

Support for the Haldane conjecture: Gap for magnetic excitations in the quasi-one-dimensional $S=1$ Heisenberg antiferromagnet AgVP_2S_6

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(Received 28 December 1988)

The low-temperature magnetic-excitation spectrum of polycrystalline AgVP_2S_6 begins above a gap ($E_g=27.4$ meV) with a form typical of a one-dimensional singularity. Powder-diffraction patterns show no long-range magnetic order but only a diffuse feature consistent with one-dimensional magnetic correlations. These observations are in agreement with the prediction of Haldane concerning the quantum gap of one-dimensional Heisenberg antiferromagnets with integer values of spin.

Interest in quasi-one-dimensional magnetism has been stimulated recently by the work of Haldane¹ who suggested that the one-dimensional Heisenberg antiferromagnets (1D HAF) with integer values of spin (S) should have an excitation spectrum separated by a gap (E_g) from the ground state, in contrast to those with half-integer S . This conjecture has since been examined by calculations on finite systems which have given support for the original proposition of Haldane.² Some of the numerical methods have been occasionally criticized³ and experimental results are clearly needed. Significant results have been obtained on two materials investigated by single-crystal neutron scattering techniques. In CsNiCl_3 a gap mode with a transverse dispersion was observed slightly above the 3D ordering temperature, with the average gap value in reasonable agreement with the one extrapolated from finite-system calculations.⁴ In $\text{Ni}(\text{C}_2\text{HgN})_2\text{NO}_2(\text{ClO}_4)$, briefly called NENP [nickel (II) di-ethylenediamine nitrito percholate] two gap modes were found⁵ and this doubling was associated with the planar anisotropy of the system. A transverse dispersion prevails in NENP too, even though it is a better quasi-1D system than CsNiCl_3 from the point of view of the interchain coupling. In both of these studies the transverse dispersion of the gap mode was associated with the interchain coupling.

The experimental ambiguities related to the 3D ordering or to the non-Heisenberg character of the magnetic chains call for systems that have a weak transversal coupling as well as small exchange and single-ion anisotropy compared with the intrachain interactions. In this respect the quasi-1D $S=1$ antiferromagnet AgVP_2S_6 is a good candidate.^{6,7} By the classical procedure, where no quantum gap is taken into account, the exchange parameter of the V^{3+} chains ($H=J\sum_i S_i S_{i+1}$) was estimated from the susceptibility data to be equal to $J\approx -400$ K, but no sign of long-range ordering was observed in $\chi(T)$ down to 5 K. The presence of a gap for magnetic excitations was presumed because the "intrinsic" susceptibility, obtained after subtracting a small amount of defect-induced Curie-like paramagnetism, extrapolates to zero when T approaches zero. The same defects, about 500 ppm free

spins with a zero-field splitting of $D/k_B\approx 5$ K, can explain the small susceptibility anisotropy observed at low temperatures.⁸ For AgCrP_2S_6 (Refs. 9 and 10), the $S=\frac{3}{2}$ isostructural counterpart with Cr^{3+} chains, a smaller $J=-100$ K was evaluated and the susceptibility showed the usual quasi-1D temperature dependence. The onset of magnetic order at about $T_N=7$ K was inferred from the susceptibility and confirmed by preliminary neutron powder diffraction¹⁰ that showed signs of doubling of the b and c parameters. In the light of these results the neutron scattering studies that will be presented below are of major interest in connection with the Haldane conjecture, especially because of the possibility of comparing the two isostructural quasi-1D systems with $S=1$ and $S=\frac{3}{2}$. In order to examine the eventual signs of magnetic ordering and to check whether a crystallographic distortion could explain the susceptibility behavior at lower temperatures, a powder-neutron-diffraction study on the $S=1$ system was undertaken. Time-of-flight neutron scattering was carried out with the aim of getting evidence on the gap directly and comparing the magnetic excitation spectra of the two systems.

The polycrystalline AgVP_2S_6 and AgCrP_2S_6 samples were synthesized using the procedure described in Ref. 6. Neutron-diffraction patterns on the vanadium compound were recorded on the D1B diffractometer ($\lambda=2.517$ Å) at the Institut Laue-Langevin (ILL) at temperatures of 300, 90, and 5 K (Fig. 1 illustrates the patterns at 5 and 300 K). The only significant modification that can be observed as the sample is cooled down from 300 to 90 K is the disappearance of the paramagnetic scattering around $2\theta=0$ and the growth of a broad diffuse hump at values of $2\theta>45^\circ$. The enhancement of this feature with decreasing temperature is a sign of magnetic correlations centered at the 1D zone boundary,¹¹ since the nearest-neighbor V-V distance projected along the chain direction is equal to $d_{1D}=2.7$ Å ($2\theta_{1D}=50.7^\circ$). There is practically no change in this feature or in the rest of the spectrum when cooling from 90 to 5 K which suggests that the 1D correlations are well developed already at 90 K and that no tendency to 3D ordering is present. The whole set of

