Raman spectra of two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnets

Stephan Haas and Elbio Dagotto
Department of Physics and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306

Jose Riera
Physics Division and Center for Computationally Intensive Physics, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6373

Roberto Merlin and Franco Nori
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

The Raman spectrum of two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnets is calculated by exactly diagonalizing clusters of up to 26 sites. The obtained spectra are compared to experimental results for various high-T_c precursors, such as La_2CuO_4 and $YBa_2Cu_3O_{6.2}$. In spite of good agreement in the position of the main excitation in the B_{1g} channel, i.e, the two-magnon peak around 0.4 eV, an additional mechanism has to be invoked to account for the broad and asymmetric shape of the overall spectrum. Here, we consider the phonon-magnon interaction which, in a quasistatic approximation, renormalizes the Heisenberg exchange integral. This mechanism is motivated in part by recent experimental observations that the Raman linewidth broadens with increasing temperature. Our results are in good agreement with Raman scattering experiments performed by various groups; in particular, the calculations reproduce the broad line shape of the two-magnon peak, the asymmetry about its maximum, the existence of spectral weight at high energies, and the observation of nominally forbidden A_{1g} scattering.

Raman scattering is a powerful technique for the study of electronic excitations in strongly correlated systems. Recently, much attention has been given to the anomalous magnetic scattering with a very broad and asymmetric line shape observed in the Raman spectra of high-T_c precursors, such as La_2CuO_4, and $YBa_2Cu_3O_{6.2}$ at around 3230 and 3080 cm^{-1}, respectively.[1] The selection rules associated with this peak are also anomalous. While the spin-pair excitations scatter predominantly in the allowed B_{1g} channel, there is also a significant contribution in the nominally forbidden A_{1g} configuration.[1]

Previous theoretical studies[2–4] of Raman scattering in the nearest-neighbor spin-$\frac{1}{2}$ Heisenberg model on a two-dimensional square lattice have shown good agreement with experiments in the position of the two-magnon peak, but they have failed to account for the enhanced width observed in the spectra. Several schemes have been proposed to resolve this problem. Initially, it was believed that strong quantum fluctuations were responsible for the broadening.[3] However, recent studies of spin-pair excitations in a spin-1 insulator, $NiPS_3$, show a relative width comparable to that of two-dimensional cuprates.[5] This leads us to question the view that the observed anomaly is due to large quantum fluctuations intrinsic to spin-$\frac{1}{2}$ systems. Instead, we propose that a magnon-phonon coupling is responsible for the experimentally observed large widths. We remark that the measured widths are 3–4 times larger than the ones predicted within the spin-wave theory using the Dyson-Maleev transformation, even when processes involving up to four magnons are taken into account.[4]

The isotropic Heisenberg Hamiltonian is given by

$$H_0=J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1}$$

where the notation is standard, and only nearest-neighbor interaction is assumed. For the cuprates, the exchange integral is $J\simeq1450$ K$\simeq0.12$ eV.

In our study, we obtained the ground state $|\phi_0\rangle$ of H_0 using a Lanczos algorithm on finite two-dimensional square clusters ($N=16$, 18, 20, and 26) with periodic boundary conditions. We studied zero-temperature spectra associated with the scattering Hamiltonian[1–4]

$$H_{\mathrm{Raman}}=\sum_{\langle ij\rangle}(\mathbf{E}_{\mathrm{inc}}\cdot\hat{\sigma}_{ij})(\mathbf{E}_{\mathrm{sc}}\cdot\hat{\sigma}_{ij})\mathbf{S}_i\cdot\mathbf{S}_j, \tag{2}$$

where $\mathbf{E}_{\mathrm{inc,sc}}$ corresponds to the electric field of the incident and scattered photons, and $\hat{\sigma}_{ij}$ is the unit vector connecting sites $\mathbf{i}$ and $\mathbf{j}$. We concentrated on the case of polarizations perpendicular to each other, $\mathbf{E}_{\mathrm{inc}}\propto\hat{\mathbf{x}}+\hat{\mathbf{y}}$ and $\mathbf{E}_{\mathrm{sc}}\propto\hat{\mathbf{x}}-\hat{\mathbf{y}}$, giving B_{1g} scattering.

