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Two-magnon light scattering in the layered antiferromagnet $NiPS_3$: Spin-$\frac{1}{2}$-like anomalies in a spin-1 system

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Raman spectra of $NiPS_3$ (spin $S=1$) reveal an anomalously broad two-magnon feature whose relative width is comparable to that shown by La_2CuO_4 ($S=\frac{1}{2}$) and other antiferromagnetic copper oxides. The magnetic continuum is strongly coupled to a nearby phonon, whose scattering amplitude interferes with it. These results question the view that the width enhancement in the cuprates stems from large quantum fluctuations intrinsic to $S=\frac{1}{2}$ systems. It is proposed that the anomaly is due instead to magnon decay involving strong magnetostrictive coupling to phonons.

Two-dimensional Heisenberg antiferromagnets (HAF) have been the focus of numerous studies over many years.[1] More recently, there have been renewed efforts in this area motivated by both the fact that the parent insulating compounds of the superconducting cuprates are spin $S=\frac{1}{2}$ nearest-neighbor HAF (Ref. 2) and the possibility that mechanisms relying on the spin dynamics may play a role in high-temperature superconductivity.[3] Within this context, the discovery by Lyons *et al.*[4] of an anomalous form of spin-pair Raman scattering in La_2CuO_4 generated a great deal of excitement.[5] The two-magnon (2M) peak in this and other cuprates[6] is unusual in that it exhibits widths and selection rules[7] incompatible with the established theory, which describes $S>\frac{1}{2}$ HAF extremely well.[8] In particular, the experimental widths are a factor of 3–4 larger than spin-wave predictions.[6] The interpretation of these findings has been the source of much controversy[9] centered on the question of whether or not these anomalies rely on quantum fluctuations intrinsic to $S=\frac{1}{2}$ systems.[10] In this paper, we show that $S=\frac{1}{2}$ materials are not the only ones with larger-than-usual widths. Raman spectra of the HAF $NiPS_3$ ($S=1$) show a 2M peak which, in relative units, is at least as broad as that of the Cu^{2+} compounds. Because all the known $S=1$ HAF are well accounted for by conventional models,[8] our results call for sources of widths other than those based on spin-only mechanisms. We discuss arguments showing that the magnetostrictive interaction[11,12] is a viable candidate to explain the width anomaly in both $NiPS_3$ and the cuprates.

$NiPS_3$ belongs to a large family of materials whose structure consists of MPX_3 slabs (M = transition metal and $X=S$, Se) separated by large van der Waals' gaps in a pattern closely related to that of the transition-metal dichalcogenides.[13] As illustrated in Fig. 1 for $NiPS_3$, the layers show a metal honeycomb surrounded by hexagonal P and X lattices (notice that the centers of the metal hexagons are occupied by P_2 groups). Because of the high stability of the P_2X_6 bipyramidal structure, the slabs can be described in terms of an ordered hexagonal array of $(P_2X_6)^{4-}$ anions and M^{2+} cations.[13] In $NiPS_3$ and other sulfides, the stacking of sulfur planes is fcc-like, leading to a small monoclinic distortion; the resulting unit cell contains a single layer and four formula units with space group $C2/m$. The ground state of the octahedrally coordinated nickel ions is an orbital singlet ($^3A_{2g}$). Below the Néel temperature $T_N=155$ K, $NiPS_3$ orders antiferromagnetically with the Ni^{2+} spins ($S=1$) lying perpendicular to the layers.[14] The alignment, depicted in Fig. 1, is of type I;[13,14] within a layer, it is defined by ferromagnetic double chains which couple antiferromagnetically to their neighbors. The interlayer ordering is ferromagnetic.[13,14] Although the magnitude of the exchange con-

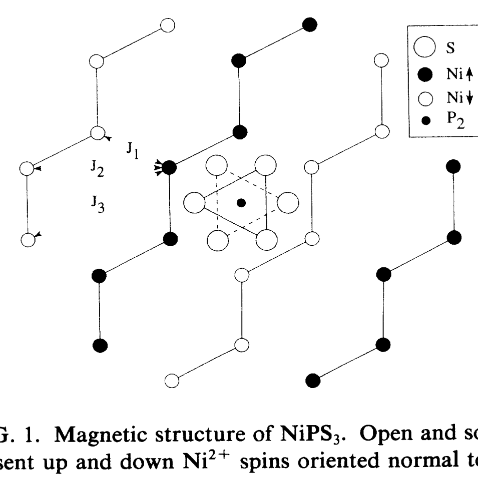

FIG. 1. Magnetic structure of $NiPS_3$. Open and solid circles represent up and down Ni^{2+} spins oriented normal to the (001) basal plane. First-, second-, and third- neighbors and associated exchange constants are also shown as well as the projection of a $(P_2S_6)^{4-}$ unit on the (001) plane.

