Direct Observation of the Haldane Gap in NENP by Far-Infrared Spectroscopy in High Magnetic Fields

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We report the first direct and comprehensive determination of the energy levels involved in the Haldane gap occurrence: the singlet ground state and the first triplet excited state. Precise values of the parameters are obtained from the analysis of the magneto-optical resonance transitions observed in the far infrared for frequencies ranging from 70 to 1000 GHz and magnetic fields up to 18 T.

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The great interest in low-dimensional magnetic systems [1] has been strongly renewed recently following a suggestion by Haldane [2] that an energy gap exists in the excitation spectrum of one-dimensional Heisenberg antiferromagnets with integer spins. Numerical simulations [3] and the proof of a solvable model [4] supported the conjecture that a quantum energy gap exists in a linear-chain Heisenberg antiferromagnet (LCHA) with integer spin between the singlet ground state and the lowest excited triplet.

Several experiments have been performed to confirm the existence of this "Haldane gap." The compound $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) is to date the best real system approaching the ideal LCHA with $S=1$. The single-ion anisotropy which in general splits the first excited state for integer $S \geq 1$ and the interchain exchange interaction constant J' responsible for three-dimensional ordering are both small compared to the intrachain exchange interaction constant J, giving the possibility for an energy gap to appear. Susceptibility measurements [5] showed a rounded maximum and an abrupt fall as the temperature was lowered below 15 K. No long-range order was observed down to 1.2 K whatever the field orientation with respect to the crystallographic axes. Two gap energies were obtained for the principal directions parallel and perpendicular to the chain axis. Inelastic neutron-scattering experiments [5] also supported the existence of an energy gap at the boundary of the Brillouin zone with values different from those extracted from the susceptibility data. More recently, magnetization experiments [6,7] in large magnetic fields showed that the magnetization, very small in the low-field region, begins to increase sharply at finite fields along the three principal axes giving evidence for the existence of the Haldane gap. Electron paramagnetic resonance (EPR) is generally considered one of the best methods to study the spin system at a microscopic level. It was used to determine the scheme of energy levels [8] and to test the Haldane gap via the introduction of impurities [9]. As a result of the limited ranges of frequencies and fields available only intraexcited triplet transitions were observed in the experiment by Date and Kindo [8] and the energy gap was obtained indirectly. Therefore it seemed useful to extend the EPR measurements to a wider range of fields and frequencies in order to obtain a comprehensive scheme of the energy levels involved in the occurrence of the Haldane gap.

We report here the first observation of optical resonance transitions between the ground state and the first excited states in the $S=1$ linear-chain Heisenberg antiferromagnet NENP giving direct evidence for the Haldane gap for $q=0$. The magnetotransmission experiments on pure and Cu-doped samples with 1% Cu were performed for the external magnetic field up to 18 T parallel to each of the principal axes a, b, and c of the crystal using monochromatic microwaves and far-infrared (FIR) radiation at temperatures between 1.6 and 4.2 K. Both Faraday and Voigt configurations were used corresponding to geometries with the wave vector of the radiation parallel and perpendicular to the external magnetic field, respectively. For the low frequencies impact avalanche transit-time diodes were used, whereas the source of FIR frequencies was a CO_2 optically pumped molecular gas laser. The integrated sample-holder–

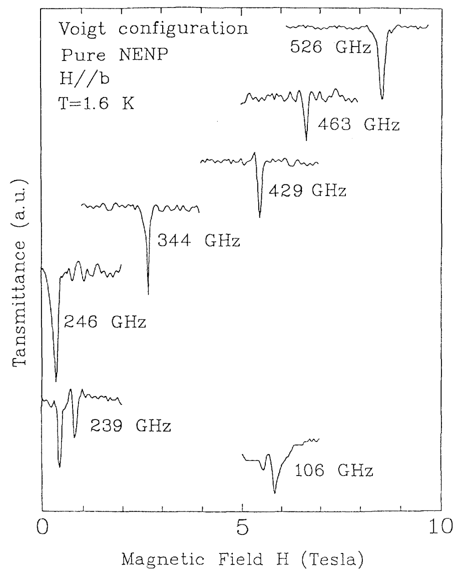

FIG. 1. Experimental data of the magnetotransmission of pure NENP at $T=1.6$ K for $\mathbf{H}\|\mathbf{b}$ in Voigt configuration for different radiation frequencies as a function of the magnetic field. The resonances are independent of the polarization in Voigt configuration. The scaling of the spectra varies with frequency, but the intensity of all resonance lines is of the order of 1% of the total transmission.

