Detection of weak emergent broken-symmetries of the Kagomé antiferromagnet from Raman spectroscopy

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We show that the magnetic Raman response of a spin-liquid is independent of the polarizations of the light for triangular symmetries. In contrast, a ground-state that has a broken symmetry shows characteristic oscillations when the polarizations are rotated. This would allow to detect weak broken symmetries and emergent order-parameters. We focus on the Kagomé antiferromagnet where no conventional long-range order has been found so far, and present the Raman cross-section of a spin-liquid and a valence bond crystal (VBC) using a random phase approximation.

Interacting spins on the Kagomé lattice are particularly interesting as a possible realization of a spin-liquid ground state. The recent discovery of a magnetic oxide, ZnCu$_3$(OH)$_6$Cl$_3$ [1], with the geometry of the Kagomé lattice has triggered renewed interest in this field [2]. All recent experiments in this compound point to the absence of long-range order, at least of conventional form, and at temperatures well below the superexchange coupling: a persistent dynamics at the lowest temperatures [3, 4], no Bragg peaks in neutron scattering [5]. This is all consistent with the prediction of a non-magnetic ground state by exact diagonalizations of the Heisenberg model [6, 7, 8]. Although other interactions (such as that of Dzyaloshinski-Moriya symmetry) may play a role [9], the nature of the ground-state of Dzyaloshinski-Moriya symmetry [10] is all consistent with the prediction of a non-magnetic spin-liquid (that does not break any lattice symmetries), as shown below using symmetry arguments. Any departure from isotropy therefore signals a broken-symmetry state.

The problem of the energy dependence of the Raman cross-section [1] is also of particular interest: what form of singlet response do we expect for a non-magnetic ground-state? In a conventional ordered-state with $\langle \mathbf{S}_i \rangle \neq 0$, the response [1] is dominated by two-magnon excitations at low energy and can be calculated accordingly [23]. Since this cannot obviously apply to a state with $\langle \mathbf{S}_i \rangle = 0$, we have developed the simplest random phase approximation (RPA) for the singlet dynamics of putative spin-liquid or VBC states. RPA is a rather drastic approximation that cannot reproduce the large singlet sector of the Kagomé lattice [1, 13]. Nonetheless it gives simple well-defined excitations that illustrate the polarization properties explicited above and which can be fur-
...for various lattices.  

First, we discuss general selection rules and the polarization-dependent terms of the cross-section using symmetry arguments. For this, the Raman operator is decomposed in irreducible tensors. The point group of the Kagomé lattice at $k = 0$ is that of the triangular lattice, $C_{3v}$ (there is an additional parity since each site is an inversion center, but it does not play any role in the following). $C_{3v}$ has two one-dimensional irreducible representations (IR) $A_1$ and $A_2$ and one two-dimensional IR $E$. The Raman operator does not have a projection onto $A_2$ so we have

$$H_R = (\hat{e}_{in} \cdot \hat{e}_{out})O_{A_1} + \mathbf{M} \cdot \mathbf{O}_E$$  \hspace{1cm} (3)$$

where $O_{A_1}$ and $\mathbf{O}_E$ are irreducible tensors that transform according to $A_1$ and $E$ respectively. $O_{A_1}$ is in fact nothing but the Heisenberg Hamiltonian so there is no scattering by $A_1$ excited states. This gives a first selection rule: if the ground state is a spin-liquid (with $A_1$ symmetry, the most general case), only the excited states belonging to $E$ (they are twice degenerate) are Raman-active. The vector $\mathbf{M}$ contains the polarization properties and is expressed by $\mathbf{M} = \sum_i (\hat{e}_{in} \cdot \hat{u}_i)(\hat{e}_{out} \cdot \hat{u}_i)\hat{u}_i$, where the sum runs over the bonds of the unit-cell, and $\hat{u}_i$ are the unit-vectors along these bonds $\hat{u}_1 = (1,0)$, $\hat{u}_2 = (-1/2, \sqrt{3}/2)$, $\hat{u}_3 = (-1/2, -\sqrt{3}/2)$. $\mathbf{M}$ can be simply reexpressed with its coordinates $\mathbf{M} \propto (\cos(\theta_{in} + \theta_{out}), \sin(\theta_{in} + \theta_{out}))$, where $\theta_{in}$ and $\theta_{out}$ are the angles of the polarization vectors of the incoming and outgoing photons with respect to the $x$-axis. The Raman cross-section at zero temperature is reduced to the Fourier transform of $|\langle 0|H_R(t)H_R(0)|0 \rangle| = \sum_{\alpha,\beta} M^\alpha M^\beta |\langle 0|O_E^\alpha(t)O_E^\beta(0)\rangle|$. We use the irreducible decomposition of $|\langle 0|O_E^\alpha(t)O_E^\beta(0)\rangle|$ and that of

