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Exchange and the "10/3 Effect" in $K_2CuCl_4 \cdot 2H_2O$ and $(NH_4)_2CuCl_4 \cdot 2H_2O$†

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The results of room-temperature EPR measurements of linewidth versus frequency in the isomorphous paramagnetic salts $K_2CuCl_4 \cdot 2H_2O$ and $(NH_4)_2CuCl_4 \cdot 2H_2O$ are described. Over the range of frequencies utilized, 3 to 60 kMc/sec, pronounced narrowing of the exchange-narrowed resonance lines is observed, due to the presence of the "10/3 effect." The observed form of the variations is in good agreement with calculations made by Tomita on these systems, and enables determinations to be made of the room-temperature values of the exchange-interaction constants, $J/k = (0.240 \pm 0.010)°K$ and $J/k = (0.197 \pm 0.008)°K$ for the potassium and ammonium salts, respectively.

INTRODUCTION

THE paramagnetic salts $K_2CuCl_4 \cdot 2H_2O$ and, to a somewhat less extent, the isomorphous $(NH_4)_2CuCl_4 \cdot 2H_2O$ have received considerable attention because they exhibit magnetic properties which are characteristic of ferromagnetic insulators having a simple Heisenberg form of exchange amongst nearest neighbors only.[1] Estimates have been made as to the magnitude of the exchange interaction in these substances by a number of authors using a variety of experimental techniques.[2] It is the purpose of this paper to describe an additional measurement of the exchange interaction derived from a seldom used technique, that of the frequency dependence of the EPR linewidths.

THE 10/3 EFFECT

The variation of linewidth versus frequency referred to here is popularly known as the "10/3 effect," and was first discussed by Anderson and Weiss,[3] but has seldom been directly observed experimentally. The first clear experimental evidence of the effect was observed by Abe *et al.*,[4] who reported the frequency dependence of the EPR linewidth of $K_2CuCl_4 \cdot 2H_2O$. Additional EPR observations of the effect have been made by one of the authors in a dilute solution of the free-radical, α, α-diphenyl β-picryl hydrazyl (DPPH)[5] and in the interesting copper salt, $Cu(NH_3)SO_4 \cdot H_2O$.[6] Recently, the effect has been used to study the nuclear-exchange interaction in the bcc phase of solid He^3.[7] In this laboratory the 10/3 effect is under investigation in a number of additional substances as a means of measuring exchange interactions.

The mechanism giving rise to the 10/3 effect may be described qualitatively as follows.

In many concentrated paramagnetic substances in which spin-lattice relaxation effects are not dominant, the primary source of linewidth is the spread in the local magnetic-field spectrum produced by dipolar and hyperfine interactions. In the presence of motion affecting the spins, the spread of local fields will be reduced by averaging if the "frequency" of motion, ω_m, exceeds the mean spread of local resonant frequencies $\gamma[\langle H_{\mathrm{loc}}^2\rangle_{\mathrm{av}}]^{1/2}$. The motional effects may arise from such sources as Brownian motion in a liquid, ion diffusion in a solid, and "spin diffusion" by means of the exchange interaction in either; the resultant resonance lines are said to be motionally narrowed or exchange narrowed. However, contributions to the local-field spectrum, and hence to the linewidth, can also arise from the normally time-averaged nonsecular (off-diagonal) part of the dipolar interaction if the time-averaging of the nonsecular components is interrupted. This will occur when the frequency characteristic of the motional spectrum (ω_m) is comparable or larger than the frequency which is characteristic of the time dependence of these nonsecular components, namely, the Larmor frequency (ω_0). The parameter $\langle H_{\mathrm{loc}}^2\rangle$ may be calculated for purely dipolar local fields by the well-known Van Vleck second-moment formalism[8]; Bloembergen, Purcell, and Pound[9] give a phenomenological expression for the motionally narrowed linewidth,

$$\Delta\omega = \gamma\langle H_{\mathrm{loc}}^2\rangle/\omega_m. \qquad (1)$$

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[1] (a) A. R. Miedema, R. F. Wielinga, and W. J. Huiskamp, Physica **31**, 1585 (1965); (b) A. R. Miedema, H. van Kempen, and W. H. Huiskamp, Physica **29**, 1266 (1963); (c) C. Domb and A. R. Miedema, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1964), Vol. IV, Ch. VI. Other related references are listed in this work.

