{DM}},S_x]]^2$. It is noted that the contribution $[H_e,[H_{\mathrm{dd}},S_x]]^2$ to M_4 has been considered by Cooper and Keffer[15] while Van Vleck[3] has considered the contribution $[H_e,[H_{\mathrm{dd}}^{\mathrm{trunc}},S_x]]^2$ to M_4. It should also be noted that the form of the $H_{\mathrm{sym\text{-}ex}}$ contribution to M_4 is exactly the same as the truncated case considered by Van Vleck, and one need only replace B_{jk} [see Eq. (21) of Ref. 3] by $D_{jk}+E_{jk}+B_{jk}$ to take account of the contribution of symmetric anisotropic exchange to M_4. An explicit calculation of $[H_e,[H_{\mathrm{DM}},S_x]]$ yields the expression

$$[H_e,[H_{\mathrm{DM}},S_x]]=\sum_{j<k}\{J_{jk}\mathfrak{D}_{jk,y}[S_{kz}(S_{jx}^2+S_{jy}^2)-S_{jz}(S_{kx}^2+S_{ky}^2)+(S_{kz}-S_{jz})(S_{jx}S_{kx}+S_{jy}S_{ky})] -J_{jk}\mathfrak{D}_{jk,z}[S_{ky}(S_{jx}^2+S_{jz}^2)-S_{jy}(S_{kx}^2+S_{kz}^2)+(S_{ky}-S_{jy})(S_{jx}S_{kx}+S_{jz}S_{kz})]\} +\sum_{\alpha,\beta}{}'\sum_{j<k<m}\{[jkm]_{\alpha,\beta}+[kmj]_{\alpha,\beta}+[mjk]_{\alpha,\beta}\}\ , \tag{9}$$

where $[jkm]_{\alpha,\beta}$ is given by

$$[jkm]_{\alpha,\beta}=\pm S_{j\alpha}(S_{kx}S_{mx}+S_{k\beta}S_{m\beta})[J_{jk}(\mathfrak{D}_{jm,\beta}-\mathfrak{D}_{km,\beta})+J_{jm}(\mathfrak{D}_{jk,\beta}+\mathfrak{D}_{km,\beta})]\ , \tag{10}$$

with the sign convention $\alpha=z,\beta=y$, plus; $\alpha=y$, $\beta=z$, minus (these are the only possibilities when taking commutators with S_x). The other two terms are obtained by permutations of the indices j,k, and m. These last terms, with summations over three different spins, have the same form as those obtained by Van Vleck[3] from the term $[H_e,[H_{\mathrm{dd}}^{\mathrm{trunc}},S_x]]$ except that here we have a summation over two such sets of terms for the two contributing components of $\vec{\mathfrak{D}}$, namely, $\mathfrak{D}_y$ and $\mathfrak{D}_z$. In order that the permuted terms $[kmj]_{\alpha,\beta}$ and $[mjk]_{\alpha,\beta}$ have the same form as $[jkm]_{\alpha,\beta}$, account must be taken of the effect of interchange of indices on the exchange parameter, i.e., $J_{jk}=J_{kj}$ and $\mathfrak{D}_{jk,\alpha}=-\mathfrak{D}_{kj,\alpha}$.

Taking the square of $[H_e,[H_{\mathrm{DM}},S_x]]$, and evaluating the traces using the expressions for $\mathrm{Tr}(S_{j\alpha}^2S_{j\beta}^2)$ and $\mathrm{Tr}(S_{j\alpha}^4)$ given by Van Vleck,[3] one obtains for this dominant contribution to M_4 the result

$$M_4=\frac{S^2(S+1)^2}{N}\left(\tfrac{4}{3}\sum_{j<k}J_{jk}^2(\mathfrak{D}_{jk,y}^2+\mathfrak{D}_{jk,z}^2)\right.$$

$$+\tfrac{1}{9}\sum_{\alpha}{}' \sum_{j<k<m} [(F_{jkm,\alpha})^2+(F_{kmj,\alpha})^2+(F_{mjk,\alpha})^2]\Big), \quad (11)$$

where

$$F_{jkm,\alpha}=J_{jk}(\mathfrak{D}_{jk,\alpha}-\mathfrak{D}_{km,\alpha})+J_{jm}(\mathfrak{D}_{jk,\alpha}+\mathfrak{D}_{km,\alpha}), \quad (12)$$

