

Detection of weak emergent broken-symmetries of the kagome antiferromagnet by Raman spectroscopy

O. Cépas,¹ J. O. Haerter,^{1,2} and C. Lhuillier¹¹*Laboratoire de Physique Théorique de la Matière Condensée, UMR 7600 CNRS, Université Pierre-et-Marie-Curie, Paris VI, 75252 Paris cedex 05, France*²*Department of Physics, University of California, Santa Cruz, California 95064, USA*

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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 one to detect weak broken-symmetries and emergent order parameters. We focus on the kagome antiferromagnet wherein 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 by using a random phase approximation.

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Interacting spins on the kagome lattice are particularly interesting as a possible realization of a spin-liquid ground state. The recent discovery of a magnetic oxide, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_3$,¹ with the geometry of the kagome 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 a conventional form, and, at temperatures well below the superexchange coupling. There is a persistent dynamics at the lowest temperatures,^{3,4} and no Bragg peaks in neutron scattering.⁵ This is all consistent with the prediction of a nonmagnetic ground state by exact diagonalizations of the Heisenberg model.^{6–8} Although other interactions (such as that of Dzyaloshinski–Moriya symmetry) may play a role in this compound,⁹ the nature of the ground state of the Heisenberg model is currently under debate. It could be a spin liquid that does not break any symmetry¹⁰ or a valence-bond crystal (VBC) that breaks translation symmetry.^{11–17} In the latter cases, however, the unit cells turn out to be rather large and the modulation of the correlations must be weak; otherwise, a large spin gap would exist. This makes the use of exact spectra to identify the broken-symmetry a difficult task,¹⁸ and no definite proof has emerged so far on the theoretical side. The question then arises as to whether it could be possible to experimentally detect such a weak broken-symmetry. Detecting the resulting emergent order parameters is indeed not easy because of the lack of direct experimental probes. Indirect ways were suggested for the chiral order parameter, for instance, through polarized neutron experiments,¹⁹ but those do not probe the singlet sector of VBCs.

In this Brief Report, we argue that the Raman scattering of light by spin excitations provides a way to distinguish between a spin liquid and a broken-symmetry state. In particular, it allows one to extract emergent order parameters in systems with no conventional magnetic long-range order. Indeed, we have found that the Raman cross section is *polarization independent* for a spin liquid governed by a Heisenberg Hamiltonian in triangular geometries, whereas, it acquires a characteristic *polarization dependence* for a broken-symmetry state with an amplitude proportional to the emergent order parameter.

Magnetic Raman scattering is a two-photon process: The (polarized) electric field of light forces the exchange of two electrons (and hence their spins), thus, creating a spin excitation in the system. The cross section of this process is given (at zero temperature) by^{20–22}

$$S(\omega, \hat{\mathbf{e}}_{\text{in}}, \hat{\mathbf{e}}_{\text{out}}) = \sum_f |\langle f | H_R | 0 \rangle|^2 \delta(\omega - \omega_f), \quad (1)$$

$$H_R = \sum_{\langle i,j \rangle} (\hat{\mathbf{e}}_{\text{in}} \cdot \mathbf{r}_{ij})(\hat{\mathbf{e}}_{\text{out}} \cdot \mathbf{r}_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j. \quad (2)$$

Equation (1) explicitly depends on the polarizations of the incoming and outgoing photons $\hat{\mathbf{e}}_{\text{in,out}}$ through the dipolar factors $\hat{\mathbf{e}} \cdot \mathbf{r}_{ij}$, where \mathbf{r}_{ij} is the bond vector of nearest-neighbor sites. The actual polarization dependence results from the symmetries: If the ground state $|0\rangle$ is a spin liquid (that does not break any lattice symmetries), one can predict the polarization-dependent terms according to the symmetries of the excited states $|f\rangle$ (of energy ω_f). For instance, in square geometries, all scattering channels depend on polarizations.²³ In triangular geometries, however, the cross section turns out to be polarization independent for a spin liquid, as shown below by using symmetry arguments. Any departure from isotropy, therefore, signals a broken-symmetry state.

