Two-magnon Raman scattering in spin-ladder geometries and the ratio of rung and leg exchange constants

P. J. Freitas and R. R. P. Singh
Department of Physics, One Shields Avenue, University of California, Davis, California 95616-8677
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We discuss ways in which the ratio of exchange constants along the rungs and legs of a spin-ladder material influences the two-magnon Raman scattering spectra and hence can be determined from it. We show that within the Fleury-Loudon-Elliott approach, the Raman line shape does not change with polarization geometries. This line shape is well known to be difficult to calculate accurately from theory. However, the Raman scattering intensities do vary with polarization geometries, which are easy to calculate. With some assumptions about the Raman scattering Hamiltonian, the latter can be used to estimate the ratio of exchange constants. We apply these results to the recent measurements of Sugai *et al.* of Raman scattering from spin-ladder materials such as $La_6Ca_8Cu_{24}O_{41}$ and $Sr_{14}Cu_{24}O_{41}$.

I. INTRODUCTION

Determining the exchange constants and establishing the microscopic spin Hamiltonian is an important step in understanding the magnetic properties of exotic new materials. In materials which have predominantly a single exchange constant, measurement of the uniform susceptibility and determination of the Curie-Weiss parameter are sufficient to obtain the exchange constant. However, in recent years, many complex materials have been synthesized which have more than one exchange constant. Furthermore, these exchange constants can be so large that the Curie-Weiss regime may not be experimentally accessible. In these cases alternative methods are needed to determine the exchange parameters. Examples of such materials are cuprate-based spin-ladder materials, cousins of high-temperature superconducting materials, for which there is a substantial literature for determining the exchange constants. The simplest methods for determining the exchange constants involve measuring the temperature dependence of the uniform susceptibility, Knight shift, or nuclear relaxation rates, which can then be compared with detailed theoretical calculations to obtain the exchange parameters. Such a fitting procedure is not very accurate, as reflected in the range of values that exist in the literature for these materials.

Recently, Sugai *et al.*[1,2] noted that Raman scattering can be used to determine the ratio of rung and leg exchange constants in spin-ladder materials. They argued that by varying the polarization direction of incident and outgoing light, one might be able to shift the Raman spectra in ways that can be related to the different exchange constants. Our study is motivated by the work of Sugai *et al.* However, we find that the arguments used by Sugai *et al.* to relate the position of the spectral peaks to the different exchange constants in the spin-ladder materials are incorrect. Within Fleury-Loudon-Elliott[3,4] theory the spectral line shape does not change with polarization at all. This gives a simple explanation why Sugai *et al.* always find a very small shift in the Raman spectra and sheds doubt on their inference that the exchange constants in all the ladder materials are close to unity.

It is well known that an accurate calculation of Raman spectra for low-dimensional spin-half antiferromagnets is very difficult due to quantum fluctuations.[5] And short of a direct comparison of the spectra with theory, it would seem that Raman spectra cannot be used to determine the ratio of exchange constants. However, we show below that the Raman scattering intensities do depend on polarization geometries in a way that is easily calculated and related to the ratio of exchange constants. Unfortunately, they come with an unknown factor, about which certain assumptions need to be made before an estimate of the ratio of rung to leg exchange constants in the ladder material can be obtained.

II. SPIN-LADDER HEISENBERG MODELS

We begin with a system described by a Heisenberg model in ladder geometry, with the Hamiltonian

$$H = J_r \sum_{\langle ij\rangle, r} \vec{S}_{\mathbf{i}} \cdot \vec{S}_{\mathbf{j}} + J_l \sum_{\langle ij\rangle, l} \vec{S}_{\mathbf{i}} \cdot \vec{S}_{\mathbf{j}}, \tag{1}$$

where J_r and J_l denote the coupling constants for the rung and leg bonds of the ladder, respectively, and the sums are only over the bonds in the indicated directions. Our primary goal is to examine the dependence of Raman scattering on the ratio of exchange constants J_r and J_l.

Within the Fleury-Loudon-Elliott approach, magnetic Raman scattering is described by an effective Raman Hamiltonian or operator:[6]

$$\mathcal{H}_R = \sum_{\langle ij\rangle} J'_{ij} (\hat{\boldsymbol{\epsilon}}_{in} \cdot \hat{r}_{ij})(\hat{\boldsymbol{\epsilon}}_{out} \cdot \hat{r}_{ij}) \vec{S}_{\mathbf{i}} \cdot \vec{S}_{\mathbf{j}}, \tag{2}$$

where the $\hat{r}_{ij}$ are unit vectors along the bond directions, and $\hat{\boldsymbol{\epsilon}}_{in}$ and $\hat{\boldsymbol{\epsilon}}_{out}$ are unit vectors indicating the direction of polarization of the incident and scattered light, respectively. The J'_{ij} are constants representing the strength of the Raman scattering interaction between spins *i* and *j*. In previous studies of the spin-ladder geometry,[2,7] it has been assumed that J_{ij} has a constant value for nearest-neighbor bonds and is zero otherwise. Thus it can be taken out of the summation.

