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Second-order effects of magnetic hyperfine interaction on NMR spectra in the $M_2CuX_4 \cdot 2H_2O$ compounds. I. Pseudoquadrupolar interaction

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The nuclear pseudoquadrupolar interaction is one of the less known and, until now, never observed peculiar effects in magnetic materials that arise from the magnetic coupling between nuclear spins and electron spins. In this paper the experimental observation of this interaction is presented for ^{17}O in $Rb_2CuCl_4 \cdot 2H_2O$ and isomorphous compounds. A short theoretical description of the pseudoquadrupolar interaction is given that is in full agreement with experiment.

I. INTRODUCTION

During the last few years an extensive nuclear-magnetic-resonance study has been carried out on the series of isomorphous ferromagnetic compounds with the $M_2CuX_4 \cdot 2H_2O$ composition (MX stands for KCl, NH_4Cl, CsCl, NH_4Br, and RbBr, respectively). The aim of these investigations is to determine the magnetic and electric quadrupolar interactions of all nuclei. From the values of these interactions a spatial distribution of unpaired spins and charges is calculated that can be related to the superexchange interaction. Since all compounds in this series contain the same magnetic ion, the influence of the diamagnetic ligands on the superexchange can be studied in particular.

In the course of these experiments we observed in the NMR spectra of those ligand nuclei which have a large transferred hyperfine coupling a few remarkable features. In one of our foregoing papers[1] we mentioned a complicated fine structure in some chlorine resonance lines. Several possible origins for this line splitting were suggested, but none of them was found to give a complete explanation of the observed features.

Recently, we reported on the ^{17}O hyperfine interaction in these compounds.[2] We observed that the angular dependence of the quadrupolar splittings in the ^{17}O NMR spectrum ($I = \frac{5}{2}$) cannot be described on the basis of the usual nuclear spin Hamiltonian in which the magnetic hyperfine interaction between the nuclear spin and the electron spin is approximated by its time-averaged value. In the present paper we will show that a correct treatment of the full hyperfine coupling gives rise to a pseudoquadrupolar interaction. This interaction, together with the normal electric quadrupolar interaction, describes accurately the observed "quadrupolar" splittings in the ^{17}O NMR spectra.

Apart from this pseudoquadrupolar interaction an indirect coupling between nuclear spins is found to exist. The (super)hyperfine interactions and the exchange coupling in the $M_2CuX_4 \cdot 2H_2O$ compounds are such that in a large field region the indirect coupling leads to a discrete fine structure of the NMR lines rather than to a line broadening as originally described by Suhl and Nakamura.[3,4] This fine structure will be the subject of Paper II.

II. PSEUDOQUADRUPOLAR INTERACTION

The physical origin of the pseudoquadrupolar interaction is essentially the same as that of the Suhl-Nakamura line broadening. Theories on this subject always consider a saturated (anti)ferromagnet, in which the properties of the electric-spin system are described in the spin-wave approximation. The experiments presented here are carried out in an external field, larger than the exchange field $J/g\mu_B$. As a consequence, in a first approximation, the electron spins may be regarded as isolated spins. A sketch of the derivation of the pseudoquadrupolar interaction will therefore be given, starting with a simple (paramagnetic) system of one electron spin and one nuclear spin, which may belong either to the magnetic ion or to a ligand. Subsequently, the influence of the exchange interaction is discussed.

The spin Hamiltonian of a system consisting of one electron spin $S = \frac{1}{2}$ and one nuclear spin $I > \frac{1}{2}$ in a magnetic field is represented by

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{SI} + \mathcal{H}_I + \mathcal{H}_Q \ , \qquad (1)$$

where $\mathcal{H}_S = \overleftrightarrow{g}\mu_B \cdot \vec{H} \cdot \vec{S}$ is the Zeeman energy of the electron spin and $\mathcal{H}_{SI} = \vec{I} \cdot \overleftrightarrow{A} \cdot \vec{S}$ is the (transferred) hyperfine interaction between $\vec{I}$ and $\vec{S}$. $\mathcal{H}_I = \gamma_I \hbar \vec{H} \cdot \vec{I}$ is the Zeeman energy of the nuclear spin and

$$\mathcal{H}_Q = \tfrac{1}{6}\nu_Q[3I_z^2 - I(I+1) + \tfrac{1}{2}\eta(I_+^2 + I_-^2)]$$

is the nuclear quadrupolar interaction in the electric field resulting from the charge distribution in the crystal.

