Abstract

Infrared transmission measurements on the $S = 1$ antiferromagnetic chain compound NENP in applied magnetic fields show a sharp absorption line at the field-shifted Haldane gap. This violates a wave-vector selection rule of the Hamiltonian normally used for NENP, as the gap excitations occur at the Brillouin zone boundary. We argue that the crystal structure admits terms which can explain the absorption lines. In addition, in an applied field, staggered orientations of the g-tensors produce a staggered magnetic field. This can explain the observation of a finite gap at all applied fields.
The one dimensional $S = 1$ antiferromagnet NENP has provided detailed experimental evidence [1]-[3] for the current theoretical picture [7]-[10] of $S = 1$ antiferromagnetic chains, and continues to be the subject of a number of investigations. However, there remain some puzzling experimental results. One of these involves infrared transmission measurements [2] in an applied magnetic field in which a sharp absorption line has been observed at the field-shifted Haldane gap. This violates the wave-vector selection rule present in the simple model Hamiltonian generally employed to describe the system. In addition, the measured gap does not vanish at a critical magnetic field but appears to turn around after reaching a finite minimum value. We propose that the data can be understood by including in the Hamiltonian terms arising from a staggered crystal structure which lift the wavevector selection rule. When a uniform field is applied, the staggered $g$-tensor effectively produces a staggered magnetic field, preventing the energy gap from closing.

We begin by comparing the resonance energies from the transmission experiments [2] with the field-shifted gaps at the zone boundary from neutron scattering experiments [4] (Figure 1(a)). The transmission experiments are at a temperature $1.6K$, much smaller than the gap energy ($14K$), so that the absorption is dominated by transitions out of the ground state. The correspondence of the data demonstrates that light creates excitations out of the $k = 0$ ground state into $k = \pi/a$ excited states at the zone boundary. This violates the momentum selection rule of the following Hamiltonian, generally employed for NENP:

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + D \sum_i (S^z_i)^2 + E \sum_i \left[ (S^x_i)^2 - (S^y_i)^2 \right] - \mu_B \sum_i \vec{S}_i \cdot \vec{gH}$$

(1)

where $J$ is the $Ni^{2+}-Ni^{2+}$ exchange, $D$ and $E$ are single ion anisotropies and $\vec{g}$ is the gyromagnetic tensor. The $z$-axis is chosen along the chain axis and $a$ is the spacing between the $Ni^{2+}$ ions. However the correct crystal symmetry of NENP at
low temperatures is given by the space group $Pn2_1a$ \[3\]. This contains the symmetry element $2_1$, which is a two-fold screw axis consisting of a displacement $a$ along the chain, combined with a $180^\circ$ rotation about the chain. The screw axis arises from the alternating orientation of the NO$_2$ groups between the Ni$^{2+}$ ions, which is indicated schematically in Fig.2. The arrangement of NO$_2$ groups on any given chain leads to a uniform electric dipole moment along the chain, and an alternating electric dipole perpendicular to the chain. It also implies that the $D$ and the $g$ tensors of two successive Ni$^{2+}$ atoms on a chain have differently oriented principal axes. The correct Hamiltonian should therefore be

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + \sum_{i \in (1)} [\vec{S}_i \cdot \vec{D}_1 \vec{S}_i - \mu_B \vec{S}_i \cdot \vec{g}_1 \vec{H}] + [\sum_{i \in (2)} \vec{S}_i \cdot \vec{D}_2 \vec{S}_i - \mu_B \vec{S}_i \cdot \vec{g}_2 \vec{H}]$$ (2)