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stants are not well known, studies indicate that $NiPS_3$ is an HAF with negligible interlayer coupling and weak two-dimensional anisotropy.[13,14] Later, it will be shown that the intralayer exchange is dominated by second-neighbor antiferromagnetic coupling.

The experiments were performed on single crystals of $NiPS_3$. Samples were loaded into a closed-loop helium or a liquid nitrogen optical cryostat for measurements in the range 15–100 K and 85–300 K, respectively. Raman spectra with ~ 3 cm^{-1} resolution were obtained using a Dilor-*XY* multichannel system and 30 mW of 4765 Å. To prevent laser heating, a cylindrical lens was used to focus the beam on the sample. The polarizations of the incident and scattered light were parallel to the layers, i.e., perpendicular to [001]. Given that effects due to the monoclinic deformation on the lattice dynamics and magnetic properties are relatively minor,[13] it is appropriate to assume that the relevant point group is D_{3d}, i.e., the ideal single-layer one, instead of the actual group C_{2h}. The corresponding irreducible symmetric $A_{1g}(\Gamma_1^+)$, $E_g(\Gamma_3^+)$, and antisymmetric $A_{2g}(\Gamma_2^+)$ scattering components were determined using both linearly and circularly polarized light. In D_{3d}, conventional (any-order) phonon and second-order magnon scattering transform like A_{1g} or E_g while the expected symmetry of one-magnon scattering (spin only) is A_{2g}; note that A_{2g} phonons are *not* Raman active.[15]

Figures 2 and 3 summarize our results. In Fig. 2, the broad line positioned at $\approx 400-550$ cm^{-1} is due to 2M scattering. The relatively narrow peaks above ~ 150 cm^{-1} are internal $(P_2S_6)^{4-}$ modes of A_{1g} or E_g symmetry.[16] As shown in Fig. 2, the 2M feature shifts to lower energies with increasing temperature and its width (intensity) increases (decreases). The magnetic structure of $NiPS_3$ gives one (doubly degenerate) optical magnon branch which, in principle, is Raman allowed at the zone center. However, the spectra do not show any evidence of the A_{2g} component identifying one-magnon scattering. Within experimental uncertainty and consistent with the 2M identification, the broad feature transforms like E_g. As first observed by Balkanski *et al.*,[17] the inset of Fig. 2 reproduces the asymmetric line shape resulting from mixing of the 2M continuum with the internal E_g mode at 558 cm^{-1}.[18] The fact that the spectrum is well behaved in the vicinity of the 585 cm^{-1} A_{1g} phonon is consistent with the symmetry analysis since the E_g character of the 2M line precludes its coupling to all but E_g modes. Other than for the interaction with the 2M continuum, our data reveal no apparent correlation between phonon scattering and magnetic ordering.

The 2M assignment of the broad feature is based on various considerations. Most important is the correlation between the T dependence of the peak frequency Ω and the magnetic ordering shown in Fig. 3. Relative to T_N and the extrapolated $\Omega_0 \equiv \Omega(T=0)$, the behavior of the $NiPS_3$ line is very similar to that of the 2M peak in the prototypical two-dimensional HAF K_2NiF_4.[19] Parenthetically, we recall that three-dimensional systems exhibit a much stronger T dependence so that 2M scattering can hardly be observed for $T \gtrsim T_N$;[8] this is unlike two-dimensional compounds where magnetic correla-

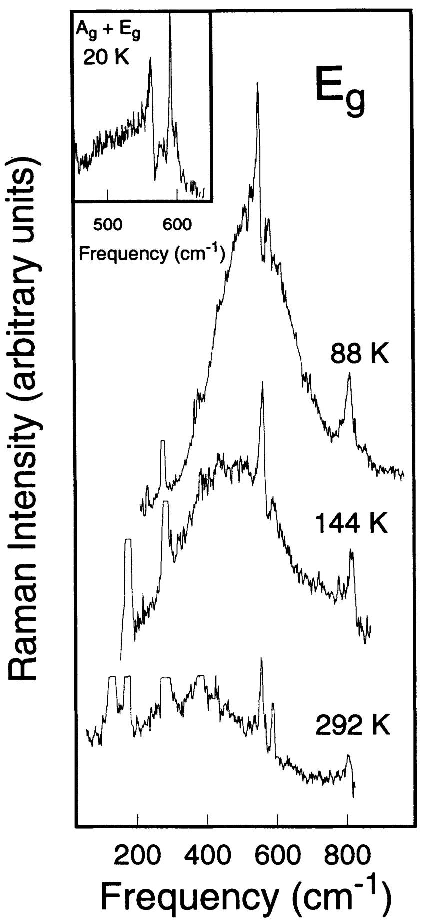

FIG. 2. Raman spectra (E_g symmetry) at various temperatures. The broad feature with maximum in the range 400–550 cm^{-1} is due to 2M scattering. For clarity, phonon peaks below ≈ 400 cm^{-1} have been truncated. Inset: Fano-type interference between the 2M continuum and the E_g phonon at 558 cm^{-1}. The noninteracting A_g mode at 585 cm^{-1} is also shown.