The electron Zeeman term $\mathcal{H}_S$ is as a rule much larger than the hyperfine term $\mathcal{H}_{SI}$. Therefore, usually the components of the hyperfine interaction perpendicular to the external field are omitted in the description of NMR spectra. To calculate the effects of these terms, the Hamiltonian (1) is written in the form

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}' ,$$

where

$$\mathcal{H}^0 = g_{zz}\mu_B H S_z + I_z A_{zz} S_z + \mathcal{H}_I + \mathcal{H}_Q \tag{2}$$

is the unperturbed Hamiltonian, which is diagonal in S_z, and

$$\mathcal{H}' = \tfrac{1}{4}(A_{xx}+A_{yy})(I_+S_- + I_-S_+) + \tfrac{1}{4}(A_{xx}-A_{yy})(I_+S_+ + I_-S_-) \tag{3}$$

is the perturbation due to the nondiagonal elements of H_{SI}. The external field H is applied along the z principal axis of $\overline{A}$. According to second-order perturbation theory, the correction to the unperturbed energy $E^{(0)}_{m_S,m_I}$ of $\mathcal{H}^0$ due to $\mathcal{H}'$ is given by the general expression

$$E^{(2)}_{m_S,m_I} = \sum_{m_S' \neq m_S}\ \sum_{m_I' \neq m_I} \frac{\langle m_S m_I|\mathcal{H}'|m_S' m_I'\rangle \langle m_S' m_I'|\mathcal{H}'|m_S m_I\rangle}{E^{(0)}_{m_S' m_I'} - E^{(0)}_{m_S m_I}} . \tag{4}$$

The Cu^{2+} ions have an electron spin $S = \frac{1}{2}$. The ground state of the electron-spin system is then characterized by $m_S = -\frac{1}{2}$, and the sum over m_S' involves only one term, i.e., $m_S' = +\frac{1}{2}$. The nonzero elements in Eq. (4) are proportional to

$$\sum_{m_I'} \langle m_I|I_\alpha|m_I'\rangle \langle m_I'|I_\beta|m_I\rangle = \langle m_I|I_\alpha I_\beta|m_I\rangle ,$$

where I_α and I_β stand for $I_\pm$. These matrix elements can be regarded as the diagonal elements of an effective nuclear Hamiltonian

$$\mathcal{H}_I^{\text{eff}} = [(A_{xx}+A_{yy})^2 I_+I_- + (A_{xx}-A_{yy})^2 I_-I_+ + (A_{xx}^2 - A_{yy}^2)(I_+^2 + I_-^2)](4g_{zz}\mu_B H)^{-1} .$$

Here, it has been assumed that $g_{zz}\mu_B H >> A_{zz}$. Noting that $I_\pm = I_x \pm iI_y$, $\mathcal{H}_I^{\text{eff}}$ can be rewritten in the form

$$\mathcal{H}_I^{\text{eff}} = h' I_z + \tfrac{1}{6}\nu_Q'[3I_z^2 - I(I+1) + \tfrac{1}{2}\eta'(I_+^2 + I_-^2)] ,$$

with

$$\begin{aligned} \nu_Q' &= -4\Delta(A_{xx}^2 + A_{yy}^2) , \\ \eta' &= -3(A_{xx}^2 - A_{yy}^2)(A_{xx}^2 + A_{yy}^2)^{-1} , \\ h' &= 2\Delta A_{xx}A_{yy} , \\ \Delta &= (16 g_{zz}\mu_B H)^{-1} . \end{aligned} \tag{5}$$

The term $h'I_z$ gives a small correction to the nuclear Larmor frequency $\nu_L = (\gamma_I/2\pi)H + (1/h)A_{zz}m_S$, which follows from the unperturbed Hamiltonian (2). The second term in Eq (5) has been expressed in the form of an electric quadrupolar interaction. As it is, however, of magnetic origin, we call it a pseudoquadrupolar interaction. Since ν_Q' and η' depend on the components of $\overline{A}$ perpendicular to the external field, the pseudoquadrupolar interaction depends on the direction of the external field with respect to the crystal. Because of the field dependence of Δ, also the magnitude of ν_Q' depends on the strength of H. These effects distinguish the pseudoquadrupolar interaction from the electric quadrupolar interaction which depends only on the charge distribution in the lattice.

Now we extend the calculation to a ferromagnetic system. Then the electron spins are exchange coupled and expression (2) for the unperturbed Hamiltonian becomes

$$\mathcal{H}^0 = \sum_{i,j} J_{ij}\vec{S}^i \cdot \vec{S}^j + \sum_i g_{zz}\mu_B H S_z^i + \sum_i I_z^i A_{zz} S_z^i + \sum_i \mathcal{H}_I^i + \sum_i \mathcal{H}_Q^i . \tag{6}$$