$$M^\alpha M^\beta = \frac{1}{2} M^2 \delta_{\alpha \beta} + \frac{1}{2} \sigma^{\alpha \beta} (M^{\alpha 2} - M^{\beta 2}) + \sigma_{\alpha \beta} M^\alpha M^\beta$$  \hspace{1cm} (4)$

where the $\sigma^{\alpha \beta}$ are the Pauli matrices. The first term belongs to $A_1$ and the last two terms to $E$, there is no projection onto $A_2$. Each term of (4) is multiplied by the matrix element $|\langle 0|O_E^\alpha(t)O_E^\beta(0)\rangle|$ of the same symmetry. This matrix element is zero or not depending on the symmetry of the ground state. (i) The ground-state is assumed to be a spin-liquid, i.e. it does not break any crystal symmetry (the wave-function $|0\rangle$ transforms according to, e.g., $A_1$). In this case the Raman cross-section reduces to the $A_1$ terms in the decomposition, $M^2(0)|O_E^\alpha(t) \cdot O_E^\beta(0)|$. Remarkably, $M^2$ does not depend on $\hat{e}_{in}$ or $\hat{e}_{out}$. Therefore, the Raman cross-section of a spin-liquid is rotationally invariant:

$$Spin \ \text{liquid} : \ \ S(\omega, \hat{e}_{in}, \hat{e}_{out}) = A(\omega)$$

This is a special property of the triangular symmetry that cannot be general: for example, on the square lattice all scattering channels are polarization-dependent. Now suppose that the ground state spontaneously breaks a symmetry of the crystal. For instance we could have a Néel state or a VBC. In both cases the wave-function contains a superposition of degenerate states belonging to different IR, $|0\rangle = a|A_1\rangle + b|A_2\rangle + c|E\rangle$. As a consequence, the Raman cross-section contains the additional terms of $M^{x 2} - M^{y 2} = \cos(2(\theta_{in} + \theta_{out}))$ and $M^x M^y = \sin(2(\theta_{in} + \theta_{out}))$ with a prefactor that depends on the cross-terms $ac^*$, etc.:

$$Broken \ \text{lattice symmetry :} \ \ S(\omega, \hat{e}_{in}, \hat{e}_{out}) = A(\omega) + E(\omega) \cos(2(\theta_{in} + \theta_{out}) + \phi_\omega)$$

The result depends explicitly on $\theta_{in}$ and $\theta_{out}$ through the cos term ($\phi_\omega$ is a phase factor independent of $\theta_{in}$ and $\theta_{out}$). The amplitude of the oscillation $E(\omega)$ is related to the order-parameter of the broken-symmetry ground-state and it is weak if the symmetry is weakly broken. It appears as a measure of the cross-terms of the ground-state wave-function. Furthermore if the symmetry is broken, we can possibly see individual excited states $|f\rangle$ with a transition probability given by $|\langle f|\mathbf{M} \cdot \mathbf{O}_E|0\rangle|^2 \sim \cos^2(\theta_{in} + \theta_{out} + \phi_f)$. If it is possible to resolve individual peaks experimentally then the variation with polarizations is strong, otherwise the sum of them reduces to the expression above.

