Dynamic Structure Factor $[S(Q,\omega)]$ of the $S=1$ Quasi-One-Dimensional Heisenberg Antiferromagnet: Neutron-Scattering Study on $AgVP_2S_6$

H. Mutka,[1] C. Payen,[2] P. Molinié,[2] J. L. Soubeyroux,[1] P. Colombet,[2] and A. D. Taylor[3]
[1]*Institut Laue-Langevin, 156X, 38402 Grenoble CEDEX, France*
[2]*Institut des Matériaux de Nantes, 2 rue de la Houssinière, 44072 Nantes CEDEX 03, France*
[3]*Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom*
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The spin correlations of the $S=1$ Heisenberg antiferromagnetic chains in $AgVP_2S_6$ have been studied by neutron scattering at temperatures of the order of $T\sim 10^{-2}J/k_B$. On the polycrystalline samples, with a careful choice of experimental conditions, we have observed a Haldane gap of $E_g=26$ meV at the antiferromagnetic point at $q=\pi$. The excitation spectra are consistent with a mode that has a spin-wave velocity $C=150$ meV and a correlation length $\xi\approx 5.5$, close to C/E_g. These results are in quantitative agreement with the predictions and numerical results on the Haldane state.

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Haldane's predictions [1,2] concerning the behavior of the isotropic-exchange, spin $S=1$, antiferromagnetic chains triggered a continuous attraction to this apparently simple but strong statement that distinguishes between the integer and half-integer spin systems, with and without a gap for elementary excitations, respectively. The consequent numerical work as well as the results on exactly solvable models have been reviewed recently by Affleck [3]. The numerous quantum Monte Carlo calculations seem to give a consistent set of data in what concerns both the energy scale of the excitation spectrum and the dynamic correlations in the Haldane state [4–8]. The experimental work in this fascinating field has mostly concentrated on two $S=1$ chain compounds, $CsNiCl_3$ and $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, or NENP. After the first demonstration of the existence of the Haldane gap by neutron inelastic scattering [9,10] the more detailed investigations using neutrons [11–14], as well as results on high-field magnetization [15,16], on electron paramagnetic resonance [17], and on nuclear magnetic resonance [18], for example, have pointed out the particular properties of the $S=1$ spin chains.

Another $S=1$ chain compound with a gap for magnetic excitation is $AgVP_2S_6$, with well separated V^{3+} chains embedded in a layer matrix [19]. Originally observed by magnetic susceptibility [20], the gap was confirmed in a preliminary inelastic-neutron-scattering study a while ago [21]. These results stimulated the more detailed investigation reported in the present Letter. The drawback of $AgVP_2S_6$ for neutron-scattering studies is that it can be prepared in sufficient quantity only in polycrystalline form. However, as will be shown below, the powder-averaged data obtained on the powerful time-of-flight spectrometers at Institut Laue-Langevin (ILL) and Rutherford Appleton Laboratory (RAL) give rather detailed information on the dynamic spin correlations. Especially, we are able to demonstrate that the gap mode does start from the $q=\pi$ 1D reciprocal point. Furthermore, applying a simple spin-wave model we can extract a value for the correlation length and for the spin-wave velocity of the excitations. All these results give a consistent picture that agrees quantitatively with the quantum Monte Carlo predictions [4–8].

The static magnetic properties of $AgVP_2S_6$ have been examined by both magnetic-susceptibility measurements on polycrystals and small single crystals and by neutron powder diffraction. These results have evidenced the remarkable isotropic character of the strong antiferromagnetic exchange occurring in the chains together with the small V^{3+} single-ion anisotropy D [22]. A Haldane-gap behavior is deduced from the nonclassical low-temperature dependence of the susceptibility that cannot be explained by single-ion or exchange-anisotropy effects. A very important observation is that there is no sign of any 3D magnetic ordering down to 2 K, although an ordering temperature $T_N=10$–15 K would be expected from the ratio of the intrachain to interchain coupling constants that was obtained by considering the broadening of the 1D singularity of the density of magnetic states [21]. This absence of long-range order has been confirmed by the neutron-diffraction patterns that were recorded with a polycrystalline sample on the D1B diffractometer at ILL at temperatures ranging from 120 to 2 K (in steps of about 3 K). The whole set of lines and their intensities were refined using the profile refinement technique starting from the nuclear structure deduced from single-crystal x-ray diffraction at room temperature. The unweighted reliability factors varied in the range 0.023 to 0.024 without any systematic trends with temperature. We want to stress that absolutely no elastic magnetic contribution was observed in this very careful study, in opposition to the preliminary results reported earlier [21]. Thus, no sign of static magnetic correlations, neither 3D nor 1D, were found in $AgVP_2S_6$ down to 2 K. This feature is as expected because of the disordered 1D character of the Haldane ground state that prevents the onset of 3D order at least up to a critical value of the interchain coupling. This point has been discussed both qualitatively and quantitatively by several authors [23,24]. The static magnetic parameters of $AgVP_2S_6$ are summarized