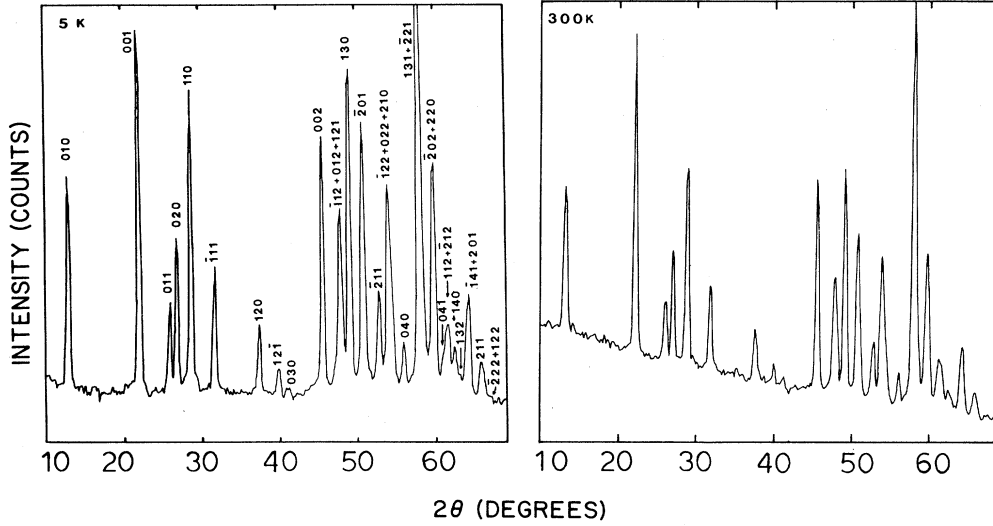


FIG. 1. Neutron powder-diffraction patterns of AgVP_2S_6 at 5 and 300 K. Note the increase at 5 K of the diffuse contribution at $2\theta > 45^\circ$ which indicates correlations centered at the 1D zone boundary at 2.13 \AA^{-1} ($2\theta = 50.6^\circ$).

lines and their intensities was reproduced and refined using the profile refinement technique¹² considering only the crystallographic structure (space group $P2/a$) as previously determined using single-crystal x-ray diffraction at room temperature.⁶ The unweighted reliability factors were 0.041, 0.043, and 0.034 at 300, 90, and 5 K, respectively. Thus, in the temperature range studied diffraction peaks can be explained by the room-temperature nuclear structure without any additional distortion that could be associated with a dimerized spin system.

The time-of-flight inelastic neutron scattering was performed at the Institut Laue-Langevin using the IN4 spectrometer. Time-of-flight spectra of the polycrystalline samples were collected in the angular ranges from 6.8° to 51.3° and from 85.5° to 101.3° , at incident energies of 16.8 and 67.2 meV. After correction for the instrumental background the data were transformed in $S(Q, \omega)$ at fixed angles and summed to cover appropriate (Q, ω) ranges that will be discussed below. Figure 2 shows an example of the data obtained at low scattering angles and at higher angles for AgVP_2S_6 at incident energy $E_i = 67.2$ meV. In the low- Q data a remarkably sharp steplike rise is seen at about 27 meV and the intensity then decreases smoothly all the way to the end of the spectral range investigated. In the energy region below the sharp edge the form of the low- Q spectrum follows closely the one measured at high- Q values which should have no magnetic contribution because the magnetic form factor is zero. As a consequence, we assume that the signal below about 25 meV in the low- Q data is due to phonons. Accordingly, it is possible to describe the whole spectrum as a magnetic-excitation spectrum superposed on a phonon background whose weight can be determined in the lower-energy range. We suppose that the magnetic-excitation spectrum is described by the 1D dispersion relation

$$\hbar \omega^2(q) = E_g^2 + C^2 \sin^2(q), \quad (1)$$

where q is the wave vector along the 1D chains, E_g is the

excitation gap, and C is an effective dispersion constant related to the exchange J . The scattering law averaged over all Q values will be proportional to the density-of-states function $g(\omega)$ of the dispersion relation of Eq. (1):

$$S(\omega) \propto \left(\frac{1}{2} \pm \frac{1}{2} + \langle n \rangle\right) \int dQ \delta(\omega - \omega(q)) G(Q, S) \\ \propto \left(\frac{1}{2} \pm \frac{1}{2} + \langle n \rangle\right) \int dQ g(\omega) F(Q). \quad (2)$$

