Resonant two-magnon Raman scattering at high pressures in the layered antiferromagnetic $NiPS_3$

S. S. Rosenblum* and R. Merlin
Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120
(Received 24 July 1998)

We have measured the Raman spectra of $NiPS_3$ for pressures up to 27 GPa at 120 K and room temperature using various lines from an argon ion laser. $NiPS_3$ is an $S=1$, insulating, two-dimensional antiferromagnet which shows an anomalously broad two-magnon excitation. At high pressures, we observe a strong dependence of the intensity, line shape, and frequency of the magnetic spectrum as a function of laser wavelength, reflecting pressure tuning of electronic transitions. $NiPS_3$ is the only material exhibiting resonant two-magnon scattering other than the parent compounds of the cuprate superconductors. [S0163-1829(99)06009-9]

I. INTRODUCTION

$NiPS_3$ belongs to the family of metal thiophosphates which are layered compounds that possess interesting magnetic[1] and cathodic[2] properties. At ambient pressure, this material undergoes an antiferromagnetic transition at $T_N = 150$ K (T_N is the Néel temperature). With a planar hexagonal structure, the in-plane magnetic behavior in these materials is characterized by three magnetic exchange constants involving first, second, and third neighbors. Competition between these constants leads to a variety of magnetic structures.[1] In $NiPS_3$, the spins align ferromagnetically along chains, with coplanar chains aligned antiferromagnetically to one another, and ferromagnetically in the direction perpendicular to the planes.[1] Previous work in $NiPS_3$ has shown that the next-nearest neighbor exchange dominates. Early Raman studies of $NiPS_3$ revealed a broad spectral feature at 530 cm^{-1} that was originally assigned to electronic scattering[3] but later shown to be due to two-magnon (2M) excitations.[4] The 2M band exhibits an anomaly in that its linewidth is nearly four times larger than that predicted from standard 2M theory.[5–7]

The 2M-width anomaly in $NiPS_3$ is similar to that observed in the parent compounds of the cuprate superconductors.[8,9] Standard 2M theory (see, for example, Parkinson[10] for work on a square-planar lattice) predicts a peak width of $\approx 10\%$ of the peak frequency (Ω_{2M}). The line shape of second-order magnon scattering is determined by a magnon density of states, modified to account for magnon-magnon interactions.[11,12] In the cuprates, the peak width is approximately three times larger than what standard theory predicts[8] and, originally, the anomaly was attributed to spin $S=1/2$ fluctuations.[9] However, the observation of a similar anomaly in $NiPS_3$ (Ref. 4) with $S=1$, coupled with other theoretical[13,14] and experimental[15] work, showed this interpretation to be incorrect. In particular, numerical simulations by Haas *et al.*[16,17] found that fluctuations in the exchange due to magnon-phonon coupling could account for the observed line shape as well as for the selection rules. This work[16,17] relied on the fact that the magnetic exchange energy in the cuprates is much greater than the phonon energies, a situation that does not apply to $NiPS_3$ for which the exchange and optical phonon energies have the same magnitude. In this work, we study the dependence of the 2M scattering in $NiPS_3$ as a function of pressure and laser wavelength (ω_L). It is well-known that hydrostatic pressure generally produces larger relative shifts for the magnetic constants than for the phonons (i.e., the Grüneisen parameters are larger for magnons).[18–22] Our data on $NiPS_3$ is consistent with the general trend, and provides additional support for the 2M assignment. Pressure can also be used to tune the material's band structure. We have observed a manifestation of such tuning in the form of a pronounced resonant enhancement of the 2M excitation at high pressures. As in the case of resonant two-phonon Raman scattering,[23] we observe that the central frequency of the magnetic scattering varies with ω_L. This dependence arises most likely from differences in the resonant behavior of magnon pairs at different critical points of the Brillouin zone.