The spectrum of the scattering operator can be written as

$$I(\omega)=\sum_n|\langle\phi_n|H_{\mathrm{Raman}}|\phi_0\rangle|^2\delta(\omega-(E_n-E_0)), \tag{3}$$

where ϕ_n denotes the eigenvectors of the Heisenberg Hamiltonian with energy E_n. In practice, the dynamical spectrum $I(\omega)$ is extracted from a continued-fraction expansion of the quantity

$$I(\omega)=-\frac{1}{\pi}\,\mathrm{Im}\langle\phi_0|H_{\mathrm{Raman}}\frac{1}{\omega+E_0+i\epsilon-H_0}H_{\mathrm{Raman}}|\phi_0\rangle, \tag{4}$$

where ϵ is a small real number introduced in the calculation to shift the poles of Eq. (4) into the complex plane.

Our results for B_{1g} scattering are shown in Figs. 1 and 2. The experimentally observed two-magnon excitation lies around $3J$, which is in good agreement with the location of the main peak in the exactly diagonalized 16-site square lat-

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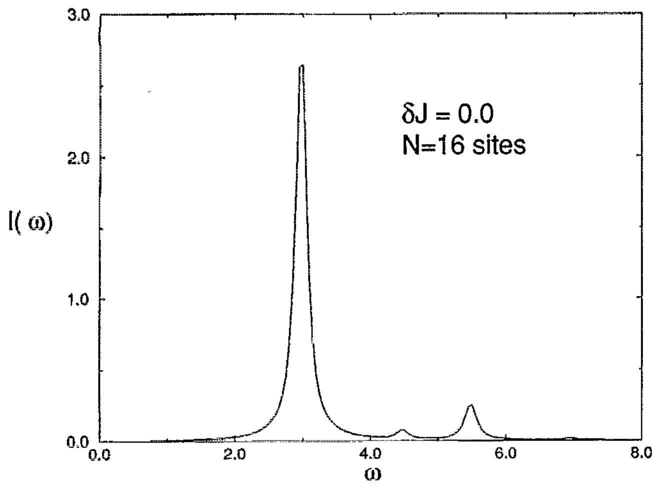

FIG. 1. B_{1g} Raman spectrum in the 4×4 lattice for the pure Heisenberg model. The peaks have been given a finite width $\epsilon=0.1J$, and ω is given in units of J.

tice shown in Fig. 1. The position of this peak can be understood in terms of the Ising model, which corresponds to the limit of the anisotropic Heisenberg Hamiltonian where no quantum fluctuations are present. In its ground state, the Ising spins align antiferromagnetically for $J>0$. Within this model and for a two-dimensional (2D) square lattice, it is well known that the incoming light creates a local spin-pair flip at an energy $3J$ higher than the ground-state energy. This argument remains valid even in the presence of quantum fluctuations. Our results indicate that the two-magnon excitation is at $2.957J$, $3.4260J$, and $3.0370J$ for the 16-, 20-, and 26-site square lattices, respectively. We believe that the somewhat large shift for the 20-site cluster is due to an artifact inherent to the symmetry of the cluster.

While there is good agreement with experiments in regard to the two-magnon peak position, the calculated widths are too small. Thus, it seems necessary to invoke an additional process to account for the observed wide and asymmetric line shape. Here, we propose that the important interaction is between the magnon pair and phonons. The phonons distort the lattice and renormalize the spin-spin exchange interaction in H_0. This mechanism relates to that proposed by Halley[6] to account for two-magnon infrared absorption in, e.g., MnF_2. The calculations in Fig. 2 correspond to the Raman spectra of a disordered lattice, or alternatively, to the quenched phonon approximation. This approximation is valid for the cuprates because there is a clear separation of energies between the fast modes (magnons) and the slow modes (phonons). For instance, in $YBa_2Cu_3O_6$ the characteristic Debye frequency is about 340 cm^{-1} while the two-magnon excitation is $\approx$3080 cm^{-1}. The Born-Oppenheimer approximation focuses on the fast modes and freezes the slow ones.

In our approach, we consider quantum fluctuations and, more important, finite temperatures, which distort the lattice. In turn, these lattice distortions induce changes, δJ_{ij}, in the exchange integral J of the perfect undistorted lattice. Here, δJ_{ij} represents the instantaneous value of $\mathbf{Q}\cdot\nabla_{\mathbf{Q}}J_{ij}(\mathbf{R})$, where $\mathbf{R}$ denotes the equilibrium position of the ion carrying the spin, and $\mathbf{Q}$ is the deviation from the equilibrium. In the quenched disorder approximation, we obtain the effective Hamiltonian

$$H_i=\sum_{\langle ij\rangle}(J+\delta J_{ij})\mathbf{S}_i\cdot\mathbf{S}_j, \tag{5}$$

where $|\delta J_{ij}|<J$ is a random variable reflecting the motion of the ions. Owing to this motion, the translational invariance of the original Heisenberg Hamiltonian [Eq. (1)] breaks down. This corresponds to taking a snapshot of the lattice, i.e., to a Born-Oppenheimer-type approximation which focuses on the fast (high-energy) modes and freezes the slow (low-energy) phonon modes.