The problem of the energy dependence of the Raman cross section [Eq. (1)] is also of particular interest: What form of singlet response do we expect for a nonmagnetic ground state? In a conventional ordered state with $\langle \mathbf{S}_i \rangle \neq 0$, the response [Eq. (1)] is dominated by two-magnon excitations at low energy and can be accordingly calculated.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. The RPA is a rather drastic approximation that cannot reproduce the large singlet sector of the Kagome lattice.^{7,8} Nonetheless, it gives simple well-defined excitations that illustrate the polarization properties explicated above and which can be further tested for various lattices.

First, we discuss general selection rules and the polarization-dependent terms of the cross section by using

symmetry arguments. For this, the Raman operator [Eq. (2)] is decomposed in irreducible tensors. The point group of the kagome lattice at $\mathbf{k}=0$ 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 (IRs) 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

$$H_R = (\hat{\mathbf{e}}_{\text{in}} \cdot \hat{\mathbf{e}}_{\text{out}}) O_{A_1} + \mathbf{M} \cdot \mathbf{O}_E, \quad (3)$$

where O_{A_1} and 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, which is the most general case), only the excited states belonging to E (they are twice degenerate) are Raman active. The vector M contains the polarization properties and is expressed by $M = \sum_i (\hat{\mathbf{e}}_{\text{in}} \cdot \hat{\mathbf{u}}_i) (\hat{\mathbf{e}}_{\text{out}} \cdot \hat{\mathbf{u}}_i) \hat{\mathbf{u}}_i$, where the sum runs over the bonds of the unit cell and $\hat{\mathbf{u}}_i$ are the unit vectors along the bonds $\hat{\mathbf{u}}_1 = (1, 0)$, $\hat{\mathbf{u}}_2 = (-1/2, \sqrt{3}/2)$, and $\hat{\mathbf{u}}_3 = (-1/2, -\sqrt{3}/2)$. M can be simply re-expressed with its coordinates $M \propto [\cos(\theta_{\text{in}} + \theta_{\text{out}}), \sin(\theta_{\text{in}} + \theta_{\text{out}})]$, where θ_{in} and θ_{out} are the angles of the polarization vectors of the incoming and outgoing photons with respect to the x axis. The Raman cross section [Eq. (1)] at zero temperature is reduced to the Fourier transform $\langle 0 | H_R(t) H_R(0) | 0 \rangle = \sum_{\alpha\beta} M^\alpha M^\beta \langle 0 | O_E^\alpha(t) O_E^\beta(0) \rangle$. We use the irreducible decomposition of $\langle 0 | O_E^\alpha(t) O_E^\beta(0) \rangle$ and that of

$$M^\alpha M^\beta = \frac{1}{2} M^2 \delta_{\alpha\beta} + \frac{1}{2} \sigma_{\alpha\beta}^x (M^{x^2} - M^{y^2}) + \sigma_{\alpha\beta}^x M^x M^y, \quad (4)$$

where the $\sigma^{x,z}$ are the Pauli matrices. The first term belongs to A_1 and the last two terms belongs to E ; there is no projection onto A_2 . Each term of Eq. (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 $M^2 \langle 0 | O_E(t) \cdot O_E(0) \rangle$. Remarkably, M^2 does not depend on $\hat{\mathbf{e}}_{\text{in}}$ or $\hat{\mathbf{e}}_{\text{out}}$. Therefore, the Raman cross section of a spin liquid is rotationally invariant:

Spin liquid:

$$S(\omega, \hat{\mathbf{e}}_{\text{in}}, \hat{\mathbf{e}}_{\text{out}}) = A(\omega).$$

