Spin susceptibility and low-lying excitations in the Haldane-gap compound Y_2BaNiO_5

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^{89}Y NMR frequency shifts K and spin-lattice relaxation rates $1/T_1$ have been measured in the chain nickelate Y_2BaNiO_5. Between 40 and 300 K the anisotropic shift is proportional to the isotropic shift K_{iso}, which is incompatible with existing theory of the spin susceptibility in Haldane-gap antiferromagnets. In addition, different energy gaps are obtained from shift and spin-lattice relaxation data: $E_g(K_{iso}) = 80 \pm 5$ K, whereas $E_g(1/T_1) = 122 \pm 8$ K. This is also unexpected, and indicates that the dynamic susceptibility $\chi(q,\omega)$ is more strongly gapped for large q than for $q = 0$.

The theory of the one-dimensional Heisenberg antiferromagnet has been developed considerably since the suggestion of Haldane[1] that for integer spin an energy gap E_g exists between the spin-liquid ground state and spin excitations. Calculations have been carried out for progressively more realistic models, including various anisotropic Hamiltonians and finite length of the spin chain. Experimental tests of these theories have generally led to satisfactory agreement, although the number of suitable materials is limited; the most thoroughly studied is the organometallic compound $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP).[2,3] A recent addition to the list of Haldane-gap antiferromagnets is the chain nickelate Y_2BaNiO_5,[4,5] which is structurally simpler than NENP and in addition opens the possibility of controlled hole doping of the spin-liquid state.[6] Neither of these materials shows any evidence for magnetic ordering.

This paper reports the use of ^{89}Y nuclear magnetic resonance (NMR) as a microscopic probe of the Ni^{2+} spin susceptibility[7–9] and magnetic excitations in undoped Y_2BaNiO_5. NMR has three important advantages over the bulk magnetic susceptibility χ_{bulk} for such a study. First, a Curie-Weiss term in χ_{bulk},[10,11] due to a dilute concentration of defect-related spins, hinders measurement of χ_s at low temperatures. For a random distribution of defect spins this paramagnetism broadens the NMR line but does not contribute to the NMR shift tensor $\mathbf{K}$.[12] Second, nuclei of nonmagnetic ions do not couple appreciably to nonspin contributions to the bulk susceptibility, particularly the Van Vleck orbital susceptibility, which are anisotropic and confuse determination of the anisotropy of χ_s. Third, the anisotropy of $\mathbf{K}$ can be determined in a powder specimen[13] when, as in the present case, high-quality single crystals are difficult to prepare.

In Y_2BaNiO_5 the anisotropic component of $\mathbf{K}$ is found to be proportional to the isotropic or centroid shift $K_{iso} \equiv 1/3$ tr $\mathbf{K}$ over nearly a decade of temperature around E_g. This is in serious disagreement with existing theory of the susceptibility,[7,9] which predicts considerably more complex behavior of the anisotropy and which agrees with susceptibility measurements in NENP.[3,7,9] Furthermore, the Van Vleck contribution is found to be a significant fraction of the measured low-temperature susceptibility, so that the ground-state spin susceptibility anisotropy is much smaller than the theoretical prediction. We also observe an unanticipated difference between the temperature dependences of the ^{89}Y NMR frequency shift and the spin-lattice relaxation rate, which should both exhibit the same activation energy E_g. The NMR data clearly differentiate between effects of Ni^{2+} spins in the chains and the defect spins;[14] the anomalous results described above are characteristic of the chains. One possibility is that the anomalies are related to dimerization of the Ni chains by a Peierls-like structural distortion, but no sign of this has been reported in neutron or x-ray-diffraction experiments. NMR, which is more sensitive than diffraction to the local spin susceptibility, does not exhibit the line splitting expected from a doubling of the unit cell. We conclude, provisionally at least, that Y_2BaNiO_5 is a Haldane-gap antiferromagnet which does not entirely behave according to theory.