TABLE I. Magnetic parameters of $AgVP_2S_6$ ($H = J\sum S_i \times S_{i+1}$, $J > 0$; for notations see text).

π/d (Å^{-1})	J [a] (meV)	J'/J [b]	D/J	E_g (meV)	C (meV)	ξ
1.07	58 ± 4	$\leq 10^{-5}$	2×10^{-4}	26	150 ± 10	5.5 ± 1

[a]Calculated from $C = 2.6J$.
[b]Taking the broadening $\Delta = 1.4$ meV as transverse dispersion, i.e., equal to $8(JJ')^{1/2}$.

in Table I ($H = J\sum S_i S_{i+1}$, $J > 0$).

Time-of-flight neutron-scattering experiments were performed at ILL using the IN4 spectrometer and at RAL using the HET spectrometer, at temperatures of $T = 5$ and 20 K, respectively. The combined use of the two instruments gives an extensive set of incident energies E_i and scattering angles θ that allows us to choose the (Q,ω) range of particular interest. Especially the high incident energy available on the HET instrument was crucial in examining the excitations at low values of momentum transfer Q. In consequence, in spite of the powder character of the samples, we can observe and analyze the dispersive features of the excitations. After correcting for instrumental background the data were transformed into $S(Q,\omega)$ at fixed angles and, when needed, summed to cover an appropriate (Q,ω) range. Measurements on vanadium samples taken in similar conditions were used in the data analysis to correct for instrumental resolution. All measurements were done with highly transmitting samples (transmission $\geq 95\%$) in order to avoid multiple-phonon-scattering background at the low-Q region (up to ~ 3 Å^{-1}) that is of interest for the magnetic contribution. In consequence, the magnetic excitation spectrum is superposed on a weak phonon background that can be subtracted using high-Q data, as discussed before [21].

On the polycrystalline samples the inelastic-neutron-scattering spectra are integrals in (Q,ω) space, over a domain defined by the E_i and θ values in use. At a fixed scattering angle θ the energy-transfer-dependent scattered intensity is proportional to $S(\theta,\omega)$ of the form

$$S(\theta,\omega) = S(Q,\omega)_{Q=Q(E_i,\theta,\omega)}. \quad (1)$$

In this expression $S(Q,\omega)$ is the powder average of the dynamic spin-spin correlation function $S(\mathbf{Q},\omega)$ of the magnetic system, i.e.,

$$S(Q,\omega) = \frac{1}{4\pi Q^2} T(\omega)|F(Q)|^2 \int_{\mathbf{Q}=\mathbf{q}+\mathbf{q}_p} S(\mathbf{Q},\omega)\,d\mathbf{Q}. \quad (2)$$

Here the momentum transfer $\mathbf{Q}$ is decomposed to a component $\mathbf{q}$ along the chain and $\mathbf{q}_p$ perpendicular to it as convenient for a quasi-1D system, $T(\omega)$ is the temperature factor ($T(\omega) = [1 - \exp(-\hbar\omega/k_B T)]^{-1}$ for our neutron energy-loss spectra), $F(Q)$ is the ionic form factor, and the integral is taken over the accessible values in the phase space.

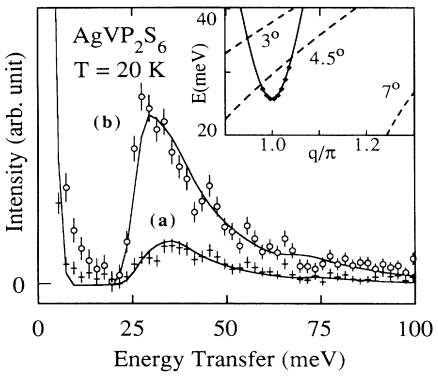

FIG. 1. Magnetic excitation spectra on $AgVP_2S_6$ (HET with $E_i = 220$ meV): Curve *a* for the angular range $3 < \theta < 4.5$ deg; curve *b*, for $3 < \theta < 7$ deg. The (Q,ω) traces of the neutrons (dashed lines) in the inset show that case *a* excludes the valley with the characteristic 1D singularity at the point (π, E_g). The continuous lines are fits with the model explained in the text, summing up the theoretical intensity over the appropriate angular range.