with α summed over y and z only. Only the squares of the individual terms in Eq. (9) contribute to M_4 since the traces of all cross terms in $[H_e,[H_{\mathrm{DM}},S_x]]^2$ vanish. The spin (S) dependence of all these terms is the same, contrary to what Van Vleck[3] found for $[H_e,[H_{\mathrm{dd}}^{\mathrm{trunc}},S_x]]^2$. These terms do not vanish for any value of S (in Van Vleck's case, the analogous first term $\sum_{j<k}J_{jk}^2B_{jk}^2$ vanished identically for $S=\frac{1}{2}$, and the analogous latter terms vanished if $B_{jk}=B$ independently of the subscripts). In the present case both the two-spin and three-spin terms in Eq. (11) make important contributions to M_4. One can also show that the fourth-moment contribution from $[H_e,[H_{\mathrm{dd}},S_x]]^2$ has a different spin dependence than for the truncated case and will not vanish for $S=\frac{1}{2}$.

C. EPR Linewidth in Terms of Calculated Moments

In the case of very large isotropic exchange, $M_4/M_2^2\gg 3$ and the line shape of the exchange-narrowed EPR line is expected to be Lorentzian except in the extreme wings of the line, where the shape function must fall off more rapidly than a Lorentzian for the moments M_2, M_4, etc., to remain finite. The relationship between the half-intensity frequency half-width $\Delta\nu_{1/2}$ and the moments, in the limit that the exchange frequency $\nu_e=J/h\gg\Delta\nu_{1/2}$, is given by the expression

$$\Delta\nu_{1/2}\simeq CM_2(M_2/M_4)^{1/2}\simeq C'M_2/(J/h)\ , \quad (13)$$

where C and C' are dimensionless constants of order unity. The case usually considered[16] is the cutoff Lorentzian, the cutoff frequency being of order ν_e (the result is insensitive to the exact cutoff frequency as long as the cutoff frequency is very much larger than $\Delta\nu_{1/2}$). The cutoff Lorentzian yields $C=\frac{1}{2}\pi/(3)^{1/2}$. However, this choise is rather arbitrary and certainly is not as realistic a line shape as a Lorentzian times a Gaussian $\{\exp[-(\nu-\nu_0)^2/2\nu_e^2]\}$, or a Lorentzian times a simple exponential $[\exp(-|\nu-\nu_0|/\nu_e)]$. The values of C and C' and also the ratios M_4/M_2 for these different line shapes are shown in Table I. The results indicate an increasing value of C as the line shape drops off more slowly in the wings; however, there is relatively little change in C' with line-shape changes, justifying the simple choice of order M_2/J for the exchange-narrowed linewidth. One means of determining the most appropriate line-shape function is to compare the theoretically calculated value of M_4/M_2 (from the spin Hamiltonian) with the values for the assumed line shape.

TABLE I. Exchange-narrowed EPR linewidth parameters. Line shape $\Delta\nu_{1/2}=CM_2(M_2/M_4)$ and $\Delta\nu_{1/2}=C'(M_2/J)$.

	C	M_4/M_2	C'
Cutoff Lorentzian	$\frac{1}{2}\pi/(3)^{1/2}$	J^2	$\pi/2$
Lorentzian times Gaussian	$(\pi/2)^{1/2}$	J^2	$(\pi/2)^{1/2}$
Lorentzian times exponential	$\pi/(2)^{1/2}$	$2J^2$	$\pi/2$

III. TEMPERATURE DEPENDENCE OF EXCHANGE-NARROWED EPR LINEWIDTH

The paramagnetic resonance linewidth for $Cu(HCOO)_2\cdot 4H_2O$ has been shown previously[11] to have a temperature dependence of the form