[2] See Tables III and IV.

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

[4] H. Abe, K. Ono, I. Hagashi, J. Shimada, and K. Iwanaga, J. Phys. Soc. Japan **9**, 814 (1954).

[5] R. N. Rogers, M. E. Anderson, and G. E. Pake, Bull. Am. Phys. Soc. **6**, 261 (1959).

[6] R. N. Rogers, J. K. Pribram, and P. D. Lazay, Bull. Am. Phys. Soc. **9**, 740 (1964).

[7] R. C. Richardson, E. Hunt, and H. Meyer, Phys. Rev. **138**, A1326 (1965).

[8] J. H. Van Vleck, Phys. Rev. **76**, 1168 (1948).

[9] B. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 695 (1948).

As discussed by Van Vleck, under normal circumstances $\gamma\langle H_{\mathrm{loc}}^2\rangle$ is properly calculated using the "truncated" dipolar Hamiltonian. Truncation eliminates the off-diagonal terms, and it is the re-introduction of just these terms through motional effects which gives rise to the 10/3 effect.[10]

The detailed comparisons of the variation of linewidth require treatment in terms of one of the general theories of magnetic-resonance absorption. In particular, the formulation of Kubo and Tomita[11] considers the effects of exchange narrowing and the 10/3 effect explicitly, and Tomita[12] has applied KT to the case of $K_2CuCl_4 \cdot 2H_2O$.

The KT theory calculates to second order the correlation function of the transverse magnetization which in the high-temperature approximation is given by

$$\chi''(\omega)=\frac{\omega}{2kt}\int_{-\infty}^{\infty} G(t)e^{-i\omega t}dt, \tag{2}$$

where $G(t)$ is the correlation function of the transverse magnetization,

$$G(t)=\langle M_x(t+\tau)M_x(t)\rangle_\tau .$$

KT calculate $G(t)$ by a perturbation expansion in powers of $\mathcal{H}'$ which is here the dipole-dipole interaction. The first-order contribution is of no interest as it is independent of motional effects. The second-order contribution to $G(t)$ is found to be approximated by

$$G(t)=\langle|M_x|^2\rangle e^{i\omega_0 t}\exp\left\{\sum_{\lambda=-1}^{2} -t\sigma_\lambda{}^2\int_0^\infty f_\lambda(\tau)\cos(\lambda\omega_0\tau)d\tau \right.$$
$$\left. +it\sum_{\lambda=-1}^{2}\sigma_\lambda{}^2\int_0^\infty f_\lambda(\tau)\sin(\lambda\omega_0\tau)d\tau\right\}, \tag{3}$$

where

$$\sigma_\lambda{}^2=\frac{\langle|[M_x,\mathcal{H}_\lambda']|^2\rangle}{\langle|M_x|^2\rangle},$$

and

$$f_\lambda(\tau)=\frac{\langle[M_x,\mathcal{H}_\lambda']e^{i\mathcal{H}_{\mathrm{ex}}\tau}[M_x,\mathcal{H}_\lambda']^t e^{-i\mathcal{H}_{\mathrm{ex}}\tau}\rangle}{\langle|[M_x,\mathcal{H}_\lambda']^2\rangle}.$$

Equation (3) predicts a linewidth

$$\Delta\omega=\sum_{\lambda=-1}^{2}\sigma_\lambda{}^2\int_0^\infty f_\lambda(\tau)\cos(\lambda\omega_0\tau)d\tau, \tag{4}$$

and a line shift

$$\delta=\sum_{\lambda=-1}^{2}\sigma_\lambda{}^2\int_0^\infty f_\lambda(\tau)\sin(\lambda\omega_0\tau)d\tau. \tag{5}$$