where $1, 2$ refers to the two sublattices on the chain, corresponding the two orientations of the principle axes of the $D, g$ tensors, and we have neglected the staggered anisotropy of the exchange interaction. The presence of the twofold screw axis implies that $\vec{D}_2, \vec{g}_2$ are obtained from $\vec{D}_1, \vec{g}_1$ by a $180^\circ$ rotation about the chain axis. As a function of the applied field, (1) and (2) have different phase diagrams: for (1), there exists a critical field strength $H_c$ \[8\] for any orientation of the field, such that for $H < H_c$ there is no spontaneous staggered polarisation. As $H$ crosses $H_c$, there is an Ising transition into a state with staggered polarisation. For the Hamiltonian (2), the symmetry is explicitly broken, and a staggered polarisation exists for any $H \neq 0$. Moreover, we shall argue below that consistent with the actual symmetry of NENP and Eq.2, there exists a non-zero electric dipole matrix element leading to infrared absorption at the Haldane gap even at $H = 0$, whose magnitude could be large enough to explain the observations. Magnetic dipole transitions implied by Eq.2 could also be important at large $H$.

The Zeeman term in (2) can be written as $\sum_i \vec{h} \cdot \vec{S}_i + (-1)^i \vec{h}_s \cdot \vec{S}_i$ where $\vec{h} = \ldots$
\( \mu_B \vec{H}(g_1 + g_2)/2 \) is the effective uniform field and \( \vec{h}_s = \mu_B \vec{H}(g_1 - g_2)/2 \) is the effective staggered magnetic field. \( \vec{h}_s \) mixes the ground state with the zone boundary excited states and prevents the energy gap from closing at a critical field. This staggered field has been invoked previously by Chiba et al. \[5\] to understand the field-dependent splittings of NMR frequencies observed below the critical field in NENP. These authors estimate \( \delta g_{yz}/g = 0.01 \).

We have employed an approximate model in order to estimate the quantitative effects of the staggered magnetic field on the triplet energies. For simplicity, we ignore here the staggering of the \( D- \) tensor. We model the low lying excitations via a bosonic quantum field theory, which is modified somewhat from the one proposed by Affleck \[8\]. In absence of a staggered field, the field-shifted gaps from our Lagrangian coincide with results of a fermionic field theory proposed by Tsvelik \[9\], which appears to give better agreement with experiment than the unmodified boson theory. We do not use the fermion theory because there the staggered polarisation is a non-local operator.

The Lagrangian we use is (\( h \equiv 1 \)):

\[
\mathcal{L} = \int dt \, dx \left[ \frac{1}{2v} \left( \frac{\partial \vec{\phi}}{\partial t} \right)^2 - \frac{v}{2} \left( \frac{\partial \vec{\phi}}{\partial x} \right)^2 - \sum_i \frac{\Delta_i^2}{2v} \phi_i^2 + \sum_{ijkl} \epsilon_{ijkl} \frac{h_i}{v} \sqrt{\frac{\Delta_i}{\Delta_l}} \phi_j \phi_l 
+ \frac{1}{2v} \sum_{ijklm} \epsilon_{ijk} \epsilon_{klm} \sqrt{\frac{\Delta_j \Delta_m}{\Delta_k}} h_i h_l \phi_j \phi_m - \lambda (\vec{\phi}^2)^2 - \vec{h}_s \cdot \rho \vec{\phi} \right], \tag{3}
\]

where the spin-wave velocity \( v \) and the gaps \( \Delta_i \ (i = 1, 2, 3) \) at the zone boundary are taken as phenomenological inputs. We use the values \( v = 110K, \Delta_1 = 15.7K, \Delta_2 = 13.6K, \Delta_3 = 29K \) \[1\], \[4\]. \( \rho \) is a constant relating \( \phi \) to the staggered polarisation \( m_s = N^{-1} \sum_{i=1}^{N} (-1)^i \vec{S}_i \), so that \( m_s = \rho \phi \). We estimate \( \rho \) from the numerically determined staggered susceptibility \[10\] \( \chi_s = 20/J \) (\( g \mu_B \equiv 1 \)) for the isotropic model.