$$\Delta H(T)=\alpha+\beta T+\gamma/|T-T_N|^p\ , \quad (14)$$

where the third term is only important near the Néel temperature and apparently results from critical fluctuations near the phase transition. Figure 1 shows the temperature-dependent EPR linewidth measured at 36 GHz for two different crystal axes. The temperature dependence is closely linear from $T=50\,^{\circ}\mathrm{K}$ ($3T_N$) to room temperature. The intercept as $T\to 0$ gives a temperature-independent contribution α, which at 36 GHz contains an 11-Oe contribution due to exchange broadening.[14] It is noted that the slope β is independent of magnetic field between 3 and 20 kOe. A detailed discussion of these EPR linewidth data is given in Ref. 11. In most magnetic crystals with significant exchange narrowing, the EPR linewidth asymptotically approaches some constant value well above T_c and this value is given approximately by M_2/J. This implies $\beta\simeq 0$, i.e., there is no linear temperature dependence. This is the case[17] for MnF_2 and other antiferromagnets. However, for $Cu(HCOO)_2\cdot 4H_2O$ the linear term is almost an order of magnitude larger than the constant term α at room temperature and is the dominant contribution to the linewidth for $T\gg T_N$. The origin of this large linear temperature dependence has been attributed[11] to single-phonon absorption and emission processes which involve spin flips and changes in the exchange energy. These spin flips, which change the exchange energy, result only from the phonon modulation of the DM antisymmetric exchange terms. Employing a model analogous to one used by Statz, Weber, Rimai, Demars, and Koster[18] for the spin-lattice relaxation of Cr^{3+} pairs, the present authors previously[11]

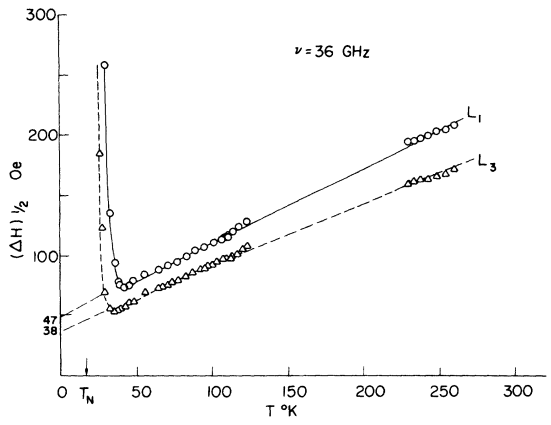

FIG. 1. $\Delta H_{1/2}(T)$ for $Cu(HCOO)_2 \cdot 4H_2O$ for the L_1 and L_3 crystal directions measured at 36 GHz. 11 Oe results from exchange broadening and must be subtracted to obtain the field-independent linewidth. The linewidth extrapolated to $T = 0$ °K from the paramagnetic range $kT > J$ represents the temperature-independent exchange-narrowed linewidth.

derived an expression for the linewidth temperature dependence due to a lifetime limitation (an effective T_2) of spin states resulting from spin flips between states differing in energy by J. We note that the single-phonon process (which in this case is independent of magnetic field and involves phonons of frequency J/h) dominates over two-phonon Raman processes at temperatures of order $T \sim \Theta_D$ because of the very large density of phonon states $[\rho_\nu(\nu = J/h)]$ for $J \sim 71$ °K. The author's expression[11] for the magnetic field half-width (Lorentzian line shape, $\Delta H = 1/\gamma T_{2\,\mathrm{eff}}$) is given by

$$\Delta H_{\mathrm{linear}\,T} \simeq \frac{4}{9}\frac{z}{g\mu_B}\frac{(\lambda R)^2|\vec{\mathfrak{D}}^2|J^2}{\rho\hbar^3}\left\langle\frac{1}{c_t^5}+\frac{2}{3}\frac{1}{c_l^5}\right\rangle_\Omega kT\,, \tag{15}$$

where z is the number of independent copper pairs (magnetic coordination number) formed by an individual copper ion, R is the distance between nearest-neighbor copper ions, λ results from the change of J with copper ion separation, i.e., $\partial J/\partial r \sim \lambda J$, ρ is the crystal density, and the quantity in brackets is the angular average of the usual function of phonon velocities for a single-phonon process. We emphasize that Eq. (15) is only an estimate of this process and note that correlation effects between different pairs of spins have been neglected.

IV. CASE OF $Cu(HCOO)_2\ 4H_2O$

The layerlike $Cu(HCOO)_2 \cdot 4H_2O$ is monoclinic[19] (type $P2_1/a$, with $a = 8.18$ Å, $b = 8.15$ Å, and $c = 6.35$ Å) in which layers of water molecules lie between the layers of copper and formate ions in the a-b plane. However, the planes of the individual formate molecule ions are tilted out of the a-b plane in a complex manner. Thus none of Moriya's symmetry rules[7] can be applied to find the vector direction of $\vec{\mathfrak{D}}_{jk}$ with respect to $\vec{R}_{jk}$ (the vector joining the neighboring jth and kth copper ions in the a-b plane) and two directions orthogonal to $\vec{R}_{jk}$, one in the a-b plane and one normal to the a-b plane. Although for the crystal in the antiferromagnetic state the b axis is a twofold axis and $\vec{\mathfrak{D}}_{\mathrm{unit\ cell}} \perp b$ axis, no such statement can be made about the individual $\vec{\mathfrak{D}}_{jk}$. The strong superexchange interaction between copper ions is via the formate ions and it is thought that the exchange interaction between copper ions in different layers is negligible. This belief is supported by the temperature dependence of the susceptibility,[8,9] which suggests two-dimensional long-range ordering below 65 °K.