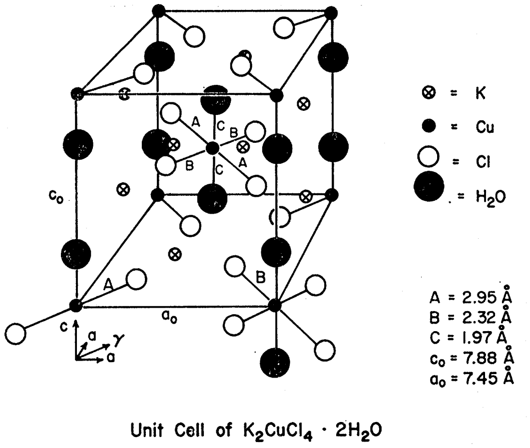

FIG. 1. The unit cell of $K_2CuCl_4 \cdot 2H_2O$. For the ammonium salt, $a=7.58$ Å, $c=7.95$ Å.

The parameter λ labels the various secular or nonsecular components of the perturbation involved (e.g., $\lambda=0$ for secular components).

The quantity $f_\lambda(\tau)$ is the normalized correlation function describing the stochastic behavior of the dipolar perturbation of the energy levels under the influence of the random processes responsible for the narrowing. In the case of the tumbling of a molecule in a liquid, it can be shown that a good approximation to the correct correlation function is the "Lorenztian," $f(\tau)=e^{-|\tau|\omega_m}$.[13] For exchange motion, Anderson and Weiss argue that $f(\tau)$ should be well represented by a Gaussian form, $f(\tau)=e^{-\frac{1}{2}\omega_e{}^2\tau^2}$. With this latter choice, the linewidth expression can be evaluated immediately to give [cf. Eq. (1)]

$$\Delta\omega_{1/2}=(\pi/2)^{1/2}\sum_{\lambda=-1}^{2}\frac{\sigma_\lambda{}^2}{\omega_{e\lambda}}e^{-\frac{1}{2}(\lambda\omega_0)^2/\omega_{e\lambda}{}^2}. \tag{6}$$

The lattice sums contained in σ_λ and $\omega_{e\lambda}$ have been calculated by Tomita for the specific case of $K_2CuCl_4 \cdot 2H_2O$ with the applied field along the c axis. When substituted into the expression for linewidth, his values give

$$\Delta H_{1/2}=\Delta H_0\{1+3.462\exp[-(\hbar\omega_0)^2/(11.447J^2)]$$
$$+1.090\exp[-(\hbar\omega_0)^2/(2.847J^2)]\}, \tag{7}$$

where $\Delta H_0=4.278\, g_c h/J$ G, and where J is the exchange energy defined by the Heisenberg isotropic exchange Hamiltonian,

$$\mathcal{H}_{\mathrm{ex}}=-J\sum_{i,j}\mathbf{s}_i\cdot\mathbf{s}_j. \tag{8}$$

EXPERIMENTAL

Samples

Potassium cupric chloride, $K_2CuCl_4 \cdot 2H_2O$, and ammonium cupric chloride, $(NH_4)_2CuCl_4 \cdot 2H_2O$, form

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[10] $\gamma\langle H_{\mathrm{loc}}^2\rangle_{\mathrm{nontruncated}}/\gamma\langle H_{\mathrm{loc}}^2\rangle_{\mathrm{truncated}}=10/3$ for a powder of an isotopic material (Ref. 8), and thus the name of the effect. In general, however, the ratio will depend upon the particular crystal structure and the angle of the applied magnetic field.

[11] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954); hereafter referred to as KT.

[12] K. Tomita, in *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September, 1953* (Science Council of Japan, Tokyo, 1954), p. 800.

[13] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Sec. VIII E.