II. EXPERIMENTAL

The absorption edge of $NiPS_3$ is ≈ 1.6 eV.[24] Single crystals grow in sheets a few millimeters on a side, and exhibit a shiny, metallic appearance when cleaved along the planes separated by the van der Waals' gaps. All samples used in this study were cleaved prior to the Raman measurements, cut to 50–70 μm on a side, and loaded into a Mao-Bell diamond anvil cell (DAC) along with a small ruby chip. The cell used a stainless steel gasket with a 200 μm sample hole. The DAC was cryogenically loaded with liquid argon which is known to provide a nearly hydrostatic medium over the pressure and temperature ranges of interest.[25–27]

For the low-temperature runs, we used a home-made optical cryostat which provided temperatures down to ~ 100 K through a liquid-N cold finger. The cryostat allows for the pressure to be adjusted from outside using a mechanical feedthrough.[18] We calibrated the pressure by comparing the $R1$ luminescence of the ruby chip inside the gasket to that of a piece of ruby mounted outside the DAC. Raman data were obtained using the available lines of an argon-ion laser with approximately 40–60 mW of focused light at the DAC. We note that our early ambient pressure studies of $NiPS_3$ (Ref. 4) were limited to much lower powers (<10 mW). The argon pressure medium and the diamond anvils provide a good

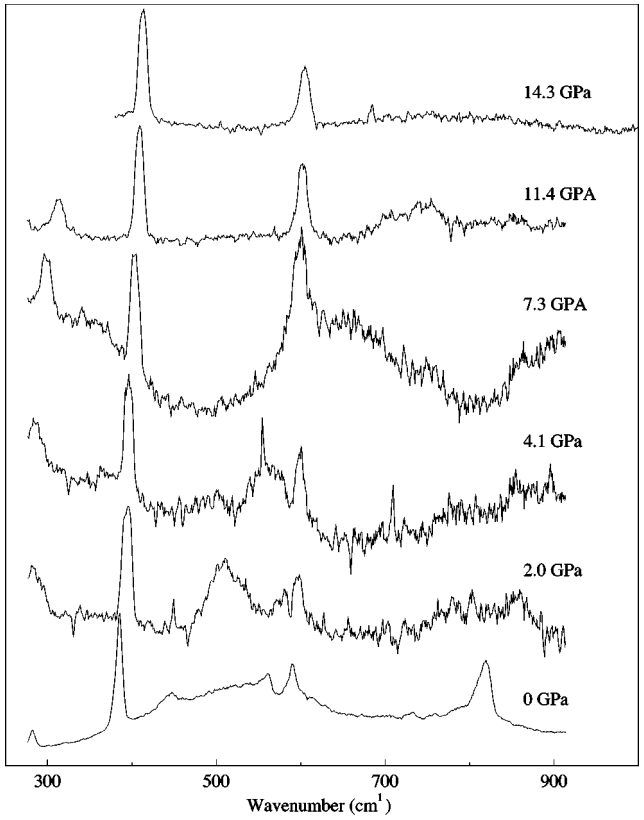

FIG. 1. Low temperature $NiPS_3$ spectra as a function of pressure. The temperature of the high-pressure data is $\approx$120 K, while the ambient pressure data was taken at 88 K. The spectra have had a linear background subtracted from them, and have been normalized to the 380 cm^{-1} phonon for clarity. Pressure values in this apparatus are known to within 6% (Ref. 42).