In conclusion, Raman spectroscopy appears as an appropriate probe to show whether the ground-state breaks the crystal symmetries or not: if the response is rotationally-invariant we can conclude that the ground state is a spin-liquid; if not the ground-state should break the symmetry of the crystal. In this case, the amplitude of the modulation gives access to the order-parameter. In the case of the Kagomé system where no ordered moment has been found, this may help experimentally to distinguish between a spin-liquid and a VBC for instance.

This discussion also applies to the triangular lattice. Incidentally, the Raman response of the Heisenberg antiferromagnet on the triangular lattice has been calculated recently using exact diagonalizations of small clusters. It is important to stress that this result cannot be seen as reflecting the Raman response of the ordered state in the thermodynamic limit: the oscillation has been missed because in a finite-size system the ground state belongs to the trivial representation of the group. One would need to construct the semi-classical Néel state by summing wave-functions of different IR with the correct amplitudes. The selection rules and the polarization dependence should then reflect the properties given above.

In order to have more precise predictions for the Raman spectrum, we now present the results of a random phase approximation. The approach consists of writing down hierarchical equations of motion for the singlet operator $\mathbf{S}_i(t) \cdot \mathbf{S}_j(t)$ (with $i$ and $j$ anywhere on the lattice) and the four-spin susceptibility associated with $|\langle 0|O_E^\alpha(t) \cdot O_E^\beta(0)| |$.
The closure of the hierarchy is done in such a way as to use two-point correlation functions, \( \langle S_i \cdot S_j \rangle \) as decoupling parameters instead of the local magnetizations \( \langle S_i \rangle \) that are assumed to vanish in the system. This involves writing down the equation of motion to second-order in the time-derivative. The closed equation of motion then contains c-numbers that are the Fourier components of \( \langle S_i \cdot S_j \rangle \). These numbers are unknown and must be determined self-consistently using sum-rules. This is similar to the Kondo-Yamaji decoupling in one-dimensional systems, and can be viewed as a random phase approximation. For the Kagomé lattice with no broken symmetry, the self-consistent parameters were previously determined \([28, 29]\). In addition, we can construct a phenomenological theory of a VBC that breaks the spatial symmetries, simply by imposing an ad hoc modulation of the \( \langle S_i \cdot S_j \rangle \) over the previous parameters. For both systems, the equations of motion are solved numerically in the reciprocal space and the Raman cross-section \([11]\) is extracted at \( k = 0 \) (the system contains up to 2700 sites).

By comparing with preliminary exact results of the dimer dynamical response of small clusters \([30]\), we believe that the response in the single peak at \( \omega \sim 0.8 J \) can in fact be broadened. This would be interesting as an indication that the present simple excitation is coupled to other low-energy singlet modes and would decay accordingly. Of course, the present approach has neglected this effect in closing the hierarchy of higher-order Green’s functions.

![Graph](image-url)

**FIG. 1:** (color online). Magnetic Raman cross-section of the Kagomé lattice calculated within RPA, assuming a spin-liquid ground-state. The response does not depend on the orientation of the incoming and outgoing photon polarizations, \( \mathbf{e}_{in} \) or \( \mathbf{e}_{out} \). Each individual delta function is slightly broadened with a Lorentzian.

In Fig. \( \text{[1]} \) we give the result of the RPA calculation of \( S(\omega, \mathbf{e}_{in}, \mathbf{e}_{out}) \) for the Kagomé lattice, assuming that \( \langle S_i \cdot S_j \rangle \) do not break the crystal symmetries (we replace the \( \delta \) functions in Eq. \( \text{[1]} \) by Lorentzians). We find that the spectrum consists of several peaks, the intensity of which decreases strongly when the energy increases. The main intensity is in fact quite concentrated in a single mode at about 0.8J. The result is fully in agreement with the group theory arguments given above: (i) all Raman-active modes are twice degenerate, so their wavefunctions can be labelled with the IR \( E \), (ii) we have rotated the photon polarizations \( \mathbf{e}_{in} \) and \( \mathbf{e}_{out} \) and have found that the intensities in Fig. \( \text{[1]} \) do not change at all.