To keep the calculations simple, it is assumed that each nuclear spin I^i is coupled to only one electron spin, which is usually a good approximation for the compounds discussed here. At sufficiently low temperature, where the magnetization is nearly saturated even in a weak field, the electron-spin system can be described by a spin wave or excitation model. The ground state is now the state with no spin waves. The lowest excited states are the states with one spin wave of wave vector $\vec{k}$. The correction $E^{(2)}$ to the ground-state energy $E^{(0)}$ due to $\mathcal{H}'$ is calculated in a similar way as before. In formula (4) the sum over m_S' is now replaced by the sum over all wave numbers $\vec{k}$ in the first Brillouin zone of the reciprocal lattice. The effective Hamiltonian $\mathcal{H}_I^{\text{eff}}$ still has the same form (5), but now Δ is replaced by

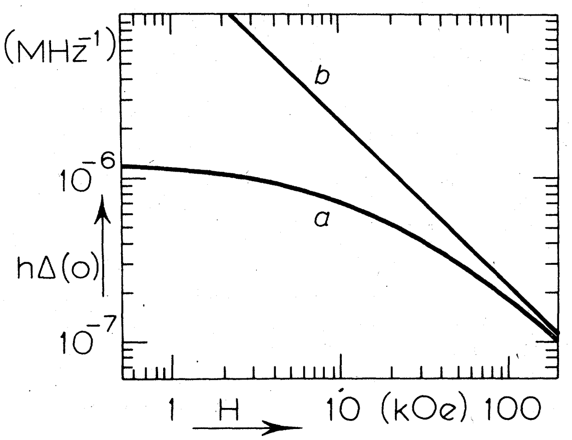

FIG. 1. Calculated field dependence of $h\Delta(0)$ for $T_c = 1$ K. The straight line b represents $\Delta = (16g\mu_B H)^{-1}$ with $g = 2$.

$$\Delta(0) = \left[\sum_{\vec{k}} 16N\omega_{\vec{k}}\right]^{-1} . \qquad (7)$$

Here N is the number of wave vectors in the first Brillouin zone and $\hbar\omega_{\vec{k}}$ is the energy of a spin wave with wave vector $\vec{k}$. In Fig. 1 the field dependence of $h\Delta(0)$ is shown by curve a (h is Planck's constant), calculated by a numerical evaluation of the summation over $\vec{k}$. Only nearest-neighbor exchange interaction has been assumed, which leads to

$$\omega_{\vec{k}} = 2JS\left[z - \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}\right] + g_{zz}\mu_B H .$$

The summation over $\vec{\delta}$ runs over the z nearest-neighbor vectors. To obtain a value for J from the transition temperature T_c, the result of the high-temperature series calculation by Swendsen has been used, i.e., $k_B T_c/J = 2.603$.[5] It can be seen from Fig. 1 that in the high-field limit, $g\mu_B H >> J$, the ideal paramagnetic case is obtained again, and $\Delta(0)$ tends to $\Delta = (16g_{zz}\mu_B H)^{-1}$ as already found in Eq. (5). In Fig. 1 the field dependence of $h\Delta$ is represented by the straight line (b). The effect of the exchange coupling is thus to reduce the pseudoquadrupolar interaction compared to the paramagnetic situation, expecially in a low field.

III. EXPERIMENTAL EVIDENCE OF PSEUDOQUADRUPOLAR INTERACTION

In general, the pseudoquadrupolar interaction is small. Only when the magnetic hyperfine interaction contains one or more large components the pseudoquadrupolar interaction cannot be ignored. However, in such a situation, as will be shown in Paper II, usually also a large line broadening due to a Shul-Nakamura interaction arises, which makes the determination of the pseudoquadrupolar interaction inaccurate or even impossible. In the $M_2CuX_4\cdot 2H_2O$ compounds, the ^{17}O hyperfine interaction is rather large compared to the quadrupolar interaction. In Table I the experimental results from Ref. 2 are given for two compounds, both obtained at $T = 1.22$ K and $H = 5.8$ kOe. In Paper II it will be shown that at this temperature and in this field the ^{17}O lines are hardly broadened by indirect interactions. The ^{17}O NMR spectrum consists of five lines ($I = \frac{5}{2}$).

In Ref. 2 it is discussed that the frequency difference between the outer satellite lines ($\nu_5 - \nu_1$), when due to the electric quadrupolar interaction only, can be approximated by the well-known first-order expression

$$\nu_5 - \nu_1 = 2\nu_Q(3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi) . \qquad (8)$$

The values of $\nu_5 - \nu_1$, observed with the total magnetic field directed along the three principal axes of

TABLE I. ^{17}O magnetic and quadrupolar interaction parameters. X, Y, and Z are the principal axes of the EFG tensor.