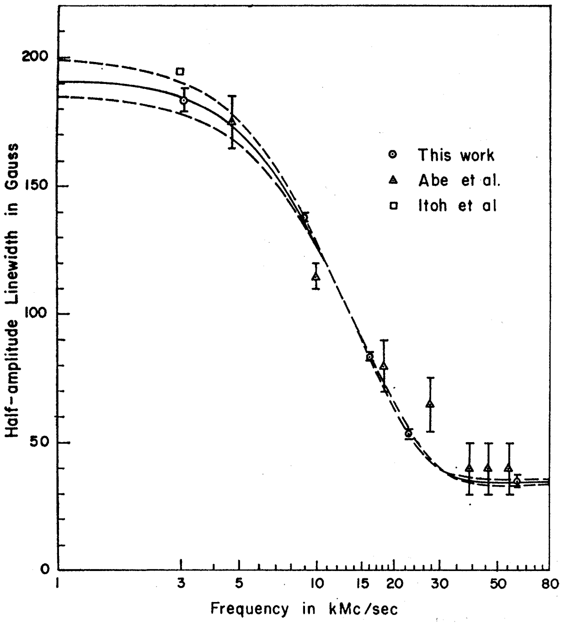

FIG. 2. Variation of linewidth versus frequency for $K_2CuCl_4 \cdot 2H_2O$ with the magnetic field applied along the c axis. The theoretical curves are based on Tomita [see Eqs. (6) and (7)] and use the Gaussian form for the dipole-dipole correlation function. The dotted curves show the resultant variation of the fitted theoretical curves with $\Delta H_0=33.0$ G, $J/k=0.250$°K for the lower curve and $\Delta H_0=36.0$ G, $J/k=0.230$°K for the upper curve. For the best fitting (solid) curve, $\Delta H_0=34.7$ *G*, $J/k=0.240$°K.

crystals of the tetragonal system. The light yellowish-green potassium salt has the unit cell dimensions $a=7.45$ Å, $c=7.88$ Å, while corresponding dimensions of the light greenish-blue ammonium salt are $a=7.58$ Å, $c=7.95$ Å.[14] (See Fig. 1.) There are two Cu^{++} ions per unit cell at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, each coordinated nearly octahedrally by four chlorines and two water molecules with the water molecules above and below along the c axis, and the chlorines in the perpendicular plane at the corners of a rhomboid. The atomic environment at one Cu^{++} site is related to the other by a 90° rotation about the c axis; thus the sites are magnetically inequivalent except when the field is applied in the c direction. The magnetic sublattice is very nearly body-centered cubic $(c/a)=1.06$).

TABLE I. Observed linewidths and g values for $K_2CuCl_4 \cdot 2H_2O$. (Values in parentheses are from Abe *et al.*[a] or from Itoh *et al.*[b])

Frequency (k Mc/sec)	Half-amplitude linewidth along c axis (gauss)	g_c
(3.0)[b]	(195)[b]	(2.06)
3.107	183 ±5	2.088±0.007
(4.76)	(175 ±10)	
9.080	138.0±1.8	2.074±0.001
		[$g_a=2.236\pm0.003$]
(9.97)	(115 ±5)	
16.090	83.7±1.8	2.061±0.001
(18.18)	(80 ±10)	
22.845	53.7±1.8	2.059±0.003
(27.5)	(65 ±10)	
(39.0)	(40 ±10)	
(46.1)	(40 ±10)	
(55.6)	(40 ±10)	
59.75	35.1±1.8	2.050±0.001

[a] Reference 3.
[b] J. Itoh, M. Fujimoto, and H. Ibamoto, Phys. Rev. 83, 852 (1951).

TABLE II. Observed linewidths and g values for $(NH_4)CuCl_4 \cdot 2H_2O$.

Frequency (k Mc/sec)	Half-amplitude linewidth along c axis (G)	g_c
3.103	160 ±6	2.10±0.01
9.065	106.5±1.8	2.075±0.001
16.094	57.9±1.5	2.058±0.001
59.73	31.2±1.5	2.050±0.001

Measurements

EPR cavity spectrometers of conventional design were used in the measurements. The magnetic field was supplied by a Varian Model V4007, 6-in. electromagnet at 3 and 9 kMc/sec and by a Harvey-Wells Model L128, 12-in. electromagnet with tapered pole caps at the higher frequencies. At all frequencies other than the lowest, TE011 reflection cavities were used, while at 3 kMc/sec, a rectangular transmission TE102 cavity was used. High-Q cavities were employed even at the highest frequencies so that the sample size could be kept to a minimum to avoid inhomogeneous field broadening. A 10-kc/sec klystron stabilizer of standard design was employed to keep the klystron frequency