![Graph](image-url)

**FIG. 2:** (color online). Magnetic Raman cross-section of the Kagomé lattice with weak broken-symmetry, within RPA. The ground-state is supposed to be the valence bond crystal depicted in the inset, that breaks the rotation symmetry (the correlations are assumed to be stronger on horizontal bonds). Different curves correspond to different orientations of the polarization vector \( \mathbf{e}_{in}(\parallel \mathbf{e}_{out}) \).

Furthermore, we now choose a VBC ground-state with a spontaneous broken symmetry in the two-point correlation functions. For simple illustration, we impose the same weak perturbation of slightly stronger \( \langle S_i \cdot S_j \rangle \) on all horizontal bonds (30 % stronger in the following calculation) (see inset of Fig. \( \text{[2]} \)). Since the equation of motion within RPA breaks the \( C_{3v} \) symmetry, the two-fold degeneracy of the \( E \)-states is lifted and we have pairs of peaks. The intensities now display strong orientation dependence when \( \mathbf{e}_{in} \parallel \mathbf{e}_{out} \) is rotated in the plane, as shown by the different curves in Fig. \( \text{[2]} \). The intensities of the two peaks change mainly like \( \cos^2 2\theta \) \( (\theta_{in} = \theta_{out} = \theta) \) for one component and \( \sin^2 2\theta \) for the other with different prefactors as long as the order-parameter is non-zero. If the peaks cannot be resolved experimentally, the cross-section measures the sum of the two intensities that therefore reduces to \( A(\omega_0) + E(\omega_0) \cos 4\theta \), in agreement with the general argument given above. It should be emphasized that even if the symmetry is weakly broken, the sum still displays a weak characteristic oscillation, the amplitude of which gives access to the order-parameter of the broken symmetry state \([31]\). We have shown this on the simplest example of a VBC, but we believe this will remain true for more complicated superstructures.
with $k \neq 0$, such as those suggested in the literature \cite{11,12,13,14,15}. It is interesting to note that a VBC will be presumably accompanied by lattice distortions of the same symmetry, which can be tested independently by X-rays.

We conclude with a simple selection rule for Raman spectroscopy in triangular geometries: if the ground state is a spin-liquid, the Raman response is independent of the polarizations of the incoming and outgoing photons. However if the ground state has a broken lattice symmetry, it should depend, in most cases \cite{25}, on the polarizations of the light. The dependence is given by $\cos(2(\theta_{in} + \theta_{out}) + \phi)$ with an amplitude that measures the strength of the emergent order-parameter. Raman spectroscopy can therefore test directly the presence of such broken symmetries. This may help in clarifying the ground state of the Kagomé system ZnCu$_3$(OH)$_6$Cl$_3$ and especially to discriminate between a real spin-liquid and a ground state of the Kagomé system ZnCu$_3$(OH)$_6$Cl$_3$ and especially to discriminate between a real spin-liquid and a valence-bond-crystal. Other particularly interesting candidates are the possible spin-liquids on triangular lattices: the organic material $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (it is nearly an isotropic triangular lattice) \cite{32}, or NiGa$_2$S$_4$ \cite{33}. Here again the issue of emergent broken-symmetry is of particular interest.

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\bibitem{25} A word of caution : if the ground-state is a superposition of A$_1$ and A$_2$ only (and not E), the symmetry is broken, but since \cite{25} does not have projections on A$_2$, the cross-section will not depend on $\theta_{in, out}$ either. This may be the case in the VBC of refs. \cite{14,16}, but certainly not the case of the Néel state nor of the VBCs of refs. \cite{11,12} which remain the most plausible VBC candidates to describe the Kagomé antiferromagnet.

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