Theory of phonon-assisted “forbidden” optical transitions in spin-gapped systems

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We consider the absorption of light with emission of one $S_{\text{tot}} = 1$ magnetic excitation in systems with a spin gap induced by quantum fluctuations. We argue that an electric dipole transition is allowed on the condition that a virtual phonon instantaneously breaks the inversion symmetry. We derive an effective operator for the transition and argue that the proposed theory explains the polarized experiments in CuGeO\textsubscript{3} and SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2}.

I. INTRODUCTION

Techniques of using the interactions between light and spin-waves to study the excitations of magnetic solids were developed shortly after the invention of the laser. Single magnon scattering of photons was first predicted from the Zeeman coupling of the magnetic field of the photon field to the magnetic spins, leading to magnetic dipole transitions.\textsuperscript{1} Later it was pointed out that the electric field of the electromagnetic radiation could also couple to the spin, by an indirect process in which spin-orbit interactions act on electronic states excited virtually by electric-dipole transitions. Experiments in antiferromagnets\textsuperscript{2,3} showed that this latter mechanism dominated the magnetic-dipole transitions to single magnon excitations. The Raman spectrum also revealed relatively strong two-magnon scattering. This was argued to be due to an independent mechanism: excited-state exchange interactions. The same mechanism, by which the magnetic exchange interaction is modified by electric-dipole excitation of the magnetic electrons, was advanced to explain far-infrared absorption. A variant is to replace the virtual electronic excitation by a virtual lattice distortion that modifies the magnetic exchange.\textsuperscript{4} The intensities of such transitions can be calculated by writing effective operators for absorption or Raman scattering in terms of the spin operators.\textsuperscript{5} This theory is considered generally to give good account of inelastic light scattering and optical absorption. For an isotropic system the effective operator conserves total spin and what is commonly called the “Fleury-Loudon” theory is used to analyse the spectroscopy of spin conserving transitions.

Optical techniques are now well established as probes of magnetic excitations, whether it be by Raman scattering, i.e. inelastic scattering of optical frequencies, electron spin resonance (ESR), i.e. resonant absorption of electromagnetic radiation with sweeping magnetic field, or by transmission measurements of infrared radiation. The techniques have been further enhanced by the increasing flexibility of light sources and detectors in the far-infrared region that is useful to much of magnetism. ESR studies using sources derived from far-infrared lasers rather than the traditional cavities are now available up to THz frequencies and may be made in large static or pulsed magnetic fields.\textsuperscript{6} Transmission studies in the far infrared range have the advantage of allowing for measurement in zero external magnetic field. While restricted to small momentum transfer, $q \approx 0$, compared to neutron inelastic scattering, the optical techniques have the advantage of much higher frequency resolution. The possibility of polarising the electromagnetic radiation means different transition mechanisms may be distinguished.