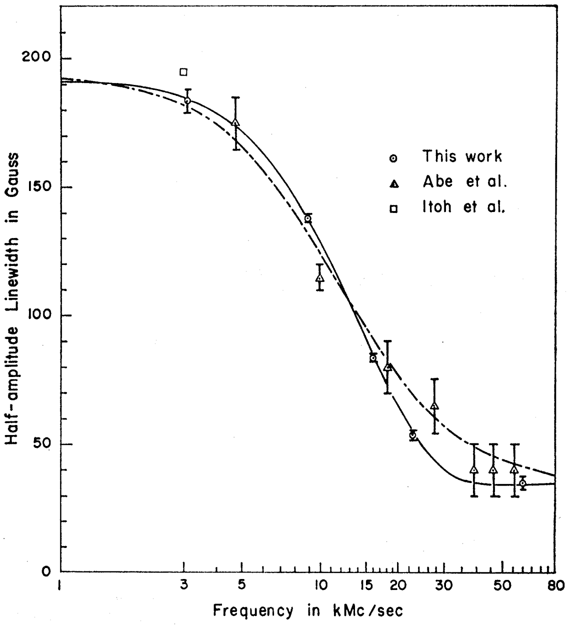

FIG. 3. A comparison of the best fitting curve of Fig. 2 with the best fitting curve using a Lorentzian correlation function. The resultant parameters for the Lorentzian curve are $\Delta H_0=35.0$ G, $J/k=0.340$°K.

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[14] L. Chrobak, Z. Krist. 88, 35 (1935); D. Harker, *ibid.* 93, 136 (1936).

TABLE III. Exchange-constant determination in $K_2CuCl_4 \cdot 2H_2O$.

J/k (°K)	Method
0.240 ± 0.010^{a}	10/3 effect ($\omega_e/2\pi = 11.9 \pm 0.5\ k$ Mc/sec)
0.30^{b}	af susceptibility ($\theta_c = 1.2$°K, $T_n = 0.88$°K)
0.295^{b}	Specific heat, $T \gg T_c$
0.33^{b}	Energy difference, paramagnetic to ferromagnetic
0.282^{b}	Specific heat, $T < T_c$ (spin-wave theory)
(0.302^{b})	(Average of above four values)
0.30^{c}	rf susceptibility ($\theta_c = 1.05$°K)
0.23^{d}	Magnetostatic mode splitting ($\theta_c = 0.9$)
0.25^{e}	NMR near $T_c (\theta_c = 1.0$°K)
0.28^{af}	Exchange broadening ($\nu_e = 11\ k$ Mc/sec)

[a] Measured at room temperature.

[b] Reference 1.

[c] J. van den Broek, L. C. van der Marel, and C. J. Gorter, Physica **27**, 661 (1961)

[d] H. Abe, H. Morigaki, and K. Koga, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 563.

[e] J. Itoh, Y. Kamiya, in *Proceeding of the International Conference on Magnetism and Crystallography* (The Physical Society of Japan, Bunkyo-Ku-Tokyo, 1962), p. 512.
1961, p. 512.

[f] K. Ono and M. Ohtsuka, Proc. Phys. Soc. Japan **13**, 206 (1958).

locked to the cavity to insure the observation of a pure absorption spectrum. Linewdiths were determined at all frequencies by repeatedly sweeping the field slowly through resonance and marking field values on a chart-recorder derivative presentation of the resonance line. The line shapes were found to be closely Lorentzian, so that the half-amplitude linewidths could be obtained from the experimentally observed derivative peak-to-peak width by multiplying by the factor $\sqrt{3}$. The field was measured with a Rawson Lush Model 820 rotating coil gaussmeter whose accuracy at a particular frequency could be checked by observing the resonance field value of a DPPH speck mounted adjacent to the sample. All linewidth measurements were made along the direction of observed minimum g and minimum linewidth, corresponding to the c axis. The sample was oriented in the magnetic field by searching for the direction of minimum g. To achieve the correct orientation, cavities were devised which allowed rotation on the sample *in situ* about a horizontal axis while the field could be rotated about a vertical axis.