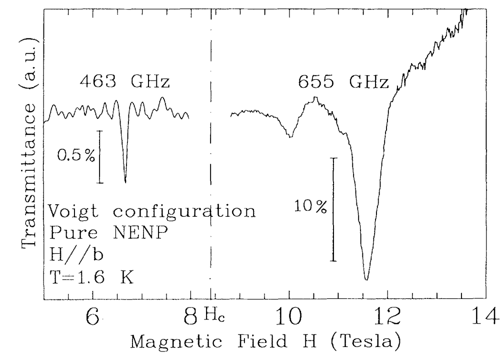

FIG. 2. The character of the magnetoresonances differs considerably below and above the phase transition at H_c. Data for pure NENP recorded in Voigt configuration at $T=1.6$ K for $\mathbf{H}\|\mathbf{b}$. Please note the different scale in intensity for both measurements indicating that the resonance below H_c is actually forbidden.

detector setup was positioned in the bore of either a 15-T superconducting solenoid or an 18-T Bitter magnet. Typical recorder traces are presented in Figs. 1 and 2 for pure NENP samples. One can see a very strong qualitative difference between the observed resonance lines. Some are very weak and narrow; others are very strong and large. This observation helps in the identification of the resonances observed at different frequencies and fields. The observed lines are weak and narrow at fields lower than $H_c \approx 8.4$ T and they are large and strong above this field. In Fig. 3 the frequency versus field chart of all resonances observed in Voigt configuration is presented for the external magnetic field applied parallel to the b axis, i.e., the chain axis. In Faraday configuration some new resonance lines appear which will not be discussed here but support fully the data obtained in Voigt configuration. Results with the external magnetic field parallel to the a and c axis were also obtained. They confirm the analysis developed below and will be presented in a more complete report together with the data obtained in Faraday geometry. Below H_c there are only two sets of resonances which extrapolate to a frequency of 260 GHz at zero field. Above H_c there are three sets of resonance lines. Two of them have the same slope, the same as the two sets observed below H_c, whereas the third one has a slope approximately double.

If one follows Haldane's conjecture for $\mathbf{H}\|\mathbf{b}$, the resonance lines arise from transitions between eigenstates of the Hamiltonian

$$\mathcal{H}=\sum_i \left\{ -J\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\mu_B S_{z_i} g_b H + D\left[S_{z_i}^2-\frac{S(S+1)}{3}\right]+E(S_{x_i}^2-S_{y_i}^2)\right\}.$$

We have calculated the eigenvalues of this Hamiltonian using a six-spin-ring model with scaling technique [10]. Basically this technique extrapolates the results from a system with a limited number of spins to the case of an infinite number of constituents. The parameters extracted from the best fit of the experimental data give the following values: $D=1.6\times10^2$ GHz$\equiv$7.8 K, $E=8.8$ GHz $\equiv$0.42 K, $J=-9.9\times10^2$ GHz$\equiv-48$ K, $g_b=2.2$, and $E_g=0.36|J|\equiv17$ K. Because of both the small linewidth of the resonances, especially those corresponding to the $|00\rangle\rightarrow|11\rangle$ transitions, and the simple fitting procedure, we estimate that the above parameters are determined within an accuracy better than 5%. The value obtained for the Haldane gap is slightly smaller than the value $E_g=0.41|J|$ [10] or the value $E_g=0.38|J|$ [11].

The continuous line in Fig. 3 represents the theoretical results. For the sake of comparison our data can be interpreted in the framework of the energy levels presented by Date and Kondo [8]. The results can be explained by assuming an effective Hamiltonian for the triplet given by

$$\mathcal{H}=\mu_B S_z g_b H + D'\left[S_z^2-\frac{S(S+1)}{3}\right] + E'(S_x^2-S_y^2)+E_g' ,$$

where $D'=-1.8D=-2.9\times10^2$ GHz$\equiv-14$ K, $E'=-1.7E=-15$ GHz$\equiv-0.72$ K, $E_g'=3.6\times10^2$ GHz

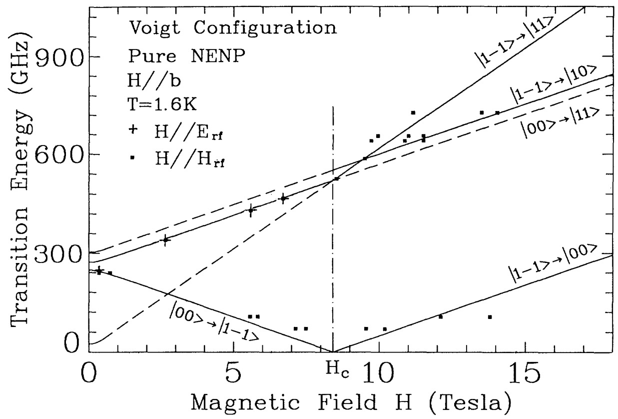

FIG. 3. Schematic of the transition energies in pure NENP for **H**‖**b** with the experimentally found resonance positions for both ordinary and extraordinary Voigt configuration. The continuous or dashed lines correspond to theoretical results. They are also shown as a guide to the eye. Note that the order of ground and excited state is inverted for magnetic fields above H_c, so that only the solid lines are realized in the experiment. The crosses are for the ordinary Voigt configuration and the squares are for the extraordinary Voigt configuration.