Optical measurements are particularly useful for precise measurements of the spin gap properties in strongly correlated systems and spin-liquid systems with magnetic singlet ground states. Because of the frequencies now available, one can apply an electromagnetic source with sufficient energy to excite the first triplet $S_{\text{tot}} = 1$ excited state from the singlet $S_{\text{tot}} = 0$ ground state. Many systems of interest are highly isotropic with respect to spin rotations and transitions between the singlet $S_{\text{tot}} = 0$ ground state of the spin-liquid to the first triplet $S_{\text{tot}} = 1$ excited state would be forbidden by symmetry in the isotropic limit. Even the weaker magnetic-dipole coupling should give zero intensity as the ground state is a spin singlet. One would then expect to see the excited singlets, i.e. two magnon states only. Nonetheless the “forbidden” transitions to the single magnon states have been observed in many spin-liquid, ranging from the $S=1/2$ quasi-one-dimensional systems CuGeO\textsubscript{3}\textsuperscript{7,8,9,10,11,12,13,14} and Na\textsubscript{2}V\textsubscript{2}O\textsubscript{5}\textsuperscript{15,16}, to 2d system such as SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2}\textsuperscript{17,18} and to the spin-1 chain compound, NENP\textsuperscript{19}. Despite detailed experiments, no clear understanding of the mechanism of these transitions has emerged. It is clear that spin-orbit coupling, that breaks the conservation of total spin, must be included as it is then possible \textit{a priori} to have a transition to a one-magnon state. As mentioned, the photon can couple to the spin degrees of freedom in different ways, via direct magnetic dipole transitions or indirect electric dipole transitions with spin-phonon or spin-orbit couplings. As one of the purposes of performing high resolution spectroscopy is to resolve the weak anisotropies, it is important to distinguish between these mechanisms, i.e. to find the one which gives the strongest absorption. As in the original studies this is done by establishing, and then verifying experimentally, selection rules. For one-magnon absorption, previous estimations favored a
purely electric dipole transition for NENP. In the case of CuGeO$_3$ the suggestion that a staggered field would give rise to a magnetic dipole transition has been ruled out by the polarized experiments. Furthermore the first order corrections to the Hamiltonian in spin-orbit coupling lead to vanishing magnetic dipole intensity owing to a lattice selection rule. In the compound SrCu$_2$(BO$_3$)$_2$ it has been shown experimentally that varying the direction of the electric field of the wave (while keeping the magnetic field of the wave fixed) changes the intensity of the absorption, suggesting that the transition is electric-dipole in nature. One would also like to know which of the two electric dipole mechanisms applies, absorption involving solely the electronic degrees of freedom or with the lattice degrees of freedom. In the original theory of Elliott and Loudon of light scattering by magnons, the electric dipole coupling indeed leads to the creation of one-magnon excitations. Although such two photon processes are not forbidden in infrared absorption, they are much smaller in intensity since they involve the weak coupling to light to second order in perturbation theory. Alternatively in the presence of strong spin-orbit coupling, it is possible to have single photon coupling to spin excitations but as this is of second order in the spin-orbit coupling, we shall assume that the linear order will dominate for these materials, which are close to isotropic. In addition lattice symmetries such as centers of inversion between the magnetic ion may eliminate such terms, or at least reduce them further, if the inversion symmetry is slightly broken, as in SrCu$_2$(BO$_3$)$_2$.

In this paper we shall show that an effective operator of Dzyaloshinski-Moriya symmetry on the spin degrees of freedom,

$$ H_E = \sum_{i,a,\beta,\gamma} E^{\beta}(t) \mathbf{A}_{\beta\gamma}(a)(\mathbf{S}_i \times \mathbf{S}_{i+a})^\gamma $$

(1)

can be used to explain the polarized experiments of CuGeO$_3$ and SrCu$_2$(BO$_3$)$_2$. Here $E^{\beta}(t)$ is the component $\beta$ of the applied electromagnetic field at time $t$. The indices $i$ and $a$ define the lattice of magnetic bonds and the coefficients $\mathbf{A}_{\beta\gamma}$ will be made explicit in section II. They couple the component $\beta$ of the electric field with the component $\gamma$ of the vector product of the spin operators. An electric dipole operator (1) can arise from an electronic mechanism, as may be the case in NENP, but centers of inversion at the middle of the Cu-Cu bonds in CuGeO$_3$ and SrCu$_2$(BO$_3$)$_2$ would forbid generation of the operator from purely electronic processes. A lattice distortion may, however, break the inversion symmetry instantaneously, and allow terms of the form in (1). We therefore consider the phonons explicitly, and in section II we derive in detail the effective transition operator, which includes an anisotropic part of the form (1). The essential physical mechanism is that the electric field excites a virtual phonon state $S_{tot} = 0$ which is coupled to the $S_{tot} = 1$ state by an anisotropic spin-phonon coupling which originates in spin-orbit coupling. An explanation involving the modulation of static Dzyaloshinski-Moriya interactions has been put forward recently for the case of NaV$_2$O$_5$. In that compound, however, no polarized experiments are available and moreover, it is difficult to distinguish with a magnetic dipole transition which turns out not to be forbidden by a lattice selection rule. The mechanism we develop here is more general in that it does not require the presence of a static Dzyaloshinski-Moriya interaction. It only needs the instantaneous breaking of the inversion center which is assured by the appropriate phonons. This allows us to consider the operator on the strongest bonds irrespective of whether the bond lacks an inversion center or not. In section II we give the selection rules and the order of magnitude of such electric dipole transitions. We compare with the experiments in CuGeO$_3$ and SrCu$_2$(BO$_3$)$_2$ in section III.