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.²⁴ (ii) 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 IRs, $|0\rangle = a|A_1\rangle + b|A_2\rangle + c|E\rangle$. As a consequence, the Raman cross

section contains the additional terms of Eq. (4), which are $M^{x^2} - M^{y^2} = \cos[2(\theta_{\text{in}} + \theta_{\text{out}})]$ and $M^x M^y = \sin[2(\theta_{\text{in}} + \theta_{\text{out}})]$, with a prefactor that depends on the cross terms ac^* , etc.:

Broken lattice symmetry:

$$S(\omega, \hat{\mathbf{e}}_{\text{in}}, \hat{\mathbf{e}}_{\text{out}}) = A(\omega) + E(\omega) \cos[2(\theta_{\text{in}} + \theta_{\text{out}}) + \phi_\omega].$$

The result explicitly depends on θ_{in} and θ_{out} through the cos term (ϕ_ω is a phase factor independent of θ_{in} and θ_{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 $|\langle f | M \cdot O_E | 0 \rangle|^2 \sim \cos^2(\theta_{\text{in}} + \theta_{\text{out}} + \phi_f)$. If it is possible to experimentally resolve individual peaks, then the variation with polarizations is strong; otherwise, their sum 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;²⁵ 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 kagome system wherein no ordered moment has been found, this may experimentally help 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 was recently calculated by using exact diagonalizations of small clusters.²⁶ It is important to stress that this result of Ref. 26 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 semiclassical Néel state by summing wave functions of different IRs 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 of a nonmagnetic state, we now present the results of a random phase approximation. The approach consists of writing down hierarchical equations of motion for the singlet operator $\mathbf{S}_i(t) \cdot \mathbf{S}_j(t)$ (where i and j are anywhere on the lattice) and the four-spin susceptibility associated with Eq. (1). The closure of the hierarchy is done in such a way as to use two-point correlation functions $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ as decoupling parameters instead of the local magnetizations $\langle \mathbf{S}_i \rangle$ 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 $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. These numbers are unknown and must be self-consistently determined by using sum rules. This is similar to the Kondo–Yamaji²⁷ decoupling in one-dimensional systems and can be viewed as a random phase approximation. For the kagome lattice with no broken-

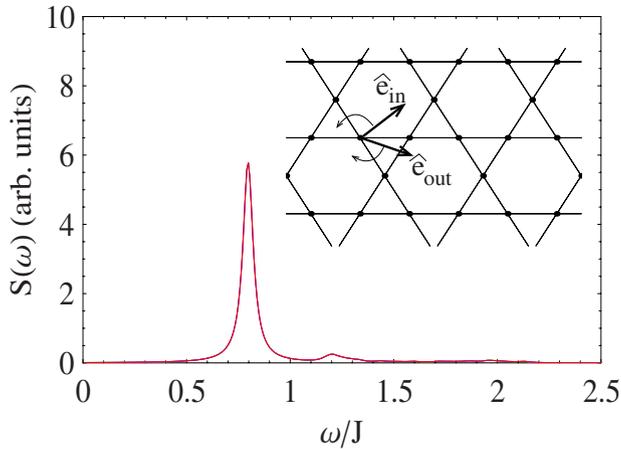


FIG. 1. (Color online) Magnetic Raman cross section of the kagome lattice calculated within the RPA, which assumes a spin-liquid ground state. The response does not depend on the orientation of the incoming and outgoing photon polarizations \hat{e}_{in} or \hat{e}_{out} . Each individual delta function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

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 $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ over the previous parameters. For both systems, the equations of motion are numerically solved in the reciprocal space and the Raman cross section [Eq. (1)] is extracted at $\mathbf{k}=0$ (the system contains up to 2700 sites).