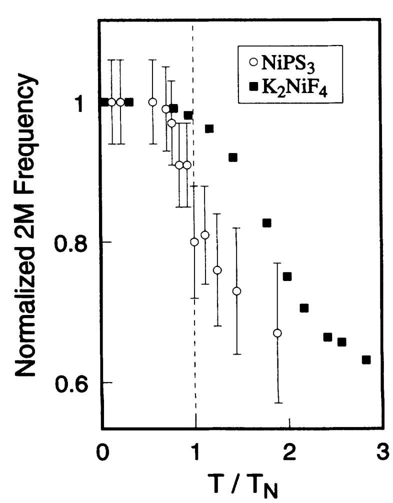

FIG. 3. The normalized 2M peak position, $\Omega(T)/\Omega(T=0)$, as a function of T/T_n. Comparison between $NiPS_3$ and K_2NiF_4 (Ref. 14).

tions typically persist well above the ordering temperature.[8] The fact that the peak symmetry is E_g and, in addition, the realization that $\Omega_0 \approx 550$ cm^{-1} is close to the magnitude of the Curie-Weiss parameter $\theta_P = -495$ cm^{-1} (Ref. 14) provide further support for the 2M interpretation A few reflections show that these seemingly independent observations are actually related. Here, the important point is not just that the line transforms in a way compatible with magnon pairs, but also that the intensity of the group-invariant component A_{1g} is negligible. As it is well known, such a behavior is characteristic of HAF systems whose properties are dominated by a *single* exchange constant.[20] In this situation, fully invariant combinations commute with the Hamiltonian and, thus, they cannot cause scattering. It follows from these arguments that a single parameter dominates in $NiPS_3$ as well. Considering the Hamiltonian $H = \frac{1}{2}\sum J_{mp}\mathbf{S}_m \cdot \mathbf{S}_p$ which includes first- (J_1), second- (J_2), and third-neighbor (J_3) exchange (see Fig. 1) and using the Ising model to describe zone-boundary magnons,[8] we find that $\theta_P = -S(S+1)(J_1 + 2J_2 + J_3)$ and $\Omega_0 \approx S(-2J_1 + 4J_2 + 6J_3)$;[21] $\mathbf{S}_l$ is the spin localized at the lth lattice site and $J_{mp}(=J_1, J_2$ or $J_3)$ are exchange integrals.[13,14] For $\Omega_0 \approx -\theta_P$, the latter expressions give $J_1 \approx J_3$. Therefore, the single dominant constant consistent with the absence of A_{1g} scattering must be J_2. The approximations $\theta_P \approx -2S(S+1)J_2$ and $\Omega_0 \approx 4SJ_2$ lead to $J_2 \approx 100-120$ cm^{-1}; J_1 and J_3 are nearly one order of magnitude smaller. It is interesting to point out that, for (strictly) $J_1 = J_3 = 0$, $NiPS_3$ becomes a frustrated two-sublattice triangular HAF.[22]

The feature we ascribe to magnon pairs was originally reported by Balkanski *et al.*[17] However, this work does not address the symmetry of the line or its correlation with magnetism. Based on the similarities between the Fano-like spectrum of $NiPS_3$ (inset, Fig. 2) and that of heavily doped *p*-type Si,[23] the authors of Ref. 17 propose an alternative identification involving electronic scattering between spin-split bands. We believe that this assignment is incorrect for several reasons. First, we find that doping-dependent scattering is difficult to reconcile with the facts that the peak is robust with respect to varying growth conditions and that spin-flip processes should transform like A_{2g} (as opposed to E_g). We further notice that the electronic transport in $NiPS_3$ is activated.[24] The free-carrier contribution to the scattering should then decrease with decreasing T, contrary to the experiments. While these arguments bear on carriers introduced by doping, it is apparent that other conventional electronic processes should also be excluded since Ω is much smaller than the optical gap or the activation energy.[24,25] We emphasize that, unlike inter- and intraband scattering, the 2M interpretation accounts naturally for the observed T dependence and symmetry. As for the Fano-character of the line shape, it is of interest to relate the present results to those on $FeBO_3$.[12] The latter HAF also shows Raman asymmetries resembling those found in *p*-type Si, but due to 2M phonon coupling.