II. EFFECTIVE MAGNETIC OPERATOR AND SELECTION RULES

In this section we show that the first-order spin-orbit correction to the spin-phonon coupling leads indeed to an effective magnetic operator for the optical transitions. We note that a phonon-assisted optical transition is the usual explanation for the occurrence of the singlet $S_{tot} = 0$ bound states of two magnon states in the spectrum of the high Tc’s cuprates. The spin-orbit correction should then lead to transition to $S_{tot} = 1$ states.

We start with a magnetic Hamiltonian for a chain or a layer of Cu atoms, for instance, that can be motivated by the usual super-exchange arguments:

$$ H = \sum_{i \sigma} \mathbf{S}_i \mathbf{J}(\{ \mathbf{u}_{id} \}) \mathbf{S}_{i+a} + H_{ph} - \mathbf{E}.\mathbf{P}_{ph} $$

(2)

where $\mathbf{S}_i$ is a spin operator, $\mathbf{u}_{id}$ is the displacement vector of the ion $d$ in the unit-cell $i$, $H_{ph}$ is the phonon Hamiltonian which takes into account the kinetic part of the ions and the spring constants, $\mathbf{P}_{ph}$ is the electric dipole of the ions and $\mathbf{E}$ is the external electric field. The magnetic couplings, $\mathbf{J}(\{ \mathbf{u}_{id} \})$, can be expanded to first order in the ion displacements. Including the first order in spin-orbit coupling, there is an extra term of Dzyaloshinski-Moriya symmetry:

$$ H_{sp} = \sum_{i \sigma \alpha \beta} g_d^{\alpha \beta} \mathbf{u}_{id} \mathbf{S}_i \mathbf{S}_{i+a} + d_d^{\alpha \beta} \mathbf{u}_{id} \mathbf{S}_i \times \mathbf{S}_{i+a} $$.  

(3)

where $g_d^{\alpha \beta}$ is the partial derivative of the diagonal part of $\mathbf{J}(\{ \mathbf{u}_{id} \})$ with respect to $\mathbf{u}_{id}$ (it depends on the bond $i, a$ but we will not write it explicitly in the following). The origin of $d_d^{\alpha \beta}$ is explained below. This is indeed a general form for the spin-phonon coupling and there is no restriction to be added on the grounds of symmetry. The static Dzyaloshinski-Moriya interaction is forbidden when there
is an inversion center at the middle of the bond. If the set of displacements $u_{id}$ is such as to remove the inversion center (which is the general case) then such an interaction takes place. For example if we take the two symmetric ninety degrees super-exchange paths Cu-O-Cu, there is a center of inversion and there is an interference between the two paths that leads to no Dzyaloshinski-Moriya interaction. Suppose now that the two oxygens move upwards. Because the hopping of the electrons is much faster than the typical phonon frequency, the electrons see a frozen distorted lattice on that time scale. The interference therefore does not occur anymore and there is an effective Dzyaloshinski-Moriya interaction in the displacements in the first order. This is the origin of the second term of (3) which involves a tensor $d^{\alpha\beta}_{d}$ since the displacements in one direction, $\alpha$, generally produce a Dzyaloshinski-Moriya vector in another direction, $\beta$. Strictly speaking, $d^{\alpha\beta}_{d}$ also depends upon the bond $i$, $\alpha$, but we do not write it explicitly. Note that this term is derived in a super-exchange approach by taking into account the spin-orbit coupling in first-order in perturbation theory in the lines of the original Moriya's article.27 We shall refer to it as a dynamical Dzyaloshinski-Moriya interaction in the following.