Such a constant simply sets the overall scale for the scattering and does not influence any other result. However, we believe that if the rung and leg exchange constants are not equal, *a priori*, we cannot assume the ratio of J' along the rung and leg directions to be equal. Thus we proceed here with a more general J'_{ij}, and later consider possible scenarios for their values, which would play an important role.

Following Sugai *et al.*, it is most useful to consider the case where the incident and scattered light have parallel polarization directions, both lying in the plane of our two-dimensional (2D) system. Thus, $\hat{\epsilon}_{in}=\hat{\epsilon}_{out}$. Most generally, we can denote the polarization with an angle θ with respect to the vertical bonds, which makes the effective Raman Hamiltonian

$$\mathcal{H}_R(\theta)=\cos^2\theta\sum_{\langle ij\rangle,r}J'_{ij}\vec{S}_{\mathbf{i}}\cdot\vec{S}_{\mathbf{j}}+\sin^2\theta\sum_{\langle ij\rangle,l}J'_{ij}\vec{S}_{\mathbf{i}}\cdot\vec{S}_{\mathbf{j}}. \quad (3)$$

For reasons of symmetry, we assume that all the J'_{ij} in each summation are the same (we call them J'_r and J'_l, respectively). Also, as a notational simplification, we define $\mathcal{H}_r=\mathcal{H}_R(0)/J'_r$ and $\mathcal{H}_l=\mathcal{H}_R(\pi/2)/J'_l$, so

$$\mathcal{H}_R(\theta)=J'_r(\cos^2\theta)\mathcal{H}_r+J'_l(\sin^2\theta)\mathcal{H}_l. \quad (4)$$

The two-magnon Raman scattering intensity as a function of frequency can be expressed using Fermi's golden rule,

$$I(\omega,\theta)=\sum_n{}'|\langle\psi_n|\mathcal{H}_R(\theta)|\psi_0\rangle|^2\delta(\omega-(E_n-E_0)), \quad (5)$$

where $|\psi_n\rangle$ and E_n are eigenvectors and eigenvalues of the Hamiltonian, and the prime indicates that the ground state is excluded from the sum.

Our key result follows from the following simple consideration: using the terminology defined above, we can express Eq. (1) as

$$\mathcal{H}_l=\frac{1}{J_l}(H-J_r\mathcal{H}_r), \quad (6)$$

which can be substituted into Eq. (4) to give

$$\mathcal{H}_R(\theta)=J'_r\left(\cos^2\theta-\frac{J_rJ'_l}{J_lJ'_r}\sin^2\theta\right)\mathcal{H}_r+\frac{J'_l\sin^2\theta}{J_l}H. \quad (7)$$

The second term of the sum is a multiple of the Hamiltonian, and thus cannot contribute to the scattering. The first term is proportional to $\mathcal{H}_r$ for all angles. Thus, within this theory, the observed two-magnon scattering spectrum will have the same line shape and peak position for all angles. This result is in direct contradiction with the arguments of Sugai *et al.*

The intensity of the spectrum is given by the expression

$$I(\omega,\theta)=\left(\cos^2\theta-\frac{J_rJ'_l}{J_lJ'_r}\sin^2\theta\right)^2I(\omega,0). \quad (8)$$

This variation of angle can be used to determine the ratio of exchange constants, provided one either knows J'_r/J'_l or can relate it to J_r/J_l. This point is discussed a little later. In principle, one can perform the experiments by varying θ continuously to obtain the above variation. One simply needs to keep the polarization directions of incoming and outgoing light fixed parallel to each other in the plane and rotate the sample. To find the ratio of exchange constants, it is sufficient to consider two angles

$$\frac{J_r}{J_l}=\frac{J'_r}{J'_l}\sqrt{\frac{I(\omega,\pi/2)}{I(\omega,0)}}. \quad (9)$$

A simple procedure for determining the ratio of coupling constants could be to measure the maximum two-magnon Raman scattering intensity, then rotate the material through an angle of 90° and measure the intensity again. The ratio of intensities would give the ratio of exchange constants, provided that one can reasonably estimate the value of the ratio of J'_r/J'_l.

III. ANALYSIS OF EXPERIMENTAL RESULTS

Experimental evidence does support the idea that the spectra do not vary much in shape as a function of angle, but do vary in intensity. For example, Sugai and Suzuki[1] measured the Raman spectra for the spin-1/2 two-leg ladder materials $La_6Ca_8Cu_{24}O_{41}$ and $Sr_{14}Cu_{24}O_{41}$ in two different configurations separated by an angle of 90°. One configuration had the incident and scattered polarizations parallel to the legs of the ladder, and the other had them parallel to the rungs. The peaks of the observed spectra for the two configurations of $La_6Ca_8Cu_{24}O_{41}$ were found at 3004 cm^{-1} and 2948 cm^{-1}, a relative difference of less than 2%, which can be neglected. The spectral shapes are largely identical as well, but the intensities are vastly different. The ratio of the intensities of the peaks of these two spectra is approximately 0.52, which is quite significant. The same measurements performed on $Sr_{14}Cu_{24}O_{41}$ yielded peaks at 3006 cm^{-1} and 3004 cm^{-1}, and an intensity ratio of approximately 0.39. The peaks are even closer together than the others studied, and the intensity ratio is smaller. Popović and collaborators[8] present scattering data for $Sr_{14}Cu_{24}O_{41}$ that shows a similar lack of peak location shift, as do measurements by Sugai and collaborators[2] on $LaCuO_{2.5}$. The small observed shift in the spectral peak could be due to impurities, phonons, or interladder couplings as well as due to other intraladder interactions not included here.[9] Note that because our result derives from an operator relation, it is not sensitive to long-range ordering in the system, and should be valid for small interladder couplings.