Our specimens of undoped Y_2BaNiO_5, which were previously used in the magnetic neutron scattering measurements of DiTusa *et al.*,[6] were prepared by solid state reaction and powdered. Y_2BaNiO_5 crystallizes in the orthorhombic *Immm* structure,[4] with a single Y site of mm point symmetry. Values of the average gap $E_g = 127$ K, the intrachain exchange coupling $J = 285$ K, and the single-ion anisotropy energy $D = 46$ K have been derived from neutron scattering measurements.[5,6]
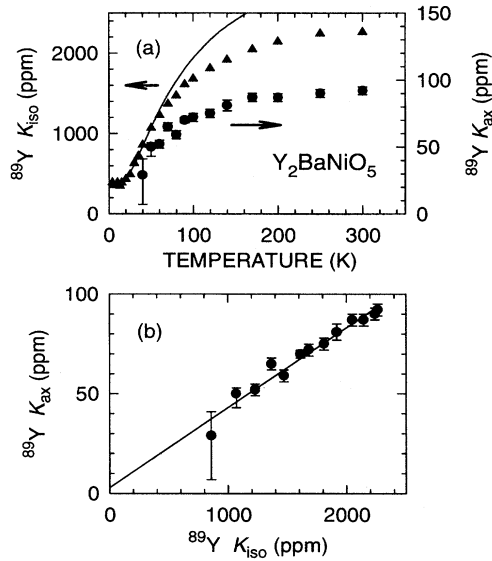
FIG. 1. (a) Temperature dependence of the ^{89}Y isotropic shift K_{iso} (triangles) and axial shift K_{ax} (circles) in Y_2BaNiO_5. Curve: fit to K_{iso} from 4 to 50 K. (b) $K_{ax}(T)$ vs $K_{iso}(T)$, with temperature an implicit parameter. Straight line: linear fit from 40 to 300 K.

^{89}Y NMR measurements were carried out in an applied field of 75 kOe. Above ~ 40 K the spectra exhibit a characteristic anisotropic powder-pattern shape[13] from which the components of K could be determined. An additional broadening, associated with the defect-spin Curie-Weiss contribution to the susceptibility,[15] increases with decreasing temperature and prevents accurate determination of the anisotropy below 40 K. ^{89}Y spectral line-shape analysis[13] indicates that to within errors the NMR shift tensor $\mathbf{K}(T)$ is axial.[16] Thus $\mathbf{K}$ is well characterized experimentally by parallel and perpendicular components $K_\parallel$ and $K_\perp$ or, equivalently, by $K_{iso} = 1/3(K_\parallel + 2K_\perp)$ and the axial shift $K_{ax} \equiv 1/3(K_\parallel - K_\perp)$.[13] This axial symmetry is surprising, since the Y-site point symmetry is lower than axial.

Values of K_{iso} and K_{ax}, obtained from fits to the spectra at each temperature, are given in Fig. 1(a). Note the absence of any Curie-Weiss behavior at low temperatures. A good fit over the temperature range 4–50 K is obtained to the form $K_{iso}(T) = K_0 + K_1 \exp(-E_g/T)$, with $K_0 = 370 \pm 10$ ppm, $K_1 = 3480 \pm 350$ ppm, and $E_g = 80 \pm 5$ K, shown as the curve in Fig. 1(a). The most striking feature of the data is the excellent linearity between $K_{ax}(T)$ and $K_{iso}(T)$ shown in Fig. 1(b). In the following we argue that this linearity indicates disagreement between the spin susceptibility anisotropy of Y_2BaNiO_5 and theory for a Haldane-gap system.

The powder-average bulk susceptibility χ_{bulk} was measured at $H = 2$ kOe and fit to the form $\chi_{bulk}(T) = \chi_0 + \chi_1 \exp(-E_g/T) + C/(T - \theta)$ over the temperature range 1.8–50 K (the values of χ_0, E_g, C, and θ were most reliably determined using this range). The fit yields $\chi_0 = (1.78 \pm 0.08) \times 10^{-4}$ emu mole^{-1}, $\chi_1 = (16 \pm 1) \times 10^{-4}$ emu mole^{-1}, $E_g = 76 \pm 2$ K, $C = (8.3 \pm 0.1) \times 10^{-3}$ emu K mole^{-1}, and $\theta = -0.43 \pm 0.02$ K. The Curie constant corresponds to a defect-spin concentration $c \simeq 0.68\%$ assuming defect spin $S = 1$.[14] The corrected chain susceptibility
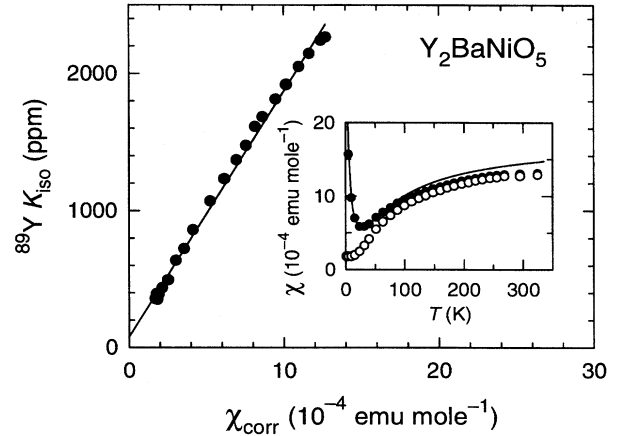