The transition probability is then given at zero temperature by the "golden rule":

$$I(\omega) = | \langle f | E, P_{ph} | 0 \rangle |^2 \delta(\omega - \omega_f)$$

(4)

where $\omega_f$ is the energy of the excitation, typically the one-magnon energy. At first order in $H_{sp}$ in perturbation theory the matrix element is written in terms of a sum over an excited states:

$$\langle f | E, P_{ph} | 0 \rangle = \sum_{n} \frac{\langle f | E, P_{ph} | n \rangle \langle n | H_{sp} | 0' \rangle}{\omega_0 - \omega_n} + \sum_{n} \frac{\langle f' | H_{sp} | n \rangle \langle n | E, P_{ph} | 0' \rangle}{\omega_f - \omega_n}$$

(5)

The intermediate states that contribute to the sum over $n$ contain one phonon (whereas the initial and final states we are interested in do not contain any phonon). The partial phonon matrix elements are calculated out, but we keep the general form for the magnetic states at this stage. In other words the phonons are integrated out and we end up with an effective matrix element acting between different magnetic states:

$$\langle f | E, P_{ph} | 0 \rangle = \langle f' | \sum_{\alpha} \gamma S_i, S_{i+a} + \delta (S_i \times S_{i+a}) | 0' \rangle$$

$$\gamma = \sum_{s} \frac{\Omega_s}{\omega_f - \Omega_s^*} g_s(D_s, E)$$

(8)

$$\delta = \sum_{s} \frac{\Omega_s}{\omega_f^2 - \Omega_s^2} d_s(D_s, E)$$

(9)

where $D_s = \sum_{d} q_d \lambda_{d,0} = 0$ is the amplitude of the instantaneous electric dipole of the unit cell due to the phonon mode $s$ with energy $\Omega_s = \Omega_{q=0,s}$. The final magnetic state has an energy $\omega_f$. $g_s = \sum_{\alpha} g_{d,\alpha} \gamma_{d,\alpha}^s$ is the amplitude of the variation of the magnetic exchange energy due the atomic distortions of the phonon $s$ ($\lambda_{d,\alpha}^s$ is the amplitude of the motion of the atom $d$, in the direction $\alpha$ due to the phonon $s$ at $q = 0$). Similarly, $d_s = \sum_{d} q_d \lambda_{d,0}^s$ is the amplitude of the instantaneous Dzyaloshinski-Moriya vector due to the phonon $s$. The resulting $\gamma$ and $\delta$ depend on the bond considered. They would usually couple the nearest neighbors, but could be introduced for neighbors at larger distances if such super-exchange processes were likely to take place. They can be introduced on the basis of the symmetry which is usually reduced with respect to the crystal symmetry by the presence of the external electric field. Thus we have written an effective operator announced in eq. (4) with $A_{d,\gamma} = \delta \delta^\gamma_{d}$. The selection rules are:

- $g_s \neq 0$: The distortion of the unit cell due to the phonon $s$ modulates the magnetic exchange between the spins. The transition at $\Delta S_{tot} = 0$ is allowed.

- $d_s \neq 0$: It implies that the distortion of the unit cell due to the phonon $s$ must break instantaneously the symmetry by inversion at the middle of the bond; so that to allow an instantaneous Dzyaloshinski-Moriya interaction which amplitude $s$ is given by $d_s$. The transitions between states that differ by the spin, $\Delta S_{tot} = 1$, are allowed and have an intensity $\sim \delta^2$.

Suppose that there is only one phonon mode $s$ which gives a major contribution to the sum. In addition, we know that this active phonon mode will appear in the infrared spectrum at the energy $\Omega_{q=0,s}$, with an intensity given by $I_{ph,s} = (D_s, E)^2$. We can therefore rewrite the intensity of the $\Delta S_{tot} = 1$ line as:

$$I_c = \frac{1}{2} \frac{\Omega_s d_s}{\omega_f^2 - \Omega_s^2} \gamma^2 I_{ph,s}$$

(10)