	i	$\frac{1}{2h}A_{ii}$ (MHz)	$(\nu_5 - \nu_1)_i$ (MHz)		
$Rb_2CuCl_4\cdot 2H_2O$	x	44.44	−1.26[a]	0.14[b]	−1.40[c]
	y	32.70	−3.33[a]	0.18[b]	−3.51[c]
	z	32.95	5.14[a]	0.18[b]	4.96[c]
$Rb_2CuBr_4\cdot 2H_2O$	x	46.23	−1.29[a]	0.08[b]	−1.37[c]
	y	34.44	−3.70[a]	0.10[b]	−3.80[c]
	z	34.79	5.23[a]	0.10[b]	5.13[c]

[a] Apparent value at $H_0 = 5.84$ kOe and $T = 1.22$ K.
[b] Calculated pseudoquadrupolar interaction.
[c] Corrected value.

the EFG tensor, respectively, are listed in Table I, third column. In contrast with what should be expected from expression (8), their sum is nonzero. This discrepancy (a few hundred kHz) is far outside the experimental accuracy (a few kHz). It must thus be concluded that another (nontraceless) interaction contributes to the observed line splittings. In Table I, fourth column, the contribution to $\nu_5-\nu_1$ due to the pseudoquadrupolar interaction is given, as calculated from formula (5), with $H=5.8$ kOe, for the rubidium-chlorine compound ($T_c=1.017$ K) and the rubidium-bromine compound ($T_c=1.874$ K). In the fifth column the values of $\nu_5-\nu_1$, corrected for these pseudoquadrupolar contributions, are given. It can easily be verified that these values indeed satisfy expression (8). This clearly proves that the observed splittings between the five resonance lines is due to an apparent quadrupolar interaction, which is the combination of the electric quadrupolar interaction and the pseudoquadrupolar interaction, as derived in this paper.

In Table II the final values for the corrected ^{17}O quadrupolar interactions are given for the complete series of compounds.

The correction h' in Eq. (5) to the magnetic hyperfine interaction is on the order of 10 kHz. This can be neglected completely compared to A_{zz}, because it is even smaller than the experimental errors in the determination of the magnetic hyperfine interaction. The ^{17}O spin densities determined in Ref. 2 remain therefore correct. In the ferromagnetic state in zero field an anisotropy field of a few hundred oersteds is present.[6] From the small field dependence of Δ in weak field (see Fig. 1) it can be expected that in the ferromagnetic state the pseudoquadrupolar interaction is about as large as in the paramagnetic state. Indeed, no significant difference in the quadrupolar splitting has been observed between the ferromagnetic and paramagnetic states.

A similar pseudoquadrupolar interaction exists for the other nuclei. Although the magnitude of this interaction is even larger for some nuclei (Cu,$\mathrm{Br_{(II)}}$) than for ^{17}O, the experimental determination proved to be impossible. Mainly because of the rather large electric quadrupolar interactions of these nuclei, the experimental error exceeds the shift of the resonance line due to the pseudoquadrupolar interaction.

TABLE II. ^{17}O quadrupolar interaction parameters after correction for pseudoquadrupolar interaction.

	ν_Q (MHz)	η
$K_2CuCl_4 \cdot 2H_2O$	1.38	0.45
$(NH_4)_2CuCl_4 \cdot 2H_2O$	1.20[a]	0.40
	1.19[a]	0.40
$Rb_2CuCl_4 \cdot 2H_2O$	1.24	0.43
$Cs_2CuCl_4 \cdot 2H_2O$	1.25	0.46
$(NH_4)_2CuBr_4 \cdot 2H_2O$	1.26[a]	0.46
	1.25[a]	0.46
$Rb_2CuBr_4 \cdot 2H_2O$	1.28	0.47

[a] In the ammonium compounds two slightly different oxygen sites are present, see Ref. 2.

IV. CONCLUSION

The pseudoquadrupolar interaction arises for all nuclei $I>\frac{1}{2}$ which have a hyperfine coupling with an unpaired electron spin. Observation will be possible only when this hyperfine interaction is large while the electric quadrupolar interaction is small or zero and the exchange interaction between the electrons is weak. These three conditions are met for the ^{17}O nuclei in $Rb_2CuCl_4 \cdot 2H_2O$ and isomorphous compounds. The observed pseudoquadrupolar interaction is in complete agreement with theory.

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[1] T. O. Klaassen, W. J. Looyestijn, and N. J. Poulis, Physica (Utrecht) 77, 43 (1974).

[2] W. J. Looyestijn, T. O. Klaassen, and N. J. Poulis, Physica (Utrecht) B 93, 349 (1978).

[3] H. Suhl, Phys. Rev. 109, 606 (1958).

[4] T. Nakamura, Prog. Theor. Phys. 20, 542 (1958).

[5] R. H. Swendsen, Phys. Rev. B 5, 116 (1972).

[6] W. J. Looyestijn, T. O. Klaassen, and N. J. Poulis, Physica (Utrecht) B 83, 169 (1976).