The simplified model we employ is one of independent noninteracting layers, each layer considered to be a face-centered square array of Cu^{++} ions (see Fig. 2), with only nearest-neighbor exchange

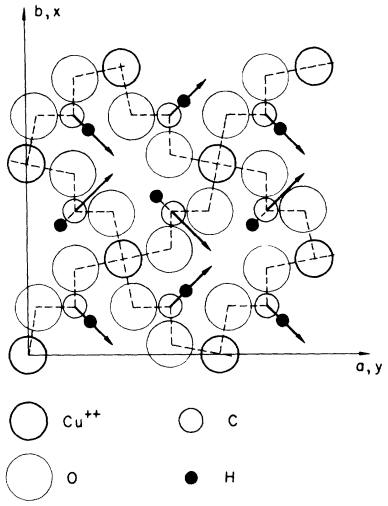

FIG. 2. Approximate model of the antisymmetric exchange vectors, $\vec{\mathfrak{D}}_{jk}$, for $Cu(HCOO)_2 \cdot 4H_2O$. The Cu^{++} ions lie in the basal (001) a-b plane in a face-centered array. The formate ions $(HCOO)^-$ are actually tilted out of the a-b plane and are projected here on the a-b plane. They are also tilted about the H-C axis, but this is neglected in this approximate model. Along a face diagonal, the $\vec{\mathfrak{D}}_{jk}$ are shown to have the same direction and the z components of the $\vec{\mathfrak{D}}_{jk}$ are all in the same direction (this choice is arbitrary depending on the indices; they could alternate parallel-antiparallel if the subscripts of every other $\vec{\mathfrak{D}}_{jk}$ along the face diagonal were interchanged since $\vec{\mathfrak{D}}_{jk} = -\vec{\mathfrak{D}}_{kj}$). This choice makes no difference in calculating the moments in the paramagnetic regime but does affect the calculation of $\vec{\mathfrak{D}}_{\mathrm{unit\ cell}}$ ($\vec{\mathfrak{D}}_{\mathrm{unit\ cell}} = \sum_{k=1}^{4} \vec{\mathfrak{D}}_{jk}$ for nearest-neighbor exchange only) present in the two-sublattice antiferromagnet. For the antiferromagnet, $\vec{\mathfrak{D}}_{\mathrm{unit\ cell}}$ is perpendicular to the twofold b axis.

between Cu^{++} ions in the same layer. Formate ions along a given face diagonal will be considered to be tilted in such a way that the $\vec{\mathfrak{D}}_{jk}$ along this diagonal are parallel (with $|\mathfrak{D}_{jk,x}| = |\mathfrak{D}_{jk,y}|$, which is probably a fairly good approximation of the actual case). The individual $\vec{\mathfrak{D}}_{jk}$ are such that for the unit cell the component of $\vec{\mathfrak{D}}_{\text{unit cell}}$ vanishes along the twofold b axis ($\vec{\mathfrak{D}}_{\text{unit cell}} = \sum_{nn=1}^{z} \vec{\mathfrak{D}}_{jk}$).

Employing Eq. (7), the second moment is found to be

$$M_2 \simeq \tfrac{2}{3} z S(S+1)[\mathfrak{D}_y^2 + \mathfrak{D}_z^2] + \cdots , \tag{16}$$

where z is the magnetic coordination number, while $\mathfrak{D}_y^2 = |\mathfrak{D}_{jk,y}|^2$ and $\mathfrak{D}_z^2 = |\mathfrak{D}_{jk,z}|^2$, the magnitude being the same for all j and k which are nearest neighbors and zero for all other pairs. Similarly the largest term in the fourth moment is shown to have the form

$$M_4 \simeq \tfrac{4}{3} z[S(S+1)]^2 J^2 (\mathfrak{D}_y^2 + \mathfrak{D}_z^2)[1 + \tfrac{1}{6}(z-1)] + \cdots , \tag{17}$$