FIG. 2. ^{89}Y K_{iso} vs susceptibility χ_{corr}, corrected for defect-spin contribution as described in the text, in Y_2BaNiO_5. Straight line: linear fit. Inset: $\chi_{bulk}(T)$ (filled circles), fit from 1.8 to 50 K (curve), and $\chi_{corr}(T)$ (open circles).

$\chi_{corr}(T)$ was then found by subtracting the Curie-Weiss contribution from χ_{bulk}. An activated temperature dependence with comparable gaps describes both $K_{iso}(T)$ and $\chi_{corr}(T)$ as expected.

Figure 2 gives the dependence of $K_{iso}(T)$ on $\chi_{corr}(T)$. [The inset shows $\chi_{bulk}(T)$, the fit described above, and $\chi_{corr}(T)$.] The good linearity indicates that K_{iso} is indeed tracking the Ni^{2+} spin susceptibility, and that the hyperfine coupling is temperature independent as expected. From the slope of this plot the isotropic transferred hyperfine field $H_{iso}^{hf} \approx N\mu_B(dK_{iso}/d\chi_{corr})$ (Ref. 17) is found to be 9.8 ± 0.4 kOe/μ_B. We have assumed that χ_{corr} is field independent, which may not be the case if the Haldane gap changes with field;[7,8] this could cause the slight curvature visible in Fig. 2.

The NMR shift and susceptibility tensors are related by the hyperfine coupling tensor $\mathbf{A}$, defined by $\mathbf{K}(T) = \mathbf{A}\chi_s(T)$. Contributions to $\mathbf{A}$ arise from the transferred hyperfine interaction, which is a property of the electronic structure, and the dipolar interaction, neither of which is temperature dependent. Although $\mathbf{K}(T)$ need not have the same symmetry as $\chi_s(T)$, the temperature dependence of $\mathbf{K}$ should reflect that of χ_s. For axial single-ion anisotropy the theoretical axial susceptibility[7,9] $\chi_s^{ax} \equiv 1/3(\chi_\parallel - \chi_\perp)$ changes sign at $T_a \sim 0.1J$ and again at $T_b \sim J$. These temperatures exhibit only a weak dependence on D, and between them, i.e., in the range ~ 30–300 K for Y_2BaNiO_5, the theoretical χ_s^{ax} varies from 0 at $T = T_a$, to a maximum of $\sim 10\%$ of the orientational average $\chi_s^{iso}(T) = \frac{1}{3}(\chi_\parallel + 2\chi_\perp)$ at $\sim T_b/2$, and back to 0 at T_b.

This behavior is not reflected in the simple linearity of Fig. 1(b). Although a low-temperature zero crossing cannot be ruled out, there is clearly no zero crossing at high temperatures, where additional broadening becomes small ($\sim 0.2K_{ax}$) and constant. Furthermore, $K_{iso}(T)$ tracks the intrinsic susceptibility $\chi_{corr}(T)$ (Fig. 2), and $K_{ax}(T)$ tracks $K_{iso}(T)$ [Fig. 1(b)]. This is unambiguous evidence that the shifts reflect intrinsic behavior.

Crystal symmetry dictates that the principal axes of $\mathbf{A}$ and χ_s be parallel to crystal axes and therefore parallel to each other. Then the anisotropy of $\mathbf{K}$ can be written in the component form

$$K_x - K_{\text{iso}} = (A_x - A_{\text{iso}})\chi_s^{\text{iso}} + (A_y - 2A_{\text{iso}})\chi_s^{\text{ax}},$$

$$K_y - K_{\text{iso}} = (A_y - A_{\text{iso}})\chi_s^{\text{iso}} + (A_x - 2A_{\text{iso}})\chi_s^{\text{ax}},$$

$$K_z - K_{\text{iso}} = (A_z - A_{\text{iso}})\chi_s^{\text{iso}} + (A_z + A_{\text{iso}})\chi_s^{\text{ax}}, \qquad (1)$$

where K_i and A_i, $i = x, y, z$, are the principal-axis components of the corresponding tensors, and $A_{\text{iso}} = \frac{1}{3}\,\text{tr}\,\mathbf{A} = H_{\text{iso}}^{\text{hf}}/N\mu_B$. Our data indicate that the anisotropic component of $\mathbf{K}(T)$ is proportional to $\chi_s^{\text{iso}}(T)$, which would be consistent with theory if in Eq. (1) the terms in χ_s^{iso} were much larger than the terms in χ_s^{ax}.