Even after powder averaging the 1D antiferromagnetic excitations are expected to show a strong intensity when the reciprocal point $q = \pi$, situated at $\pi/d = 1.07$ Å^{-1}, is contributing (the spin-spin distance along the chain is $d = 2.96$ Å). This is indeed observed as can be seen in Fig. 1, which shows how the exclusion of the point ($q = \pi$, $\hbar\omega = E_g$) cuts down the measured intensity coming from the 1D singularity at $\hbar\omega = E_g$. In addition the measurements at high enough incident energy, shown in Fig. 2, contain a strong contribution that slopes down at energy transfers centered at $\hbar\omega = 150$ meV. We attribute this

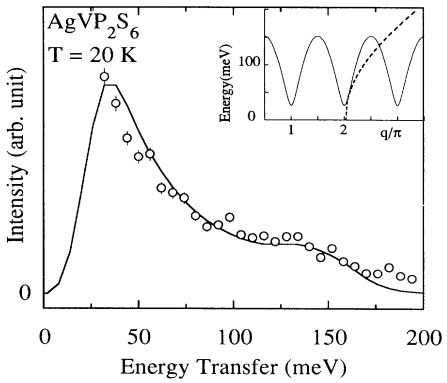

FIG. 2. Magnetic excitation spectrum on $AgVP_2S_6$ (HET, $E_i = 650$ meV), in the angular range $3 < \theta < 7$ deg, corresponding to the (Q,ω) range depicted in the inset. The high incident energy favors the observation of high-energy-transfer contributions because of the small value of Q. Accordingly the band edge around $\hbar\omega = C \approx 150$ meV becomes visible. The fitted continuous line suggests a broadening of the order of $\Delta = 30$ meV (FWHM) at the point $q = \pi/2$.

intensity to the point $q=\pi/2$ where the collective antiferromagnetic excitations have their maximum energy, deduced to be $\hbar\omega=C=2.6J$ for the $S=1$ Heisenberg chains from finite-system and quantum Monte Carlo calculations [5,6]. These model-independent results fix the energy scale of the excitations: $J\approx 150/2.6$ meV $=58$ meV, $E_g=25$–30 meV at the antiferromagnetic point. In fact, our experimental data are in good agreement with an idealized 1D model that we now explain in detail.

We apply the following 1D dispersion model:

$$\hbar^2\omega^2(q)=E_g^2+C^2\sin^2(q-\pi)\,, \tag{3}$$

where E_g is the excitation gap and C the spin-wave velocity. We assume a purely 1D scattering law with the correlation length ξ to describe the q dependence of the intensity,

$$S(q,\omega)=\delta(\omega-\omega(q))\{[(q-\pi)^2+\xi^{-2}]^{-1/2} - [(q+\pi)^2+\xi^{-2}]^{-1/2}\}\,, \tag{4}$$

with the square-root-of-Lorentzian-type q dependence inspired by the Monte Carlo results of Nomura [6] and fulfilling the condition $S(0)=0$. Then the powder-average $S(Q,\omega)$ will reduce to the density-of-states function $g(\omega)$ of the dispersion relation of Eq. (2), weighted by the instantaneous spin-spin correlation $S(q)=S(q(\omega))$, i.e.,

$$S(Q,\omega)=(4\pi Q^2)^{-1}S(q)g(\omega)T(\omega)|F(Q)|^2\,, \tag{5}$$

where the q dependence can be replaced explicitly by ω dependence by inverting the dispersion relation (3). We have fitted the experimental results with the model of Eq. (5) taking into account the instrumental resolution and calculating the $S(\theta,\omega)$ according to the experimental conditions. The agreement is very good using the known value of π/d and the fitted set of parameters C, E_g, and ξ expressed in the table. This can be seen in Figs. 1–3. Equally good fits with the same set of parameters were obtained for eight incident energy values from $E_i=45$ to 650 meV. This gives convincing evidence for the validity of our approximate treatment that supposes an ideally one-dimensional system. Accordingly, we are confident that this analysis yields meaningful values of the important parameters of the model.