There are several possiblities for the value of J'_r/J'_l that should be considered. We shall begin by examining the possibility that $J'_r/J'_l=J_r/J_l$, as follows from a large-U perturbative treatment and suggested by the work of Moriya[10] and Shastry and Shraiman.[11] If we assume that $J'_r/J'_l=J_r/J_l$, Eq. (8) becomes $I(\omega,\theta)=(\cos 2\theta)^2I(\omega,0)$. Thus, all of the maxima should be identical in magnitude. This conclusion is directly contradicted by all of the experimental results discussed previously, where the ratio was found to vary by more than a factor of 2. Clearly, direct proportionality does not exist.

A second possibility is that all of the nearest-neighbor Raman operator coupling constants are equal to one another. This has been assumed universally by almost all previous studies of these ladder materials. The bonds along the rungs and legs of the ladder are nearly identical, which is perhaps what led to this assumption. However, it leaves open the question of why this ratio will remain unity when the ratio

TABLE I. Computed J_r/J_l for the materials studied by Sugai *et al.* for the two ratios of the Raman coupling constants discussed in the text.

Material	$J_r'/J_l' \approx 1$	$J_r'/J_l' = \sqrt{J_r/J_l}$
$La_6Ca_8Cu_{24}O_{41}$	0.72	0.52
$Sr_{14}Cu_{24}O_{41}$	0.63	0.39
$LaCuO_{2.5}$	0.74	0.55

J_r/J_l deviates significantly from unity. Assuming $J_r'/J_l' \approx 1$, Eq. (9) becomes

$$\frac{J_r}{J_l} = \sqrt{\frac{I(\omega, \pi/2)}{I(\omega,0)}}. \tag{10}$$

A third possibility can be motivated by perturbation theory. If the two-magnon Raman process involves a direct exchange, it is a second order process, whereas the usual superexchange could be mediated by nonmagnetic intermediate ions and thus could be a fourth-order process in a large-U expansion. In this case, a more natural relationship between the Raman and Heisenberg coupling constants is $J' \propto \sqrt{J}$. So

$$\frac{J_r}{J_l} = \frac{I(\omega, \pi/2)}{I(\omega,0)}. \tag{11}$$

Using these two possibilities, we computed the ratio of the Heisenberg coupling constants for the materials studied by Sugai and collaborators, using their published data. The results for these materials are shown in Table I.

Let us discuss these results in light of previous studies.[12,13] Some authors have adopted the point of view that this ratio is close to unity, and have used that as the starting point of their analysis.[14] On the other hand, some local density approximation calculations[18,19] find the ratio to be closer to 0.5. A number of other studies which allow the ratio to vary, also find values close to ~ 0.5,[15–17] although a range of experimental values from 0.5 to 1.13 has been quoted.[15,20–23,25] Brehmer *et al.*[24] make an interesting attempt to reconcile the conflicting viewpoints, keeping the ratio as unity but allowing an additional biquadratic ring interaction in the Hamiltonian.

In the Sugai-Suzuki paper, the authors used an incorrect argument for the energy shift to estimate the ratio of exchange couplings along the rungs and legs of the ladder. Their ratio was determined to be 0.95 for $La_6Ca_8Cu_{24}O_{41}$ and 1 for $Sr_{14}Cu_{24}O_{41}$. It is now clear that Sugai and collaborators obtained values close to unity because, to a good approximation, the spectra do not shift at all with a change in the polarization direction. Using their data and Eq. (10) and Eq. (11), we calculate the ratio to be less than 1 in all cases. It is interesting to note that using Eq. (11), our calculated ratio agrees well with the conclusion that $J_r/J_l \sim 0.5$.

IV. CONCLUSION

We have seen how Fleury-Loudon-Elliott theory predicts that the shape of the Raman spectra in the spin-ladder geometry, with nearest-neighbor Heisenberg exchange constants, does not change with the polarization directions. Instead, there exists a relationship between the intensity of two-magnon Raman scattering in different polarizations and the ratio of Heisenberg exchange constants. With some suitable assumptions about the Raman Hamiltonian, we have used it to estimate the ratio of the rung to leg exchange constant in several cuprate materials. The full dependence of the intensity on the polarization direction can be experimentally verified and should serve as a test for Fleury-Loudon-Eliott theory.

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