in which the $\frac{1}{6}(z-1)$ contribution arises from the three-spin interaction terms $F_{jkm,\alpha}$ and $F_{mjk,\alpha}$. The middle term, $F_{kmj,\alpha}$, is the only term in Eq. (11) which can produce destructive or constructive interference, and it has the form $F_{kmj,\alpha} = J(-\mathfrak{D}_{jk,\alpha} + \mathfrak{D}_{km,\alpha})$ when the exchange interaction is restricted to nearest-neighbor Cu^{++} ions. For our simple model shown in Fig. 1, the middle terms are zero for $\alpha = y$ and z (however, these terms give a contribution $32 J^2 \mathfrak{D}_x^2$ for $\alpha = x$).

The ratio M_4/M_2 found from Eqs. (16) and (17) will be $3S(S+1) J^2$ which becomes $\frac{9}{4} J^2$ for the Cu^{++} case ($S = \frac{1}{2}$). This value is closest to the value given in Table I for a line-shape function of a Lorentzian times an exponential. Moreover, this line shape would seem more realistic than a simple cutoff Lorentzian. However, the results for the EPR linewidth are insensitive to the precise form of the line shape (or cutoff frequency) when $J^2 >>> M_2$, which is certainly the case for $Cu(HCOO)\cdot 4H_2O$.

Using Eqs. (13) and (17), setting $(\mathfrak{D}_y^2 + \mathfrak{D}_z^2) \sim \frac{2}{3}|\vec{\mathfrak{D}}|^2$ and $S = \frac{1}{2}$, one finds the exchange-narrowed temperature-independent magnetic field half-width for $Cu(HCOO)_2\cdot 4H_2O$ to be

$$\Delta H_{\text{ex-n}}(\text{"}T\text{"} \to 0) \approx \frac{\pi}{6} \frac{z}{g\mu_B} \frac{|\vec{\mathfrak{D}}|^2}{J} . \tag{18}$$

The ratio of the one-phonon temperature-dependent linewidth to the exchange-narrowed temperature-independent linewidth is of order

$$\frac{\Delta H_{\text{linear-}T}}{\Delta H_{\text{ex-n}}(\text{"}T\text{"} \to 0)} \approx \frac{24}{9\pi} \frac{(\lambda R)^2}{\rho c_{\text{eff}}^5} \left(\frac{J}{\hbar}\right)^3 kT . \tag{19}$$

This ratio[20] is independent of the DM interaction and thereby provides a useful check on the experimental results since all the quantities in (19) are known (or can be estimated) except c_{eff}.

From the formula for the half-intensity width $\Delta H_{1/2} \simeq (\pi/2g\mu_B)(M_2/J)$, the magnitude of M_2 can be found. Using $J \simeq 71.5\,^{\circ}\text{K}$ (1.06×10^6 Oe) and $\langle \Delta H_{1/2}(\text{"}T\text{"} \to 0)\rangle_{\text{av}} \approx 31$ Oe, (see Fig. 5 and Table 3 of Ref. 11) a value $M_2/g^2\mu_B^2 \simeq 9.6\times10^6\ \text{Oe}^2$ is found. An explicit calculation of the dipole-dipole contribution to M_2 [see the last term in Eq. (7)] yields $M_{2\text{dd}}/g^2\mu_B^2 \simeq 8\times10^4\ \text{Oe}^2$. $M_{2\text{dd}}$ is more than two orders of magnitude too small to account for the temperature-independent exchange-narrowed paramagnetic linewidth (the value extrapolated to zero temperature from the paramagnetic regime). Using Eq. (16), an estimate of $|\vec{\mathfrak{D}}_{jk}|$ can be made [$|\vec{\mathfrak{D}}_{jk}|^2$ approximated by $\frac{3}{2}(\mathfrak{D}_y^2 + \mathfrak{D}_z^2)$] and one obtains $|\vec{\mathfrak{D}}_{jk}|/g\mu_B \simeq 2700$ Oe.