The thermal occupation (Bose) factor $\langle n \rangle$ distinguishes between the (sample) energy gain (+) and loss (−) spectra. For a powder sample the Q and spin dependence $G(Q, S)$ of the scattering cross section reduces to the magnetic form factor $F(Q)$. In the experiment the integration over Q does not cover all the Q space. However with a proper choice of angular range a large volume around the 1D zone boundary is contributing and we get a

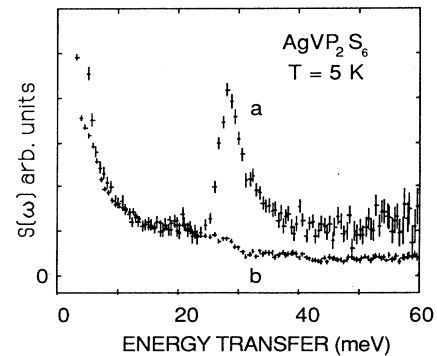


FIG. 2. Background corrected scattering law $S(Q, \omega)$ of AgVP_2S_6 at 5 K summed over the elastic Q range from (a) 1.35 to 3.1 \AA^{-1} and from (b) 7.75 to 8.8 \AA^{-1} . The high- Q data represents the phonon background that is, using a proper weight, superposed on the low- Q data in the beginning of the spectrum ($\omega < 25$ meV).

result that is representative of the low excitation energy range. The experimental results were fitted with the model of Eq. (2) using the tabulated form factor¹³ and including the instrumental resolution that broadens the 1D singularity of the density of states. The phonon contribution presented by the high- Q data was subtracted using an adjustable weight factor. Figure 3 shows that an excellent agreement is obtained in the peak region and below after allowing for a small additional broadening of 0.90 meV (Gaussian distribution) around the average gap value $E_g = 27.4$. The value of C (that will be discussed below) was fixed to 120 meV but the value of E_g is not sensitive to this choice.

In strong contrast to the $S=1$ system the Cr-containing compound with $S=\frac{3}{2}$ exhibits a continuum of excited states from the ground state. At low temperatures the development of 3D order distorts the spectrum considerably but at temperatures where 3D fluctuations are small ($T > 50$ K) the model of Eq. (2) and a narrow (0.5 meV) gap distribution centered on $E_g = 0.3$ meV is in reasonable agreement with experiment, see Fig. 4. The model fails totally at the upper limit of the spectral range (not shown). This is not surprising considering the case of the $S=\frac{1}{2}$ 1D HAF where a notable tail reaches above the exactly known lower limit that is given by Eq. (1) with $E_g = 0$ and $C = \pi J/2$ (Ref. 11). For AgVP_2S_6 the whole magnetic-excitation spectrum has not yet been measured but preliminary results on IN4 at higher incident energies ($E_i = 115$ meV, 153 meV) have shown that the spectrum extends well above 100 meV.

Three important conclusions can be drawn from the above results. First, AgVP_2S_6 behaves as a practically ideal 1D system at temperatures at least down to 5 K. Second, it has a remarkable gap in the magnetic-excitation spectrum. And third, the similar $S=\frac{3}{2}$ system has no gap, but clear modifications due to the onset of magnetic order are observed. The existence of the gap in the $S=1$ compound cannot be explained quantitatively by theories based on single-ion or exchange anisotropy.¹⁴ However, all the results are consistent with the conjecture of Haldane. The absence of long-range magnetic order becomes understandable in the picture in which the order is suppressed up to a critical value of the interchain cou-

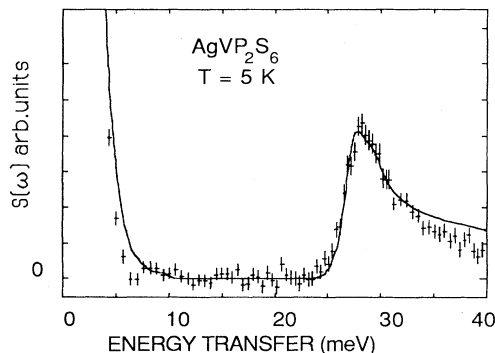


FIG. 3. Magnetic excitation spectrum of AgVP_2S_6 at 5 K. The solid line represents the fit with the model of Eq. (2) convoluted with instrumental resolution and including an additional Gaussian broadening (± 0.9 meV) of the gap $E_g = 27.4$ meV.