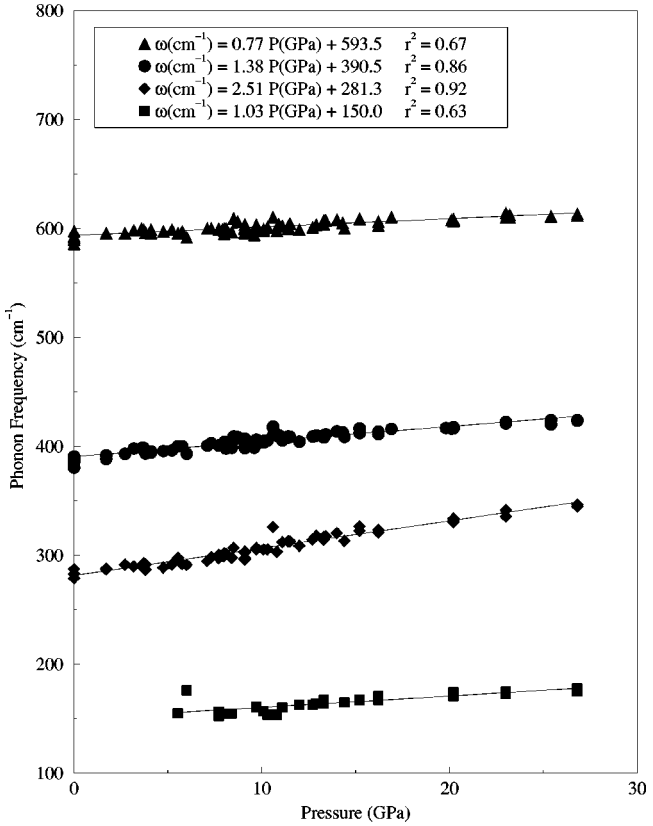

FIG. 2. $NiPS_3$ phonon shifts versus pressure. Straight lines represent linear fits. The inset gives the pressure dependence of each mode and the r^2 of the linearization. Peak frequencies are accurate to ± 2 cm^{-1}, and pressure values are known to 6%.

thermal pathway for heat dissipation, allowing for the higher power densities inside the DAC. In all cases, we recorded spectra at lower laser powers to make sure that the spectral features were not affected by the high intensities. The scattered light was collected with a confocal arrangement of photographic lenses which rejected most of the scattering from the diamond phonon. The scattered light was analyzed using a Dilor *XY* triple monochromator with an intensified photodiode array detector. On average, approximately 3 to 5 counts per second were recorded at the peak of the 2M excitation.

III. RESULTS

$NiPS_3$ crystallizes in the monoclinic structure (point group C_{2h}) and has two formula units per primitive cell, resulting in 12 infrared active and 15 Raman active vibrational modes. However, weak interlayer coupling causes the Raman spectrum to effectively exhibit the higher hexagonal symmetry of the in-plane structure (point group D_{3d}) with $3A_g+5E_g$ modes[28] (the two B_g modes of the C_{2h} point group correlate with the Raman-silent A_{2g} modes of D_{3d}). These eight modes were observed by Bernasconi *et al.*[28] In addition, and as reproduced in Fig. 1 for ambient pressure, the spectra show a Raman band at 818 cm^{-1} which we assign to second-order vibrational scattering. The 2M excitation is significantly broader than the phonons, and has an ambient-pressure frequency of 530 cm^{-1}. Figure 2 plots the phonon frequencies versus pressure calculated from all sets of high pressure data (300 and 120 K). Only the strongest $NiPS_3$ modes are observable inside the DAC. The phonons exhibit broadening over this pressure range but no splitting, an indication that no structural phase transition takes place in this range.[29] The pressure dependence of the frequency shifts are included in the inset of Fig. 2. Above 33.0 GPa, the Raman signal becomes too weak to measure.

Figure 1 shows spectra taken as a function of pressure at 488.0 nm. The temperature of the high-pressure data is $\approx$120 K, while the ambient pressure data was taken at 88 K.[30] As expected, the 2M peak shifts much more quickly with pressure than the phonons (see Fig. 3). In addition, the intensity of the 2M band increases relative to that of the fully symmetric PS_3 stretching mode. The mode at 590 cm^{-1} exhibits a similar intensity enhancement relative to the 2M band. The variation in peak intensities between spectra reflects resonant effects. In particular, note that at 11.4 GPa the 2M peak height is much smaller than that of the 380 cm^{-1} A_g phonon, while at 7.3 GPa these two peaks have comparable intensities. Also note that the mode we attribute to second order vibrational scattering (see Fig. 1) broadens and weakens at high pressures.