If we employ Eq. (19) and the experimental ratio $\Delta H_{1/2}(T)/\Delta H_{1/2}(\text{"}T\text{"} \to 0)$, an estimate of the sound velocity c_{eff} can be found since J and ρ are known and λR can be estimated.[21] Using $J \simeq 71.5\,^{\circ}\text{K}$, $\rho = 1.81\ \text{g/cm}^3$, $\lambda R = 10$ (Ref. 21), and $\langle \Delta H_{1/2}(T)/\Delta H_{1/2}(\text{"}T\text{"} \to 0)\rangle_{\text{av}} = 0.018\,T$, one finds $c_{\text{eff}} \simeq 1.8\times10^5$ cm/sec, which is a reasonable transverse velocity of sound for this crystal. The ratio $\Delta H_{1/2}(T)/\Delta H_{1/2}(\text{"}T\text{"} \to 0)$ is independent of $|\vec{\mathfrak{D}}|$ since both these quantities are closely proportional to $|\vec{\mathfrak{D}}|^2$. Lack of experimental knowledge of the individual $|\vec{\mathfrak{D}}_{jk}|$ and c_{eff} makes it difficult to calculate the individual values $\Delta H_{1/2}(T)$ and $\Delta H_{1/2}(\text{"}T\text{"} \to 0)$. Nevertheless, the ratio of these two quantities is consistent with the very large value of J, which also suggests that $|\vec{\mathfrak{D}}_{jk}|$ should be large. If one argues that the three-dimensional antiferromagnetic ordering at $17\,^{\circ}\text{K}$ suggests a value $J_{jk} \simeq 3kT_N/2zS(S+1)$ (or $J_{jk} \simeq 8.5\,^{\circ}\text{K}$), which is an eightfold reduction over the value suggested by the two-dimensional ordering, one finds c_{eff} reduced by a factor 3.5 which appears somewhat small for a transverse sound velocity. Even with this smaller estimate for J, the value of $M_{2\text{dd}}$ is still a factor of 14 too small to account for $\Delta H_{1/2}(\text{"}T\text{"} \to 0)$. We therefore conclude the best over-all fit to the static susceptibility temperature data and the EPR linewidth data is given by the large-J value inferred from the two-dimensional ordering occurring below $65\,^{\circ}\text{K}$. It is necessary to include large antisymmetric exchange contributions to M_2 to account for the magnitude of the exchange-narrowed EPR linewidth.

The ratio $|\vec{\mathfrak{D}}|/J$ inferred from the above analysis is ~ 0.005, more than a factor of 20 smaller than one would obtain from Moriya's estimate, namely, $|\vec{\mathfrak{D}}| \sim (\Delta g/g)J$. In fact Moriya's estimates for D and E [D and $E \sim (\Delta g/g)^2 J$] might appear to make them large enough to account for the magnitude of M_2. However, our AFMR study[10] suggests values of H_{DM}—an antisymmetric canting field ($H_{\text{DM}} = \mathfrak{D}_{uc,z} \times \langle S\rangle/2\mu_B$)—of order 12×10^3 Oe and of H_K—the axial

TABLE II. Copper salts which show unusual linewidths.

Salt	T_N (°K)	J (°K)	$(M_{2dd}^{trunc})^{1/2}$ (Oe)	$\frac{\pi}{2g\mu_B}\frac{M_{2dd}}{J}$ (Oe)	Expt ΔH(Oe) 300 °K	77 °K
$Cu(HCOO)_2 \cdot 4H_2O$ (Ref. 11)	17	71.5	187[a]	0.2	165	62[b]
$CuSO_4$[c]	35	33.6	570[a]	4.3	...	3460[b]
CuF_2[d]	69	34	1130[a]	16.7	498[e]	...
$CuCl_2 \cdot 2DMSO$[f]	...	> 0.07	147[a]	< 139	173	65[b] (90 °K)

[a]Only the isotropic average value is given.

[b]Data given are along a representative direction and similar behavior is observed in other principal directions.

[c]J. S. Wells, L. M. Matarresse, and D. J. Sukle, J. Chem. Phys. 47, 2259 (1967).

[d]R. J. Joenk and R. M. Bozorth, J. Appl. Phys. 36, 1167 (1965).

[e]F. W. Lancaster and W. Gordy, J. Chem. Phys. 19, 1181 (1951).

[f]T. R. Reddy and R. Srinivasan, J. Chem. Phys. 45, 2714 (1966).

anisotropy field ($H_K = D_{uc}\langle S\rangle/2\mu_B$)—of order 500 Oe, with an even smaller value for the rhombic field $H_{K'}$ ($H_{K'} = E_{uc}\langle S\rangle/2\mu_B$). These results are somewhat open to question because of the difficulty in obtaining all the exchange tensor parameters from the AFMR analysis. However, these results support the hypothesis that $|\vec{\mathfrak{D}}_{jk}| \gg \mathfrak{D}_{jk}$ and E_{jk}. All of these quantities are more than an order of magnitude smaller than given by Moriya's estimates. One possible reason for this is that the exchange integrals involving excited-state orbitals are much smaller than those for the ground-state orbitals.