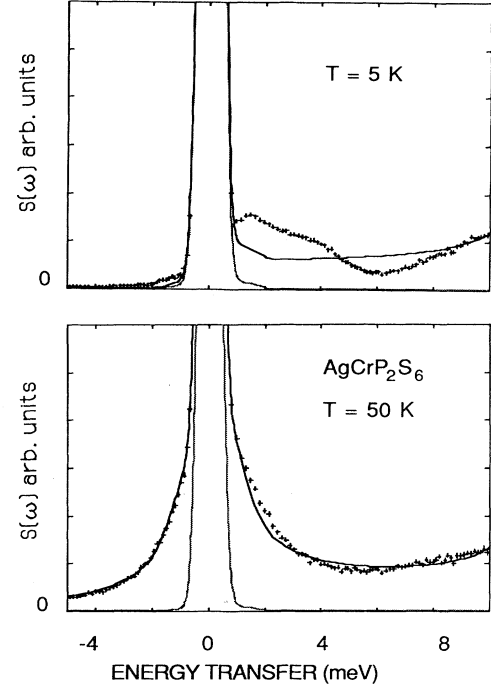


FIG. 4. Magnetic-excitation spectrum of AgCrP_2S_6 at 5 and at 50 K. At the higher temperature the spectrum can be fitted in the low-energy transfer range using the Eq. (2) and a gap distribution starting from zero value. At 5 K the magnetic order modifies the form strongly but there is still no gap.

pling¹⁵ in the presence of the gap.

In comparison with the earlier experiments that have given evidence of the Haldane gap our observations on AgVP_2S_6 stand out because the gap is extremely sharp. The 1D singularity is broadened only by 3%. If this broadening is related to the transverse coupling in the way proposed for the other two materials^{4,5} we can conclude that in AgVP_2S_6 the interchain interactions are very weak, indeed, $J'/J \approx 10^{-5}$. In CsNiCl_3 the transverse dispersion of the gap mode is a factor of 3,⁴ and in NENP a variation of 20% was measured for the lowest gap mode.⁵ Another reason for the broadening might be the planar anisotropy that was proposed to explain the two-gap situation in NENP. If this were the case in AgVP_2S_6 we can conclude that the effect is very small and in good agreement with the isotropic "intrinsic" susceptibility.¹⁰ We want to point out that our best fit was obtained with a Gaussian distribution of gaps and without detailed knowledge on the dispersion it is difficult to assign this broadening to a given mechanism. Factors like temperature or disorder cannot be excluded either.

The value of the gap is expected² to be in the range $E_g = (0.25-0.41) |J|$. Comparing the observed gap with the $J/k_B \approx -400$ K extracted from the susceptibility gives $E_g/|J| \approx 0.8$. On the other hand, our inelastic scattering results have shown that there is a roughly constant spectral weight up to at least 100 meV. This, associated with the spin-wave value of $C = 2|J|$, suggests that $|J|/k_B \approx 600$ K or more, and accordingly $E_g/|J| \approx 0.5$.

This uncertainty reflects the experimental difficulties in estimating the value of J . The chemical instability of the sample prevents heating above 500 K and, consequently, the maximum of $\chi(T)$ typical of quasi-1D chains cannot really be reached and the resulting $|J|$ is probably too small. In the case of inelastic scattering, even with the high incident energies necessary to establish the full extent of the magnetic-excitation spectrum, a value for J can be obtained only if a valid model for the spectral density were available in the range where the simple spin-wave theory fails, due to the expected broadening of excitations at a given q especially near the 1D zone boundary.¹⁶

The experiments reported above have given convincing evidence for the supposition that the $S=1$ Heisenberg antiferromagnetic chains in AgVP_2S_6 form a strongly 1D

system with a gap in the excitation spectrum. The results are consistent with the Haldane conjecture that predicts a gap for systems with integer values of spin. The energy scale and the very clean gap that was observed make this compound an attractive choice for further investigations that can help to pinpoint the particular behavior of the $S=1$ Heisenberg antiferromagnetic chains.

We thank Dr. G. Kearley for the original version of the fit routine and Mr. A. Lau for technical assistance in adapting it for our needs. We are grateful to Dr. A. Murani for comments and discussions. The Laboratoire de Chimie des Solides is Unité Associée au Centre National de la Recherche Scientifique No. 279.

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¹⁴We do not repeat here the reasoning that is similar to the ones presented in Refs. 4 and 5, with the proper parameter values of our compound.

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¹⁶The exact value of the dispersion constant C is not known for the $S=1$ HAF but it is expected to be greater than the spin-wave value $2|J|$, in analogy with the $S=\frac{1}{2}$ system. Similarly, one can expect that the excitations are not the sharp delta function peaks (see Ref. 11).