In our study, the random couplings δJ_{ij} were drawn from a Gaussian distribution

$$P(\delta J_{ij})=\frac{1}{\sqrt{2\pi}\sigma}\exp[-(\delta J_{ij})^2/2\sigma^2].$$

For a typical optical phonon frequency ($\approx$340 cm^{-1} for $YBa_2Cu_3O_6$), we expect $\sigma\simeq0.3J$.[7] $I(\omega)$ was obtained as the quenched average over $m\simeq1000$ realizations of the randomly distorted lattice. The quenched average of an operator $\hat{O}$ is defined by

$$\langle\langle\hat{O}\rangle\rangle=\frac{1}{m}\sum_{j=1}^{m}\langle\phi_0(j)|\hat{O}|\phi_0(j)\rangle, \tag{6}$$

where $\phi_0(j)$ is the ground state of the jth realization of the disordered system.

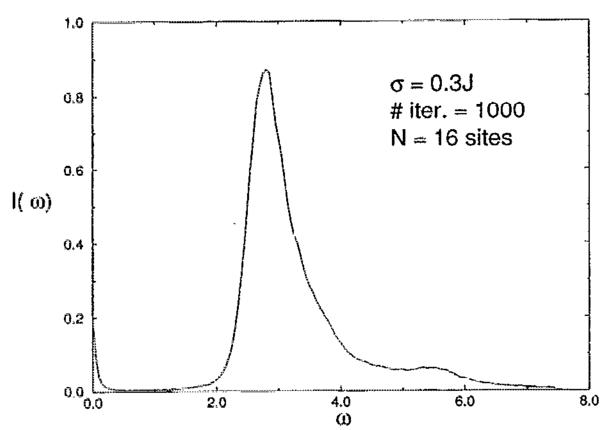

FIG. 2. B_{1g} Raman spectrum for the Heisenberg model on a 4×4 lattice in the presence of randomness in the exchange integral; this represents the effect of the spin-pair–phonon interaction; ω is given in units of J.

In Fig. 2, we show the Raman spectrum for the 16-site square lattice in the presence of random exchange couplings drawn from a Gaussian distribution with $\sigma\simeq0.3J$, which we found to agree best with experimental spectra.[1]

We find that the three main features observed in the experiments,[1] namely, the broad line shape of the two-magnon peak, the asymmetry about its maximum, and the existence of spectral weight up to $\omega\sim8J$ are well reproduced. Beyond the two-magnon peak, there is a continuum of phonon-multimagnon excitations. The small feature around $\omega \sim 5.5J$ is tentatively assigned to a four-magnon excitation. We are currently investigating this point. In addition, the calculated A_{1g} component (not shown), which becomes allowed due to disorder, also shows good agreement with experiments.

Finally, we would like to stress that not every kind of disorder gives rise to the observed broadening of the spectrum. For instance, disorder by points defects or twinning planes will not produce such an effect. Also, it is observed in experiments that the Raman linewidth broadens with increasing temperature.[8] This is a strong indication of a phonon mechanism for the broadening.

In summary, we find strong evidence of phonon-induced broadening of the two-magnon Ramam scattering peak by treating the low-energy phonons as a static random distortion of the lattice. Our results are in good agreement with experimental spectra.

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[7] For conventional transition metal oxides and halide magnets, the dependence of the superexchange integral J on the spin-spin separation r is approximately given by $J(r) \sim r^{-10}$. This decay law can be extracted from experiments probing the pressure dependence of J; see, e.g., M. J. Massey *et al.*, Phys. Rev. B **41**, 8776 (1990). However, for the cuprates the exact value of the decay exponent is still not agreed upon. For instance, recent results of M. Aronson *et al.*, Phys. Rev. B **44**, 4657 (1991), predict an exponent of about -6.4 ± 0.8. Nevertheless, *any* of these values for the decay exponent gives a very strong dependence of J on the spin-spin separation, and our estimate for σ is not significantly affected by them.

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