V. DISCUSSION AND CONCLUSIONS

The results and analysis above indicate that for $Cu(HCOO)_2 \cdot 4H_2O$ the usual ideas on the exchange-narrowed EPR linewidth need to be extended to take account of transitions between states of different exchange energy (differing in energy by J, $2J$, etc.) resulting from phonon modulation of the DM interaction. The large values of J and $\vec{\mathfrak{D}}$ for $Cu(HCOO)_2 \cdot 4H_2O$ lead to the large linear temperature dependence of the EPR linewidth. The idea of a constant exchange-narrowed EPR linewidth for $T \gg T_N$ is not valid in this case. In the moment analysis as applied to exchange narrowing, one calculates moments in the high-temperature limit which amounts to neglecting spin correlations or neglecting other terms in a series expansion[22] (expansion parameter $1/kT$), i.e., the moments correspond to the infinite-temperature limit. With strong exchange present, the expansion will be valid for $kT > J$.[22] However, this approach has not included the possibility of phonon-induced spin-flip transitions. Consequently, what is meant here by the temperature-independent exchange-narrowed EPR linewidth is the extrapolation back to $T = 0$ °K of the EPR linewidth from the paramagnetic region where $kT > J$. Whenever $\Delta H_{1/2}(T)$ in the paramagnetic regime is not constant, but contains field-independent linear temperature-dependent terms as discussed in Sec. III (or also a temperature dependence resulting from spin-lattice relaxation), it is not correct to take the usual exchange-narrowed linewidth as the high-temperature value; instead one should use the "T" → 0 extrapolated value for the linewidth $\frac{1}{2}\pi(M_2/J)$.

$Cu(HCOO)_2 \cdot 4H_2O$ may seem to be an extreme case because of the large J and $|\vec{\mathfrak{D}}|$ values. Although it is an unusually favorable case for observing the behavior discussed above, there are probably many other cases, particularly in copper salts with strong superexchange, where the DM antisymmetric exchange interaction may either contribute to the second moment and the temperature-independent exchange-narrowed EPR linewidth, or to a temperature-dependent linewidth through phonon modulation of the DM interaction. Table II lists a number of salts which show temperature-dependent linewidths (which we believe not to be due to spin-lattice relaxation[23] of the usual type), and/or which show linewidths significantly broader than $\frac{1}{2}\pi M_{2dd}/J$. While much additional work would be required (as in Ref. 11) to prove that the DM interaction was contributing to the EPR linewidth for these salts, it seems likely that antisymmetric exchange will play a role for some of these cases.

Recent work[24] on the exchange-narrowed EPR linewidths of MnF_2, $KMnF_3$, and $RbMnF_3$ has shown experimental exchange-narrowed linewidths more than a factor of 2 larger than the theoretically calculated exchange-narrowed linewidths using well-established exchange constants and values of M_{2dd}. The much smaller J values and the negligibly small g shifts for Mn^{++} in these salts suggest that the DM interaction is much too small to contribute significantly to the EPR linewidth in these cases. In fact, a possible explanation for these discrepancies,

taking into account the non-Lorentzian shape of the wings of the line and employing M_2, M_4, and M_6 has been given.[25] We note, however, that in rutile-structure crystals like MnF_2, the symmetry is such that $\vec{\mathfrak{D}}_{k \text{ unit cell}} = \sum_j^s \vec{\mathfrak{D}}_{jk} = 0$. The DM interaction resulting from nearest-neighbor exchange will not affect the AFMR modes of the antiferromagnetic phase, but can contribute in principle to the EPR linewidth.

Hitherto, the DM antisymmetric exchange interaction has only been considered to influence the properties of magnetic crystals in the ordered state. This work indicates that antisymmetric exchange can contribute to the second, fourth, and higher moments, and thus to the exchange-narrowed EPR linewidth in the paramagnetic state. For $Cu(HCOO)_2 \cdot 4H_2O$, antisymmetric exchange makes the dominant contribution to the second moment and the EPR linewidth. Although no other cases have been confirmed yet, there are other paramagnetic salts exhibiting strong superexchange where antisymmetric exchange may well contribute to the EPR linewidth.