According to the original treatment by Haldane there is an intimate connection between the correlation length ξ and the energy gap E_g. It is expected that $\xi=C/E_g$. Our study allows us to compare the correlation length deduced from the model fit to the independently obtained C/E_g ratio and the agreement is excellent. In the model that we have applied, the dynamical correlations have a square-root-of-Lorentzian-type q dependence that was first proposed by Nomura [6] after his Monte Carlo calculations. More recently, Tsvelik's field-theory treatment [25] concluded that the same kind of dynamic correlation is the appropriate form to use in the case of Haldane systems.

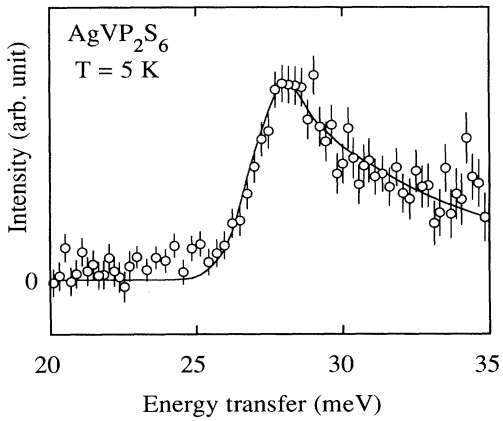

FIG. 3. The gap singularity is only broadened by $\Delta=1.4$ meV (IN4, $E_i=45$ meV, $5<\theta<26$ deg). The instrumental resolution is 1 meV. The fitted line is as described in the text.

As he noted, the use of a simple Lorentzian will give a smaller value of ξ even though the experimental data can agree equally well with either type of function; thus the choice must be guided by the theoretical results. Indeed, the square root of a Lorentzian corresponds to the asymptotic correlation-function envelope $|x|^{-1/2}\exp(-|x|/\xi)$ that was already proposed by Haldane [2]. The numerical value of ξ has been calculated by several authors [4,6,7,26,27] and the results concentrate around $\xi=6$ for the Heisenberg system at $T=0$ K. This is close to the value that best fits our data, in addition to the fact that the result is equal to the C/E_g ratio. In this respect our results on $AgVP_2S_6$ are representative because of the high value of antiferromagnetic coupling compared to the temperature ($k_BT\approx J/100$). Furthermore, the observed value of ξ agrees with the close-to-ideal Heisenberg character [7,26] of the magnetic chains that was already inferred from magnetization measurements [22].

The deviation from the simple 1D picture is visible in our results as a broadening of the excitations. The gap singularity at $q=\pi$ has a width of $\Delta=1.4$ meV (FWHM) and at $q=\pi/2$ it is $\Delta=30$ meV. The reasons for this can be looked for either in the 3D effects or in the intrinsic properties of the chains. Supposing that the effect at $q=\pi$ is due to 3D coupling only, we have estimated an upper limit for the interchain coupling constant $J'/J\leq 10^{-5}$. For the 1D system the origin of such broadening can be the finite temperature: A calculation of $S(Q,\omega)$ [28] showed a strong broadening ($\Delta/\omega=0.5$ FWHM) of $q=\pi$ excitations at a temperature of $k_BT=J/8$, to compare to the 0.04 that we observe at $k_BT\approx J/100$. Experimentally, it is known that a strongly damped behavior sets in at still higher temperatures ($k_BT\geq J/2$) where the gap mode merges in a quasielasticlike feature [12,29]. The broadening at $q=\pi/2$ is most probably a 1D effect similar to the one already seen in $CsNiCl_3$ that seems to extrapolate to a overdamped char-

acter at $q=0(\mathrm{mod}2\pi)$ [14]. We note that temperature effects and q dependence are important and calculations should be extended to a broader range.

In the present study the low-temperature magnetic excitations of the $S=1$ 1D Heisenberg antiferromagnet $AgVP_2S_6$ have been examined with time-of-flight neutron inelastic scattering. Using a broad range of experimental conditions we followed the dispersive character of the excitations on the polycrystalline samples. The results have been analyzed with a model scattering law constructed from a spin-wave-like dispersion and a square-root-of-Lorentzian dynamic structure factor. The obtained values of energy gap, spin-wave velocity, and correlation length are in quantitative agreement with the recent Monte Carlo results concerning the Haldane state.

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