Let us now focus on the width anomaly considering γ_0, the low-T FWHM (full width at half maximum) of the 2M peak. The $NiPS_3$ data give $\gamma_0/\Omega_0 \approx 0.4$ which is comparable to values found in the cuprates.[4-7] This needs to be contrasted with the standard model predicting $\gamma_0/\Omega_0 \approx 0.1$ for the contribution of a single pair of (antiferromagnetically coupled) spins.[8] Since the theoretical prediction is manifestly obeyed by a large number of HAF compounds,[8] the problem is to understand what distinguishes $NiPS_3$ *and* the cuprates from the well-behaved systems. As mentioned earlier, there is no consensus in the cuprate literature regarding this issue.[4-7,9-11] For both systems the crucial question is, can large widths be explained *solely* in terms of spin degrees of freedom? And, if not, what other interactions are involved? (we remark that the experiments rule out both explanations based on extrinsic effects[6,7] and the possibility that a set of unresolved peaks due to multiple spin-pair contributions could account for the additional broadening). In the cuprates, the spin-only assumption, represented by the work of Singh *et al.*,[10] relates the width anomaly to quantum fluctuations intrinsic to $S = \frac{1}{2}$. This explanation is supported primarily by the fact that the calculated first three spectral moments are in very good agreement with spectra.[10] However, there is evidence suggesting that the agreement may be accidental.[9] Dyson-Maleev[9] and 4×4 lattice[26] calculations reveal widths which are considerably smaller than the experimental ones even though the measured and calculated moments (appreciably modified by four-magnon contributions[9]) are very close. Competing with the spin-only interpretation are proposals attributing the larger width to magnon decay into other excitations.[11,27] The phenomenological approach of Weber and Ford[27] shows that good agreement with experiments can be obtained using the standard theory[8] provided one allows for both a weak relaxation of momentum conservation and a small imaginary part $\approx 0.05-0.1$ of the magnon energy. Reference 27 argues that scattering by free carriers is the source of the damping. Strong support for the decay picture comes from T dependent measurements on $RBa_2Cu_3O_6$ ($R =$ Eu, Y) by Knoll *et al.*[11] which show the broadening to increase with T. As amplified later, this work ascribes the finite magnon lifetime to spin-lattice coupling.[11]

While the previous discussion may leave some room for controversy in the cuprates, the case of $NiPS_3$ is a different matter. Since many $S = 1$ HAF are known to be well described by the standard model, the extra width in $NiPS_3$ necessarily stems from effects beyond spin-only mechanisms. Although one cannot possibly conclude from the $NiPS_3$ data alone, by analogy, that the anomalies of the cuprates have the same origin, it is evident that the observation of similar behavior for $S = 1$ casts serious doubts on the notion that $S = \frac{1}{2}$ is special. In light of these remarks and the available arguments for and against the spin-only interpretation,[8,9,11,26,27] it is difficult to escape the conclusion that the extra width in the cuprates is not intrinsic to $S = \frac{1}{2}$.

What is, then, unique about $NiPS_3$ and the cuprates? We agree with Refs. 11 and 27 that enhanced broadening is the result of strong magnon decay. Following Knoll *et al.*[11] and recent work on $FeBO_3$,[12] we further believe that the operating mechanism is the magnetrostrictive coupling[11,12]

$$V=\sum_{m>p}\left[\frac{\partial J_{mp}}{\partial Q}\right]_{Q=0}(\mathbf{S}_m\cdot\mathbf{S}_p)Q \quad (1)$$

relying on the modulation of exchange parameters by the vibrations; Q is a phonon coordinate operator. In the harmonic approximation, V leads to 2M-phonon coupling providing a natural avenue for magnon (and phonon[12]) decay. As discussed in Ref. 11, magnon scattering is enhanced in situations where the ratio between magnetic and vibrational energies is large. The reason is that, with increasing J, more phonon branches can participate in the process and, so, contribute to the damping. Hence, the magnetostrictive scenario associates width anomalies not with small S, but with large J. This distinguishes the cuprates and, to a lesser extent, $NiPS_3$. While large exchange favors decay, it is obvious that the lifetime is also determined by the magnitude of the coupling constant $\partial J/\partial Q$. In particular, differences in the width of compounds having similar values of J (say, La_2CuO_4 and La_2NiO_4),[6] must be attributed to differences in $\partial J/\partial Q$. In Ref. 11, it is shown that typical coupling strengths are consistent with magnon lifetimes required to explain the cuprate data. Finally, we remark that estimates of $\partial J/\partial Q$ can be gained from measurements of the effect of V on the phonons as demonstrated in Ref. 12 for $FeBO_3$. In $NiPS_3$, V manifests itself in the Fano profile of Fig. 2 reflecting phonon decay into magnon pairs.

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