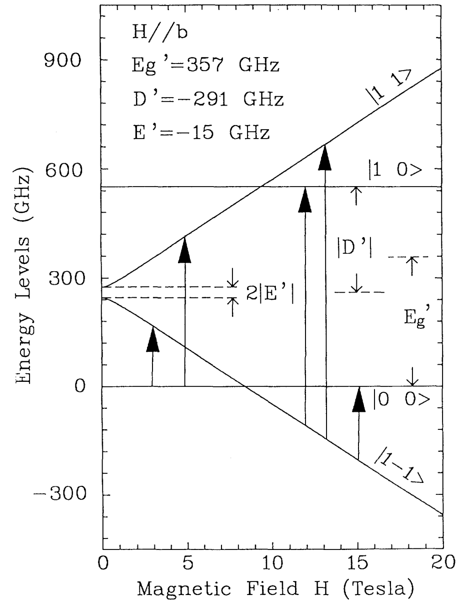

FIG. 4. Energy-level scheme for the ground-state singlet and excited-state triplet in NENP for **H**‖**b**. The arrows indicate different transitions observed between the ground-state singlet and the excited states, $|00\rangle \rightarrow |11\rangle$ and $|00\rangle \rightarrow |1\,-1\rangle$, and between the excited states, $|1\,-1\rangle \rightarrow |10\rangle$ and $|1\,-1\rangle \rightarrow |11\rangle$.

$\equiv 17$ K, $g_b = 2.2$. Therefore, including the ground state, the scheme of the four energy levels involved in the magneto-optical transitions that we have observed is presented in Fig. 4.

In principle, transitions between the subspaces ($|00\rangle$) and ($|10\rangle$, $|1\,-1\rangle$, $|11\rangle$) are forbidden for simple magnetic dipole excitation. At low temperatures only the lowest level is significantly populated. The observed transitions involve as a starting state the singlet ground state $|00\rangle$ below the crossing point at H_c and the excited triplet state $|1\,-1\rangle$ above H_c. At low fields we observe the transitions $|00\rangle \rightarrow |1\,-1\rangle$ and $|00\rangle \rightarrow |11\rangle$. These transitions are also forbidden, but one can expect that the selection rules can be lifted by higher-order terms in the Hamiltonian or due to the fact that the chains of nickel atoms are not infinitely long. For instance at the lowest frequency that we have used, the mixing of the two states $|00\rangle$ and $|1\,-1\rangle$ produces a sensitive increase in the intensity of the absorption. At higher fields the ground state is $|1\,-1\rangle$. Transitions can occur to levels $|00\rangle$ and $|10\rangle$ with strong intensity, and to level $|11\rangle$ with small intensity because it involves a $\delta S_z = 2$ transition. Around H_c the experimental data reflect an interaction between the $|00\rangle$ and $|1\,-1\rangle$ states caused by finite-size effects: The coherence length of the spins diverges and the two states are coupled [12]. It should be noted that if the resonances observed below the critical field H_c were arising from transitions from the $|1\,-1\rangle$ levels instead of arising from transitions from the $|00\rangle$ level, the intensity of the resonances would increase when occurring at higher magnetic fields because the $|11\rangle$ level becomes more populated. This is not the case, as is shown in Fig. 1.

Compared to the scheme presented by Date and Kindo there is one main difference: There seems to be no sign of the presence of the spin-wave continuum below the first excited triplet. This is supported by the fact that at high frequencies we still observe sharp resonance lines, whereas one would expect some broadening by the spin-wave continuum.

In the Cu-doped samples, besides the resonances which are described above, we have observed resonances corresponding to transitions between the two $S_z = \pm \frac{1}{2}$ states with g values between $g = 2.01$ and 2.15.

In conclusion the energy-level diagram of the four lowest energy states in the one-dimensional linear-chain Heisenberg antiferromagnet NENP has been obtained. It strongly supports the conjecture of the existence of a Haldane gap, although a rather large single-ion anisotropy exists in this material.

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