In Fig. 1, we give the result of the RPA calculation of $S(\omega, \hat{e}_{\text{in}}, \hat{e}_{\text{out}})$ for the kagome lattice assuming that $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ do not break the crystal symmetries [we replace the δ functions in Eq. (1) by Lorentzians]. We find that the spectrum consists of several peaks, the intensity of which strongly decreases when the energy increases. The main intensity is in fact quite concentrated in a single mode at about 0.8 J. The result is fully in agreement with the group theory arguments given above: (i) All Raman-active modes are twice degenerate so their wave functions can be labeled with the IR E and (ii) we have rotated the photon polarizations \hat{e}_{in} and \hat{e}_{out} and have found that the intensities in Fig. 1 do not change at all. By comparing to 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 accordingly decay. Of course, the present approach has neglected this effect in closing the hierarchy of higher-order Green's functions.

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 a slightly stronger $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ on all horizontal bonds (30% stronger in the following calculation) (see inset of Fig. 2). Since the equation of motion within the RPA breaks the C_{3v} symmetry, the twofold degeneracy of the E states is lifted and we have pairs of peaks. The intensities now display a strong orientation dependence when $\mathbf{e}_{\text{in}} \parallel \mathbf{e}_{\text{out}}$ is rotated in the plane, as shown by the different curves in

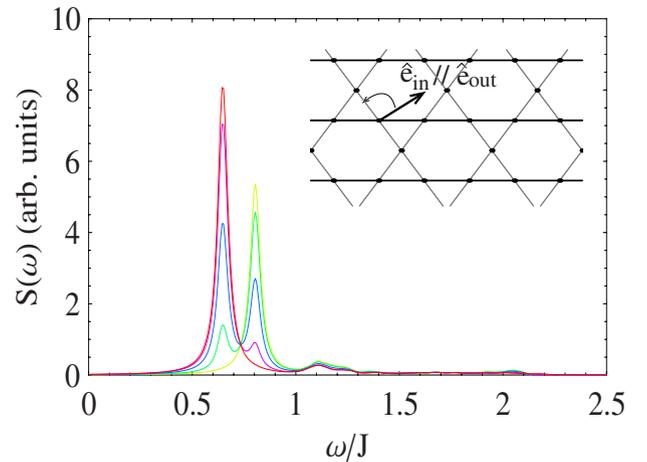


FIG. 2. (Color online) Magnetic Raman cross section of the kagome lattice with weak broken-symmetry within the RPA. The ground state is supposed to be the valence bond crystal depicted in the inset that breaks the rotation symmetry (the correlations are assumed to be stronger on horizontal bonds). The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

Fig. 2. The intensities of the two peaks mainly change like $\cos^2 2\theta$ ($\theta_{\text{in}} = \theta_{\text{out}} = \theta$) for one component and like $\sin^2 2\theta$ for the other with different prefactors as long as the order parameter is a nonzero. If the peaks cannot be experimentally resolved, the cross section measures the sum of the two intensities that therefore reduces to $A(\omega_0) + E(\omega_0) \cos 4\theta$, which is 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 $\mathbf{k} \neq 0$, such as those suggested in literature.^{11–17} It is interesting to note that a VBC will be presumably accompanied by lattice distortions of the same symmetry, which can be independently tested 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,²⁵ on the polarizations of the light. The dependence is given by $\cos[2(\theta_{\text{in}} + \theta_{\text{out}}) + \phi]$, with an amplitude that measures the strength of the emergent order parameter. Raman spectroscopy can therefore directly test the presence of such broken-symmetries. This may help in clarifying the ground state of the kagome system $\text{ZnCu}_3(\text{OH})_6\text{Cl}_3$, 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 $\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3$ (Ref. 32) (it is nearly an isotropic triangular lattice) or NiGa_2S_4 .³³ Here, again, the issue of emergent broken-symmetry is of particular interest.

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- ²⁵A word of caution: If the ground state is a superposition of A_1 and A_2 only (and not E), the symmetry is broken. However, since Eq. (2) does not have projections on A_2 , the cross section will not depend on $\hat{e}_{in,out}$ either. This may be the case in the VBC of Refs. 13 and 15, but certainly not the case of the Néel state nor of the VBCs of Refs. 14 and 16, which remain the most plausible VBC candidates to describe the kagome antiferromagnet.
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