Figure 4 shows spectra obtained at ambient pressure and 9.1 GPa for various argon laser lines. The ambient pressure spectra exhibit only modest intensity changes with ω_L while the 9.1 GPa data show dramatic variations in the 2M intensity and peak center as the excitation energy varies. These

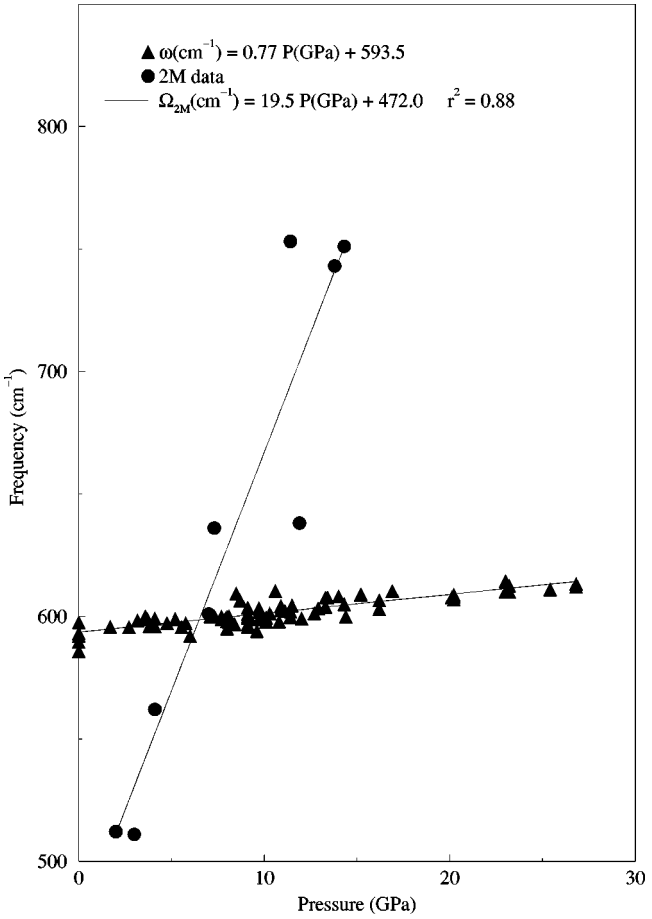

FIG. 3. Ω_{2M} versus pressure for $NiPS_3$. Circles represent actual data points. The straight line through the circles is a linear best fit, giving a slope of 19.5 cm^{-1}/GPa. Triangles represent one of the A_g phonons, and are included to show the difference in the pressure behavior of phonons and magnons. Peak frequencies are accurate to ± 2 cm^{-1}, and pressure values are known to 6%.