RESULTS AND DISCUSSION

The results of our linewidth measurements are presented in Tables I and II and Figs. 2, 3, and 4. The values of Abe *et al.* for $K_2CuCl_4 \cdot 2H_2O$ are also given. The Tomita linewidth expression with the Gaussian form of correlation function [Eqs. (6) and (7)] has been fitted to the experimental results to determine the parameters J and ΔH_0. It is seen that the agreement of the variation of linewidth with Tomita's expression, Eq. (7), is excellent. Ideally, one would like to fit by varying the single parameter J while allowing the secular part of the linewidth, ΔH_0, as well as the nonsecular variation to be predicted. However, using the value of J determined here, the calculated value of the exchange narrowed linewidth, e.g., $\Delta H_0 \simeq 18$ G for the potassium salt, is in relatively poor agreement with the

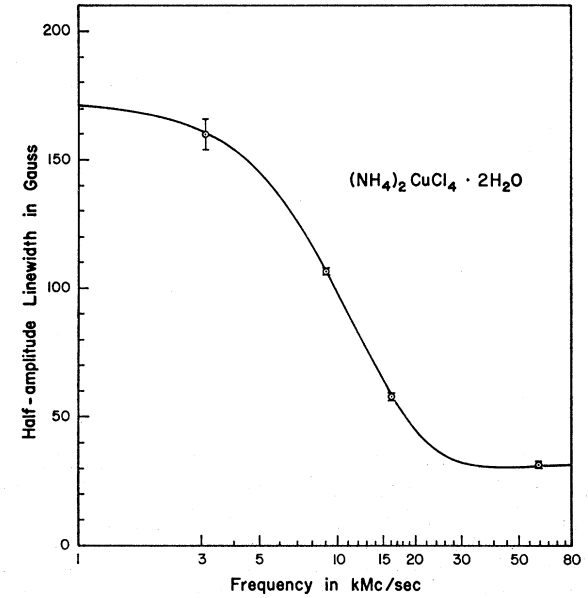

FIG. 4. Variation of linewidth versus frequency for $(NH_4)_2CuCl_4 \cdot 2H_2O$ with the magnetic field applied along the c axis. The theoretical curve is based on Tomita [see Eqs. (6) and (7)] in which a Gaussian form is used for the dipole-dipole correlation function. The fit corresponds to $\Delta H_0 = 31.0$ G, $J/k = 0.197$°K.

value determined experimentally, $\Delta H_0 \simeq 35$ G. Hence, ΔH_0 is also treated as an adjustable parameter for purposes of fitting. The disagreement of the observed secular linewidth with that predicted is not too surprising, because abslolute values of exchange narrowed linewidths are rarely given well by such moment calculations. This is presumably explained by the strong dependence of the second moment on ion separation, small crystal-field effects, and the presence of anisotropic exchange. In addition, the absolute value of linewidth calculated depends upon the actual form of the correlation $f(\tau)$. Hyperfine splittings will also affect the second moment of the line, although from estimates based on other Cu^{++} complexes, this will not be an important factor, contributing at most a few gauss to the linewidth.

In constrast to the value of ΔH_0, the relative variation of the linewidth with frequency is determined primarily by the symmetry of the lattice through the ratios of the secular to nonsecular moments. Thus, much more

TABLE IV. Exchange-constant determination in $(NH_4)_2CuCl_4 \cdot 2H_2O$.

J/k (°K)	Method
0.197 ± 0.008^{a}	10/3 effect ($\omega_e/2\pi = 9.8 \pm 0.3$ kMc/sec)
0.24^{b}	af susceptibility ($\theta_c = 0.95$°K, $T_n = 0.70$°K)
0.21^{b}	Specific heat, $T \gg T_c$
0.24^{b}	Energy difference, paramagnetic to ferromagnetic
0.222^{b}	Specific heat, $T < T_c$
(0.227^{b})	(Average of above four values)

[a] Measured at room temperature.