Now the coefficients of χ_s^{iso} in Eq. (1) are of the order of the anisotropy $\Delta A = \max(A_i) - \min(A_i)$ in $\mathbf{A}$, whereas the coefficients of χ_s^{ax} are of the order of A_{iso}. Therefore ΔA would have to be $\gtrsim A_{\text{iso}}$ for $\chi_s^{\text{iso}}(T)$ to dominate the measured $K_{\text{ax}}(T)$ if, as according to theory, $\max(\chi_s^{\text{ax}}) \sim 0.1 \chi_s^{\text{iso}}$. But then K_{ax} would be $\gtrsim K_{\text{iso}}$, whereas experimentally $K_{\text{ax}} = (0.040 \pm 0.006) K_{\text{iso}}$ [Fig. 1(b)]. This rules out such an explanation. A similar argument can be made for nonaxial χ_s. We conclude that χ_s^{ax} is either proportional to χ_s^{iso} or much smaller than predicted; in the latter case the shift anisotropy would be entirely due to the (small) anisotropy of $\mathbf{A}$. Future NMR studies of single crystals will determine ΔA directly.

The zero-temperature shift K_0 consists of a contribution $K_s(0)$ from Ni^{2+} chains and an isotropic temperature-independent chemical shift σ. From the empirical systematics found between $\sigma(^{89}\text{Y})$ and the group electronegativity of ligands in transition-metal oxides[18] we estimate $\sigma = 190 \pm 90$ ppm. Then $K_s(0) = 180 \pm 100$ ppm, and $\chi_s^{\text{iso}}(0) = (1.0 \pm 0.5) \times 10^{-4}$ emu mole^{-1} using the value of A_{iso} obtained above. We take $\chi_0 = \chi_s^{\text{iso}}(0) + \chi^{\text{VV}} + \chi_{\text{dia}}$, where χ^{VV} is the powder-averaged orbital Van Vleck susceptibility and $\chi_{\text{dia}} = -1.2 \times 10^{-4}$ emu mole^{-1} is the core diamagnetic susceptibility,[19] and obtain $\chi^{\text{VV}} = (2.0 \pm 0.5) \times 10^{-4}$ emu mole^{-1}.

According to theory[7,8] a finite spin susceptibility at $T = 0$ is due to single-ion anisotropy. But then χ^{VV} will also be anisotropic.[20] The observed susceptibility anisotropy $\Delta\chi_{\text{bulk}}(T)$ in single-crystal NENP (Ref. 3) was found to be in reasonable agreement with theory,[7] but apparently this comparison did not take the Van Vleck anisotropy $\Delta\chi^{\text{VV}}$ into account. We have estimated $\Delta\chi^{\text{VV}}$ in NENP from the single-ion anisotropy D (Refs. 3, 9, and 21) and g-shift tensor,[2] and obtained $\Delta\chi^{\text{VV}} = (1.0 \pm 0.2) \times 10^{-4}$ emu mole^{-1}. This is a significant fraction of $\Delta\chi_{\text{bulk}}(0) = 4 \times 10^{-4}$ emu mole^{-1} in NENP.[3] Taking it into account would considerably modify quantitative agreement with theory. For Y_2BaNiO_5 the calculated $\Delta\chi^{\text{VV}}$ reproduces a measurement of $\Delta\chi_{\text{bulk}}(0)$ (Ref. 11) with a reasonable reduction factor (76%) for the spin-orbit coupling parameter λ,[20] leaving little room for a large spin susceptibility anisotropy at $T = 0$. This result, if sustained, would constitute a major disagreement with theory.