In the isotropic limit of the quadratic Lagrangian, \( \chi_s \approx \rho^2 v/\Delta^2 \). Using \( v = 2J, \Delta = 0.41J \), we estimate \( \rho = 1.3 \). The above Lagrangian with \( h_s = 0, \Delta_1 = \Delta_2 \), produces the same field dependent gaps at the zone boundary as the fermionic Lagrangian in
As an illustration, for \( h_s = 0 \), \( h = h\hat{x} \), the lowest magnon branch has energy given by

\[
\omega^2(k) = k^2 + h^2 + \frac{1}{2}(\Delta_2^2 + \Delta_3^2) - \sqrt{\left(\frac{\Delta_2^2 - \Delta_3^2}{2}\right)^2 + h^2(\Delta_2 + \Delta_3)^2 + k^2 h^2 \left(\sqrt{\frac{\Delta_2}{\Delta_3}} + \sqrt{\frac{\Delta_3}{\Delta_2}}\right)^2}
\]

(4)

At \( k = 0 \), this formula is identical to Eq. 16c in [9], while the formulas differ slightly for finite \( k \). We remark that Date and Kindo [6] have discussed a model where the magnon energies at the zone boundaries are those of a single \( S = 1 \) spin in presence of uniaxial anisotropy. After proper identification of the zero-field gaps, the field-shifted gaps calculated from such a single-ion Hamiltonian are identical to (4) and Eq.16c in [9].

To estimate \( \lambda \), we need to know the non-linear staggered susceptibility. In the isotropic limit, the mean field staggered polarisation is \( m_s = \chi_s h_s - A(\chi_s h_s)^3 + O(h_s^5) \), where \( \chi_s = \rho^2 v/\Delta^2 \) and \( A = 4\lambda v/(\Delta^2 \rho^2) \). From perturbation theory, we obtain for large \( h_s \), \( m_s = 1 - (J/h_s)^2 + O((J/h_s)^4) \). Matching the large and small \( h_s \) behaviour using a simple functional form \( m_s = \chi_s h_s / (1 + B\chi^2 h_s^2 + \chi^4 h_s^4)^{1/4} \), we obtain an estimate \( A = 1, \lambda = \Delta^2 \rho^2 / (4v) \). Assuming \( \Delta = 0.41 J, v = 2J, J = 55K \) we have a rough estimate, \( \lambda = 3.7K \).

Finally, we need to estimate the staggered field produced by an applied uniform field \( h \). Consider the case where \( h \parallel \hat{z} \). Taking into account the observations of Chiba et. al., we calculate the field dependent gaps for (i) \( h = h\hat{z}, h_s = 0.01h\hat{y} \). A transverse field applied along the \( a- \)axis makes an angle of 32° with the \( x- \)axis of an individual chain. We therefore calculate field dependent gaps for (ii) \( h = h(\hat{x}\cos(32°) + \hat{y}\sin(32°)), h_s = 0.01\sin(32°)h\hat{z} \). The mean field values of the zone boundary gaps are plotted in Figures 1(a),(b), and Figure 3 shows the corresponding staggered polarisations.
We now consider the interaction Hamiltonian responsible for the absorption. The momentum selection rule can in principle be lifted by the presence of localised impurities or by having chains of finite length. However, in this case, excited states would be generated with all possible momenta, producing a threshold instead of a sharp line. The observed lines are sufficiently narrow so that this seems to be an unlikely explanation. We will restrict our attention to Hamiltonians that preserve the crystal symmetry. We consider two cases, (a) interaction Hamiltonians that violate the translational symmetry of (1), and (b) interaction Hamiltonians that maintain the translational symmetry but where the absorption is allowed in presence of a staggered polarisation when $H \neq 0$. In both cases, we consider (i) magnetic and (ii) electric dipole transition Hamiltonians. We present below results only for the dc field along the chain axis.