[b] Reference 1.

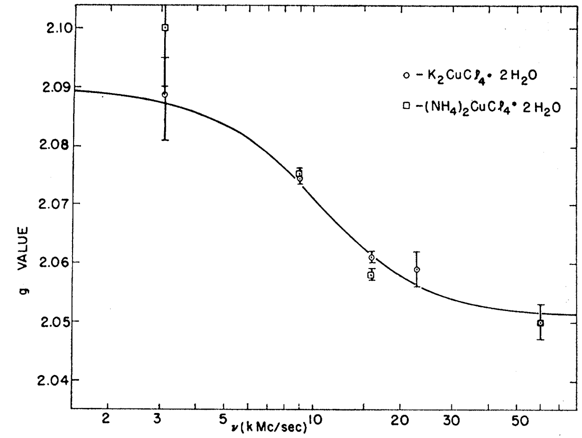

FIG. 5. The predicted g shift from Eq. (5) compared with the experimental results. The amplitude of the shift and its frequency dependence are determined from the parameters found in Figs. 2 and 4. The base line is arbitrary and is chosen to fit the high-frequency points. The curve plotted is actually that calculated for the potassium salt, although the difference in the ammonium-salt curve is not significant in view of the relative accuracy of the measurements.

confidence is felt in the form of the theoretical 10/3 curve, and the experimental results bear this out. The results obtained for the two salts from our estimated fit are compared in Tables III and IV with other measurements of J from a variety of sources

It is seen that these room-temperature values obtained for J are slightly below the consensus of values obtained by other techniques. However, estimates of the change in the exchange interaction due to thermal expansion of the lattice between low temperatures and room temperature indicate that most, if not all, of the discrepancy could be explained this way, to within experimental error.[15] It is interesting to note that the ammonium salt with about a 1% larger lattice spacing, has in fact a value for J at low temperatures very nearly equal to our room-temperature value for the potessium salt, while the expected lattice expansion for the potassium salt over the same temperature limits is estimated also to be about 1%. While this seems to be good confirmation of the proposed effect of lattice expansion on exchange, the argument breaks down when one looks at the low-temperature results of the isomorphous rubidium salt, $Rb_2CuCl_4 \cdot 2H_2O$.[1a] There, the spacing is larger again than the ammonium salt, but the exchange interaction surprisingly is larger than for the potassium salt. It is hoped that the temperature variation of J as measured using the 10/3 effect will help to clarify this situation.

As discussed previously, a particular correlation function was assumed in order to obtain the variation of linewidth. While the present data are insufficient to conclusively confirm the Gaussian form, no deviation from the Gaussian can be detected, and they do rule out the Lorentzian form mentioned above (see Fig. 3). This supports the Anderson-Weiss picture of weak-exchange processes occurring via a gradual mutual precession, rather than a stepwise, Markovian type of process. To our knowledge, this is the first such evidence concerning the nature of the exchange-correlation function to be reported.

We have also compared our measured g values with the lineshift formula of Eq. (5), using our experimentally determined values of ΔH_0 and J to determine the parameters in the equation. As can be seen in Fig. 5, the observed g values are in reasonable agreement with both the magnitude and the frequency dependence of the predicted shift. The curve is that calculated for the potassium salt; the experimental errors involved make separate comparisons extravagant. The particularly large errors of the 3 kMc/sec point arises from an observed sample dependence of the g value in the relatively large and imperfect crystals used at this low frequency.

To our knowledge, this is the first confirmation of the nonsecular g shift to be reported.

CONCLUSION

The predictions of the Kubo-Tomita theory regarding nonsecular linewidth broadening (the 10/3 effect) and the accompanying nonsecular line shift have been verified. The results indicate an EPR technique for the measurement of exchange in the high-temperature region which should give accuracy comparable to low-temperature methods for salts having simple magnetic lattices.

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[15] There also is some recent evidence that the lattice may also undergo a minor structural change upon cooling [G. Seidel and S. H. Choh, Bull. Am. Phys. Soc. 11, 186 (1966)] which could also contribute to the temperature dependence of J.