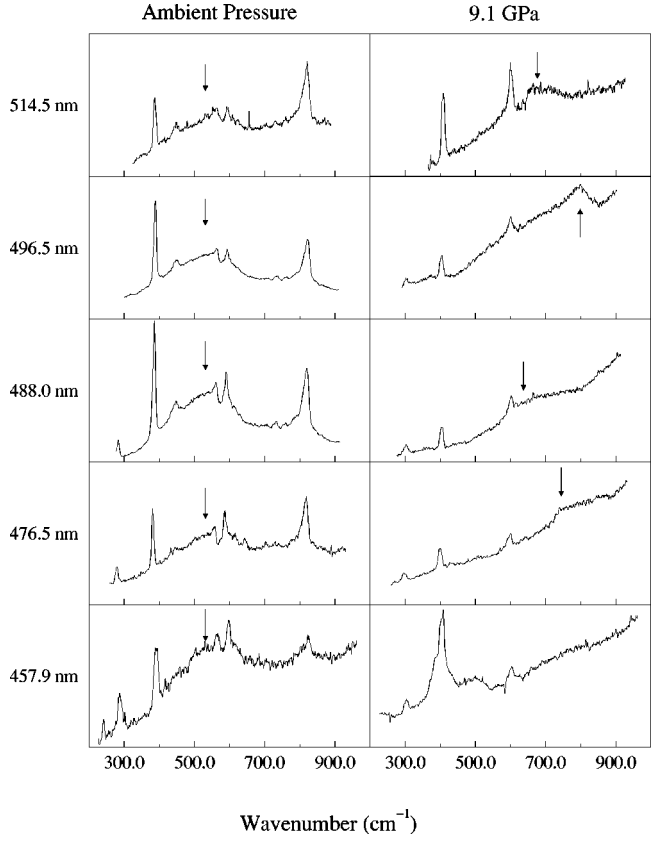

FIG. 4. $NiPS_3$ data at ambient pressure and 9.1 GPa as a function of laser excitation. Arrows denote the 2M feature. The ambient pressure data was obtained at 88 K and the 9.1 GPa data at 120 K. Spectra at ambient pressure show a weak dependence on the incident laser wavelength unlike the 9.1 GPa data which show an effect indicating the presence of an electronic resonance. The upwards slope in the 9.1 GPa spectra originates from the diamond phonon at 1330 cm^{-1}, whose intensity dwarfs that of $NiPS_3$'s signal by several orders of magnitude.

strong intensity variations indicate the presence of one (or more) electronic resonances between 457.9 and 514.5 nm for both the phonons (e.g., the 380 cm^{-1} A_g phonon in the 457.9 nm spectra) *and* the 2M excitation. As discussed later, the observed dependence of Ω_{2M} on ω_L takes on particular significance when we note that the observed 2M frequency at 496.5 nm is approximately equal to that at 476.5 nm, and that these wavelengths differ by ≈ 850 cm^{-1}, which approximately equals Ω_{2M}.

IV. DISCUSSION

The interpretation of resonant Raman experiments requires a good knowledge of the material's joint density of states. Several authors have studied the valence band of the metal thiophosphates,[24,31,2,32–37] and early work by Piacentini *et al.*[24,31] showed that the Ni^{2+} *d* states are near the top of the valence band or within the gap. Unfortunately, there have not been reports of inverse photoemission or detailed optical measurements that could help us identify the nature of the observed Raman resonance.

The assignment of the observed high-pressure behavior to resonant 2M scattering relies on three characteristics of the data. First, the zero-pressure peak position extrapolated from Fig. 3 matches that observed at 120 K in previous studies.[4] Additionally, the slope of Ω_{2M} versus *P* is close to the value of 22.1 cm^{-1}/GPa observed in the $S=1$ planar antiferromagnet K_2NiF_4 by Struzhkin *et al.*[22] These two observations indicate that the broad peak observed in the high-pressure experiments is indeed due to 2M scattering.[4] The dramatic change of the 2M band intensity with pressure (Fig. 1) and its dependence on ω_L at high pressures are ascribed to resonant effects due to transitions involving *d* states. Here, we note that the spectra in Fig. 4 provide conclusive evidence for resonant behavior. The line shape modifications due to pressure alone (Fig. 2) can also be explained by a dependence of the matrix elements (as opposed to resonant denominators) on pressure.[38] The observed shifts in Ω_{2M} with laser frequency (see Fig. 4) are also consistent with resonant behavior. As for two-phonon scattering,[23] we expect that different critical points of the two-magnon continuum will experience different dependence on ω_L and, hence, that the 2M line shape will vary with ω_L, as we observe. With this in mind, it is interesting to note that for laser lines 496.5 and 476.5 nm that are separated by Ω_{2M} the dominant frequency of the 2M band is approximately the same. We speculate that this arises as a result of an ingoing resonance at 496.5 nm, becoming an outgoing resonance at 476.5 nm.

In conclusion, we have observed resonant 2M scattering in $NiPS_3$. This, and the fact that the 2M width is anomalously broad recalls Raman work on the cuprate superconductors.[8,9,39,40] We note that, prior to its observation in the latter compounds,[39] resonant 2M Raman scattering was not conclusively identified.[41] Hence, $NiPS_3$ is the only material outside the cuprates that exhibits resonant magnon-pair scattering.

ACKNOWLEDGMENTS

The authors would like to thank Professor A. H. Francis for generously supplying $NiPS_3$ samples used for this study. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

*Present address: Kaiser Optical Systems, Inc., Ann Arbor, Michigan 48106.

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