Above ~ 40 K an exponential spin-lattice relaxation recovery function $\exp(-t/T_1)$ was observed; the relaxation rate $1/T_1$ between 40 and 300 K is shown in Fig. 3. The relaxation rate is due to thermal excitations of the Ni^{2+} chains, and can be written in the form[22]
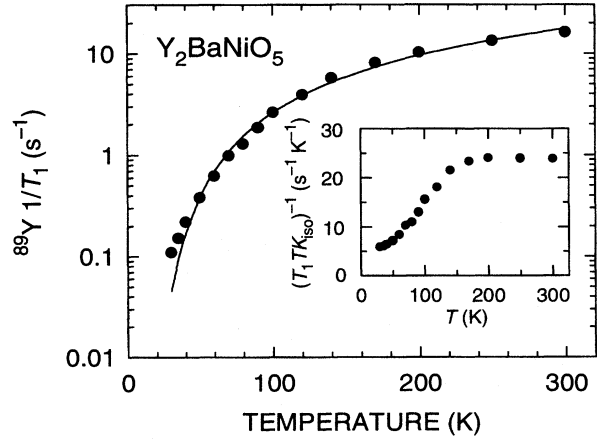

FIG. 3. Temperature dependence of ^{89}Y spin-lattice relaxation rate $1/T_1$ in Y_2BaNiO_5 above 40 K. Curve: fit described in text. Inset: temperature dependence of $(T_1 T K_{\text{iso}})^{-1}$.

$$1/T_1(T) = 2\gamma_n^2 k_B T \sum_q |A(q)|^2 \chi''(q, \omega_n)/\omega_n, \qquad (2)$$

where γ_n is the nuclear gyromagnetic ratio, $A(q)$ is the wave-vector-dependent hyperfine coupling, and $\chi''(q, \omega_n)$ is the dissipative component of the chain dynamic susceptibility evaluated at the nuclear Larmor frequency ω_n. We find $A(q)$ to be at most weakly q dependent,[23] so that $1/T_1$ samples spin fluctuations at all q.

The important feature of these data is that $(T_1 T)^{-1}$ grows much more rapidly with temperature than K_{iso}. This is shown in the inset of Fig. 3, which gives the temperature dependence of $(T_1 T)^{-1}/K_{\text{iso}}$. This ratio is constant above ~ 200 K, but decreases markedly below a temperature of the order of the energy gap. Such behavior unambiguously demonstrates that the local dissipative susceptibility $\Sigma_q \chi''(q, \omega_n)$, sampled by $(T_1 T)^{-1}$, is more strongly temperature dependent (i.e., exhibits a larger gap) than the uniform static susceptibility $\chi'(q = 0, \omega = 0)$, sampled by K_{iso}. This seems hard to reconcile with a theory in which activation over the Haldane gap at $q = \pi/a$ controls both the uniform static susceptibility[7] and the spectrum of low-lying spin excitations; in such a theory $(T_1 T)^{-1}/K_{\text{iso}}$ would be independent of temperature.

The data were fit to an activated form for $(T_1 T)^{-1}$, by analogy with the treatment of $K(T)$ and $\chi(T)$. This yields $E_g = 122 \pm 8$ K for 30 K $< T < 300$ K (curve in Fig. 3), which is consistent with the average gap obtained from neutron scattering.[5,6] It is significantly larger than the value obtained from the NMR shift, however: again, the gap which characterizes $\Sigma_q \chi''(q, \omega_n)$ is larger than that which characterizes $\chi'(0, 0)$. In NENP the gaps from susceptibility data[3] and from proton $1/T_1$ data[24] are approximately equal (~ 15 and ~ 14 K, respectively, the latter after taking field suppression of the gap into account). Thus Y_2BaNiO_5 behaves differently from NENP in this respect as well.

The fit is over higher temperatures ($T \sim E_g$) than desirable to determine the low-temperature activation energy. Activated quantities typically "soften" for temperatures near

E_g, however [see, e.g., Fig. 1(a)], so that the true value of E_g may be underestimated. Fits to an activated form for $1/T_1$ (Ref. 24) rather than $1/T_1T$ would also produce a larger gap value. The discrepancy is even more marked under either of these scenarios, and in any case the strong temperature dependence of $(T_1TK_{iso})^{-1}$ (inset of Fig. 3) makes the point independent of any fit.