In case (a)(i), the transition Hamiltonian is $H_I(t) = -\mu_B \vec{H}_{rf}(t) \cdot \delta \cdot \sum_i (-1)^i \vec{S}^i$, where $\vec{H}_{rf}$ is the magnetic field of the infrared radiation. The absorption intensity for the two lower branches from this Hamiltonian should be a maximum when $\vec{H}_{rf} \parallel \hat{z}$, and should vanish for $\vec{H}_{rf} \perp \hat{z}$. For $\vec{H}_{rf} \parallel \hat{z}$, the absorption coefficient is

$$\alpha(\omega) = \frac{\mu_0 n (\delta g_{yz} \mu_B)^2}{\hbar c} \omega \int_{-\infty}^{\infty} \frac{1}{N} \sum_{i,j} \langle (-1)^{i-j} S_y^i(t) S_y^j \rangle e^{i\omega t} dt$$

(5)

where $n$ is the density of nickel ions, $\langle \cdot \rangle$ is the ground state expectation, and $\delta g_{yz}/g \approx 0.01 \ [\text{3}].$ At zero applied field, assuming axial symmetry, $\langle (-1)^{i-j} S_y^i(t) S_y^j \rangle \approx (1/3)(e^{-i\Delta \cdot t/\hbar} + e^{-i\Delta \cdot t/\hbar})e^{-\Gamma t} f(|i - j|)$, where $f(0) = 1$, and $f(i)$ decays exponentially for large $i$ with the transverse correlation length $\xi$. At resonance, this yields for the lowest branch, $\alpha \approx (3 \times 10^{-5} m^{-1}) Q(\xi/a) \cos^2(\theta_M)$, where $Q = \Delta_+/\hbar \Gamma$ and $\vec{H}_{rf} \cdot \hat{z} = H_{rf} \cos(\theta_M)$. We estimate the $Q$ value at low fields from the experimental data $\ [\text{2}]$ to be be crudely $100$, and also $\xi/a \approx 10 \ [\text{1}].$ This yields $\alpha \approx 3 \times 10^{-2} m^{-1}$. Assuming a sample thickness of 1 $\text{mm}$, this gives an absorption dip of 0.003% of
transmitted light, small compared to the observed absorption of $\approx 0.5\%$.

In case (b)(i), the transition Hamiltonian is $H_I(t) = -\mu_B \vec{H}_{rf}(t) \cdot \vec{g} \cdot \sum_i \vec{S}_i$. The orientation dependence of the absorption is the same as in (a)(i). For $\vec{H}_{rf} \parallel \hat{z}$, the absorption coefficient can be obtained from Eq.(5) with the replacements $\delta g_{yz} \rightarrow g_{zz}$, $(−1)^{i−j} \rightarrow 1$. At low applied fields, noting that $\sum \vec{S}_i \approx (1/v) \sum \vec{\phi}_i \times \vec{\phi}_i$, we find a mean field estimate of the absorption at the lowest gap energy $\alpha \approx \alpha_M Q(\xi/a)(\Delta_+/2J)^2 < \phi_y >^2 \cos^2(\theta_M)$, where $\alpha_M = \mu_0 n (g_{zz} \mu_B)^2 / hc = 0.3 \, m^{-1}$. With parameter values as above, this value of $\alpha$ is again too small to explain the observed low field intensities. At high fields, however, the staggered polarization becomes quite large. The lowest mode then predominantly consists of angular fluctuations, and we may expect a linearised spin-wave calculation to give qualitatively correct values of $\alpha$. Such a calculation gives $\alpha \approx \alpha_M Q(2J <\phi_y>/\Delta_+) \cos^2(\theta_M)$. The line broadens at high fields, and taking parameter values to be $Q \approx 10$, $<\phi_y> \approx 0.3$, $\Delta_+ \approx 5K$, $\theta_M = 0$, we obtain $\alpha \sim 200m^{-1}$, implying an absorption coefficient of 20% for a sample 1 mm in thickness. This is consistent with the experimental absorption at high fields.