ACKNOWLEDGMENT

The authors are grateful for a private communication from Dr. P. Richards concerning this work.

*Work supported in part by the U. S. Atomic Energy Commission.

†Present address: Department of Physics, West Virginia University, Morgantown, W. Va.

[1]P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).

[2]R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).

[3]The second moment resulting from the dipole-dipole interaction was first calculated by I. Waller, Z. Physik 79, 370 (1932). A detailed analysis of the moment method taking account of dipolar broadening was given by J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[4]Several authors have mentioned this possibility. See, for example, F. Keffer, Phys. Rev. 88, 686 (1952); B. R. Cooper and F. Keffer, *ibid.* 125, 896 (1962); A. J. Henderson and R. N. Rogers, *ibid.* 152, 218 (1966); R. N. Rogers, F. Carboni, and P. M. Richards, Phys. Rev. Letters 19, 1016 (1967).

[5]Anderson and Weiss (Ref. 1) and Van Vleck (Ref. 3) note that additional broadening may result from fine-structure terms. These will not play a role for $S = \frac{1}{2}$ ions.

[6]Crystals which do not have inversion symmetry with respect to the point midway between superexchange-coupled ions.

[7]I. Dzialoshinsky, J. Phys. Chem. Solids 4, 241 (1958); T. Moriya, Phys. Rev. Letters 4, 228 (1960); Phys. Rev. 120, 91 (1960).

[8]R. B. Flippen and S. A. Friedberg, J. Chem. Phys. 38, 2652 (1963); H. Kobayashi and T. Haseda, J. Phys. Soc. Japan 18, 541 (1963).

[9]M. S. Seehra, Phys. Letters 28A, 754 (1969).

[10]M. S. Seehra and T. G. Castner, Jr., Phys. Rev. B 1, 2289 (1970).

[11]M. S. Seehra and T. G. Castner, Jr., Physik Kondensierten Materie 7, 185 (1968).

[12]Fine-structure terms do not contribute for the $S = \frac{1}{2}$ case, namely, for Cu^{++} ions.

[13]Biquadratic terms have also been observed. See E. A. Harris and J. Owen, Phys. Rev. Letters 11, 9 (1963); D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, *ibid.* 11, 10 (1963). For $S = \frac{1}{2}$ ions, these terms would just be constants and need not be included in Eq. (1).

[14]M. Yokota and S. Koide, J. Phys. Soc. Japan 9, 953 (1954).

[15]B. R. Cooper and F. Keffer, Phys. Rev. 125, 896 (1962).

[16]See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, England, 1961), p. 436.

[17]See M. S. Seehra and T. G. Castner, Jr., Solid State Commun. 8, 787 (1970).

[18]H. Statz, M. J. Weber, L. Rimai, G. A. Demars, and G. F. Koster, J. Phys. Soc. Japan 17, 430 (1962).

[19]R. Kiriyama, H. Ibamoto, and K. Matsuo, Acta Cryst. 7, 482 (1954).

[20]Using general spin-spin correlation-function arguments, including the effect of phonon modulation of these spin-spin correlation functions, P. Richards (private communication) has calculated the same ratio $\Delta H_{\text{linear-}T}/\Delta H_{\text{ex-n}}(\text{"}T\text{"} \to 0)$ given in Eq. (19) with a slightly different numerical coefficient $(3/\pi^{3/2})$. However, the DM interaction was not an essential feature of this calculation.

[21]This results from the $\frac{10}{3}$ law for the volume dependence of superexchange for many antiferromagnets; see D. Bloch, J. Phys. Chem. Solids 27, 881 (1966).

[22]See G. E. Pake, *Paramagnetic Resonance* (Benjamin, New York, 1962), Sec. 7-2.

[23]The temperature dependence of two-phonon spin-lattice relaxation processes which ordinarily dominate for $T > 0.1\ \Theta_D$ approaches T^2 for $T \sim \Theta_D$ and is much stronger for T well below Θ_D. The data concerning the temperature dependence of the linewidths given in Table II are too meager to make any conclusive statements, but there appears to be a weaker dependence than predicted by two-phonon spin-lattice relaxation processes.

[24]J. E. Gulley, B. G. Silbernagel, and V. Jaccarino, J. Appl. Phys. 40, 1318 (1969); Phys. Letters 29A, 657 (1969).

[25]J. E. Gulley, Daniel Hone, D. J. Scalapino, and B. G. Silbernagel, Phys. Rev. B 1, 1020 (1970).