In summary, [89]Y NMR measurements in Y_2BaNiO_5 reveal features of the spin susceptibility of this Haldane-gap system and considerable discrepancies with existing theory. These may possibly be related to gap formation by dimerization or some other "non-Haldane" mechanism, but this remains to be demonstrated. The proportionality of the axial NMR shift $K_{ax}(T)$ to the isotropic shift $K_{iso}(T)$ indicates that the susceptibility anisotropy $\Delta\chi$ predicted by theory and observed in other systems does not describe Y_2BaNiO_5. Moreover, the Van Vleck contribution to $\Delta\chi$ in NENP and Y_2BaNiO_5 reduces agreement with theory. The temperature dependence of $(T_1T)^{-1}$ is more rapid than that of K_{iso}, and

the activation energy deduced from the former is correspondingly greater than from the latter, whereas comparable gap values have been obtained from susceptibility and $1/T_1$ in NENP. This behavior indicates that the dynamic susceptibility $\chi(q,\omega)$ exhibits a larger gap near $q=\pi/a$ than for $q=0$. Perhaps the fact that the single-ion anisotropy is staggered in NENP but not in Y_2BaNiO_5 has something to do with these differences in behavior. In any event, the NMR data pose new challenges for the theory of Haldane-gap antiferromagnets.

[1] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).

[2] A. Meyer et al., Inorg. Chem. **21**, 1729 (1982).

[3] J. P. Renard et al., J. Appl. Phys. **63**, 3538 (1988).

[4] D. J. Buttrey, J. D. Sullivan, and A. L. Reingold, J. Solid State Chem. **88**, 291 (1990).

[5] J. Darriet and L. P. Regnault, Solid State Commun. **86**, 409 (1993).

[6] J. F. DiTusa et al., Phys. Rev. Lett. **73**, 1857 (1994); J. F. DiTusa et al. (unpublished).

[7] I. Affleck, Phys. Rev. B **41**, 6697 (1990).

[8] A. M. Tsvelik, Phys. Rev. B **42**, 10 499 (1990).

[9] T. Delica et al., Europhys. Lett. **15**, 55 (1991); S. Yamamoto and S. Miyashita, Phys. Rev. B **50**, 6277 (1994).

[10] O. Avenel et al., Phys. Rev. B **46**, 8655 (1992).

[11] B. Batlogg, S-W. Cheong, and L. W. Rupp, Physica (Amsterdam) B **194-196**, 173 (1994).

[12] R. E. Walstedt and L. R. Walker, Phys. Rev. B **9**, 4857 (1974).

[13] See, for example, G. C. Carter, L. H. Bennett, and D. J. Kahan, Prog. Mater. Sci. **20**, 1 (1977).

[14] A. P. Ramirez, S-W. Cheong, and M. L. Kaplan, Phys. Rev. Lett. **72**, 3108 (1994). Only the product $cS(S+1)$ is determined by C.

[15] The observed additional linewidth is quantitatively accounted for by dipolar coupling to randomly-distributed defect spins (Ref. 12).

[16] As an example, any nonaxial anisotropy is $\lesssim 0.1K_{ax}$ at 80 K.

[17] The correction to the relation $K_{iso}=A_{iso}\chi_{iso}$ is of order $(\Delta A/A_{iso})(\chi_{ax}/\chi_{iso})$, which is expected to be less than 1% in the present case.

[18] R. Dupree and M. E. Smith, Chem. Phys. Lett. **148**, 41 (1988); N. Janes and E. Oldfield, J. Am. Chem. Soc. **107**, 6769 (1985).

[19] Landolt-Börnstein Tables (Springer-Verlag, Berlin, 1950), Vol. I, Part 1, pp. 395–398.

[20] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon Press, Oxford, 1970), p. 398ff.

[21] W. Lu et al., Phys. Rev. Lett. **67**, 3716 (1991).

[22] T. Moriya, Prog. Theor. Phys. (Kyoto) **16**, 23 (1956).

[23] Strong q dependence of $A(q)$, i.e., $A(q)=0$ at the antiferromagnetic point in the Brillouin zone, occurs only if the dominant hyperfine coupling is the same to the two sublattices. In Y_2BaNiO_5 the Y site is equidistant from nearest-neighbor Ni sites on the same chain, but the bond angles are unfavorable for supertransferred hyperfine interactions through O ligands [E. Šimánek and Z. Sroubek, in Electron Paramagnetic Resonance, edited by S. Geschwind (Plenum, New York, 1972); T. Shimizu et al., Bull. Mag. Res. **12**, 39 (1990)]. Then next-nearest-neighbor coupling to uncorrelated fluctuations on different chains will contribute appreciably to $1/T_1$.

[24] P. Gaveau et al., Europhys. Lett. **12**, 647 (1990); N. Fujiwara et al., Phys. Rev. B **45**, 7837 (1992).