We now consider electric dipole transitions. The $Ni^{2+}$ positions lack a center of inversion symmetry [3], and electric dipole transitions are therefore allowed within the spin manifold. An appropriate Hamiltonian for case (a)(ii) is a time-dependent Dzyaloshinskii-Moriya (DM) Hamiltonian [11]

$$H_{I}^{elec} = p \vec{E}_{rf}(t) \times \hat{n}_{perp} \cdot \sum_i (-1)^i \vec{S}_i \times \vec{S}_{i+1},$$

where $\vec{E}_{rf}$ is the oscillating electric field from the light wave and $\hat{n}_{perp}$ is a unit vector along the staggered component of the internal electric field $\vec{E}_{in}$. The static DM exchange is of the order of [11] $J_A \approx J \delta g/g \sim 1K$. We write $p \equiv \eta J_A/E_{in}$, where $\eta$ is a dimensionless constant, and we estimate $E_{in}$ as the field produced by one electronic charge at a distance of 3A. This implies $p = \eta 10^{-33}C - m$. The absorption
in the lowest branches from the above Hamiltonian vanishes when $E_{rf} \perp \hat{z}$ and is a maximum when $E_{rf} \parallel \hat{z}$. For the latter case, 

$$\alpha(\omega) = \frac{np^2}{\epsilon_0 \hbar c} \omega \int_{-\infty}^{\infty} \frac{1}{N} \sum_{i,j} \langle A_i(t) A_j \rangle e^{i\omega t} dt$$

(7)

where $A_i = \hat{z} \times \hat{n}_{perp} \cdot (-1)^i \vec{S}_i \times \vec{S}_{i+1}$. From the field theoretic description it follows that $\sum (-1)^i \vec{S}_i \times \vec{S}_{i+1} \approx (1/v) \sum \phi_i \partial \phi_i / \partial t$. Noting this relation, we estimate $\alpha$ for the gap energy to be $\alpha \approx \alpha_E Q (\xi/a)(\Delta_+/2J)^2 \cos^2(\theta)$, where $E_{rf} \cdot \hat{z} = E_{rf} \cos(\theta_E)$ and $\alpha_E = np^2/\epsilon_0 \hbar c = 4\eta^2 \times 10^{-3} m^{-1}$. Taking typical values at low fields to be $Q \approx 100$, $\Delta_+ \approx 10K$ and $\xi/a \sim 10$, we obtain $\alpha \sim 0.04\eta^2 m^{-1}$. In order to obtain an absorption comparable to the experimental value of 0.05% for a 1 mm thick sample, we must take $\eta = 10$, which is large, but does not seem impossible. At high fields, a linearised spin wave theory yields for the lowest mode $\alpha \approx \alpha_E Q(2J/\Delta_+) \langle \phi_y \rangle^2 \cos^2(\theta_E)$. For $Q \approx 10$, $\eta = 10$, $\langle \phi_y \rangle \approx 0.3$, $\Delta_+ \approx 5K$, $\theta_E = 0$, we obtain an absorption coefficient of 10% for a sample 1 mm in thickness, comparable to the experimental absorption at high fields.

The Hamiltonian for case (b)(ii) includes a time dependent symmetric exchange and a time dependent on-site anisotropy. The absorption from these terms have the same selection rules at high fields as the case (a)(ii).

To summarise our observations on the absorption intensities: while these do not strictly vanish for any orientation of the polarisation plane of light, the magnetic dipole or electric dipole absorption intensities for a particular line can individually vanish for special orientations of the polarisation plane. The magnetic dipole absorption at low fields is estimated to be too weak to explain the observations, while the spin wave estimate at high field for the lowest branch produces numbers closer to the observation. We cannot estimate the electric dipole absorption with accuracy, but our crude estimate indicates that it can produce plausible absorption strengths at all the
applied fields. A priori, there is no reason why the two absorption mechanisms should have the same strength, so that one might expect significant angular dependence in the intensities. Careful studies of the angular dependence of the intensities should clarify the absorption mechanisms. The strong increase in the absorption intensities at high fields is presumably related to the appearance of a large staggered moment.

In conclusion, the experimentally observed infrared absorption in NENP at low temperatures \[2\] can be understood after taking into account the crystalline symmetry of the material. The presence of a staggered, anisotropic g-tensor produces a staggered internal field when a uniform magnetic field is turned on. This prevents the gap from closing at a critical field. Mean field calculations of the gap energies qualitatively agree with the experimental observations. Transition Hamiltonians can be found consistent with the reported crystalline symmetry of NENP that break the translational symmetry of the spin chain, and can explain the observed transitions.

The conclusions of our work are corroborated by recent spin resonance experiments \[12\] where the temperature was varied. The absorptions corresponding to those described in \[2\] rapidly disappear with increasing temperature, consistent with the depopulation of the ground state. As the temperature is raised, absorptions corresponding to flipping the spins of excited magnons increasingly become visible. One remaining mystery about the absorption, however, is the splitting of each absorption peak observed in the experiments of Ref. \[2\].

We would like to thank D. Huse, S. Geschwind, W. Lu and I. Silvera for illuminating discussions. This work was supported in part by NSF grant DMR 91-15491 and by a fellowship to PPM from the Schlumberger Corporation.
REFERENCES

[1] W. J. L. Buyers et. al. Phys. Rev. Lett. 56, 371 (1986); M. Steiner et. al. J. Appl. Phys. 61, 3953 (1987); J. P. Renard et. al. Europhys. Lett. 3, 945 (1986); J. P. Renard et. al. J. Appl. Phys. 63, 3538 (1988); K. Katsumata et. al. Phys. Rev. Lett. 63, 86 (1989); Y. Ajiro et. al. Phys. Rev. Lett. 63, 1424 (1989); M. Hagiwara et. al. Phys. Rev. Lett. 65 3181 (1990).

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

[3] A. Meyer et. al. Inorg. Chem. 21 1729 (1982).

[4] L. P. Regnault et. al. Physica B 180 188 (1992).

[5] M. Chiba et. al. Phys. Rev. B44, 2838 (1991).

[6] M. Date and K. Kindo, PRL 65, 1659 (1990);

[7] F. D. M. Haldane, Phys. Rev. Lett. 50, 1153 (1983); R. Botet, R. Jullien and M. Kolb, Phys. Rev. B28, 3914 (1983); J. B. Parkinson and J. C. Bonner, Phys. Rev. B32, 4703 (1985); M. P. Nightingale and H. W. J Blote, Phys. Rev. B33, 659 (1986); H. J. Schulz and T. Ziman, hys. Rev. Lett. 33 6545 (1986); T. Kennedy, J. Phys. Cond. Matt. 2, 5737 (1990); I. Affleck et. al. Phys. Rev. Lett. 59, 799 (1987); ibid. Commun. Math. Phys. 115, 477 (1988).

[8] Ian Affleck, Phys. Rev. B41 6697 (1990); Ian Affleck, Phys. Rev. B43 3215 (1991).

[9] A. M. Tsvelik, Phys. Rev. B42 10499 (1990).

[10] T. Sakai and M. Takahashi, Phys. Rev. B43, 13383 (1991); Phys. Rev. B43, 659 (1991).
[11] See p.90-91 in *Magnetism*, V1, Ed. G.T.Rado and H.Suhl, Academic Press, NY (1963).

[12] W.Palme *et. al.* *Int.J.Mod.Phys B*, 1016 (1993).
FIGURES

In (a), the field shifted gaps from neutron scattering (circles) for $h \parallel \hat{z}$ are compared to the positions of the absorption dips in the transmission experiment (crosses). (b) corresponds to field applied transverse to the chain, for which only neutron scattering data (circles) is available. The solid lines in (a),(b) result from the mean field calculation described in the text.

Schematic diagram of the backbone of an NENP chain, showing its staggered structure.

Mean field staggered polarisations corresponding to the gaps in Fig.1. The NMR lineshifts from Chiba et.al., are shown as dots. The lineshifts have been scaled by a constant to make one point lie on the theoretical curve.