We denote by $E$ the order of magnitude of the variation of the magnetic exchange energy due to the phonon and following Moriya we estimate $d_s \sim (\Delta q/E)$. That gives:

$$I_c \sim \left( \frac{\Delta q}{g} \right)^2 \left[ \frac{\Omega_s E}{\omega_f^2 - \Omega_s^2} \right]^2 I_{ph,s}$$

(11)
This expression gives the intensity of such a process compared to the intensity of the optically active phonon. It is reduced by two factors: the spin-orbit coupling (in the cuprate materials, \( \Delta g/g \) can be 0.1) and the ratio of the energy modulation of the magnetic exchange due to the phonon by roughly the energy of the same phonon. The latter is difficult to estimate: in CuGeO\(_3\), the first optical phonons have \( \Omega \sim 10\text{meV} \), and the modulation can be as large as \( E \sim 1\text{meV} \). That gives \( I_e \sim 10^{-4} I_{ph} \).

Another way to compare with is to consider that singlet excited states, as for example the \( S = 0 \) bound-state below the continuum in CuGeO\(_3\), appear in the optical spectrum due to the isotropic spin-phonon coupling (the \( \gamma \) term). We denote their intensity by \( I_e^{\text{singlet}} \). Then we have: \( I_e^{\text{triplet}} \sim \left( \frac{\Delta g}{g} \right)^2 I_e^{\text{singlet}} \). It means that if the singlet bound-state appears in the optical spectrum with an intensity \( I_e^{\text{singlet}} \) due to the isotropic spin-phonon coupling, the triplet states should also appear with an intensity which is roughly 100 times smaller, if Moriya’s estimate applies.

**Effect of a magnetic field.** We consider a basic triplet excitation here. A magnetic field lifts the degeneracy of the triplet into three branches. When \( \mathbf{H} \parallel \delta \ (||z) \), \( S^z \) is a good quantum number and the transition should satisfy \( \Delta S^z = 0 \). Therefore, only the mode \( S^z = 0 \) could be observed and its intensity does not depend on the strength of the field. By contrast, when the magnetic field is perpendicular to \( \delta \), the wave-function is a superposition of wave-functions with different \( S^z \):

\[
\Psi^{\pm'} = \frac{1}{\sqrt{2}} [1,0] + \frac{H_{||}}{\sqrt{2} |H_{||}|} [1,1] + \frac{H_{\perp}}{\sqrt{2} |H_{\perp}|} [1,-1]
\]

\( \Psi^0' = \frac{1}{\sqrt{2}} \left( \frac{H_{\perp}}{|H_{\perp}|} [1,1] - \frac{H_{||}}{|H_{||}|} [1,-1] \right) \) \hspace{1cm} (12)

where the vector notation stands for \([S, S^z] \). The transition is allowed to the states \( \Psi^{\pm'} \) with quantum numbers \( S^z = \pm 1 \) and the mode which energy does not depend on the field has no intensity. The magnetic field dependence is therefore very different from what is expected for magnetic dipole transitions.\(^{22}\) This is basically because the electric field conserves the \( S^z \) quantum number. As we have just seen, however, in transverse magnetic field, \( S^z \) is no longer conserved and the magnetic field-dependent branches may appear in the optical spectrum. They do indeed appear in CuGeO\(_3\)\(^{35}\).

We now compare the intensities of the magnetic dipole transitions with those of the electric dipole transitions that we have made explicit here. To make such a comparison, we consider the following two models that give intensity to the optical transitions. First a purely magnetic model and magnetic dipole transitions. In order to have an intensity, we need to add a static magnetic anisotropy, such as a Dzyaloshinski-Moriya interaction or an anisotropy in the \( g \) factor, which are both first order in the spin-orbit coupling, so that in the most favourable case (when no lattice selection rule forbids it), the matrix element is of order \( \sim \Delta g/g \) at best. In the second model, we consider an isotropic magnetic model, but we add the anisotropic spin-phonon coupling that we have considered above. The intensities of the transitions of the two models are given by:

\[
I_M = |\langle f | \mu_B \mathbf{h} S_{tot} | 0 \rangle|^2 \sim |\mu_B h|^2 \left( \frac{\Delta g}{g} \right)^2
\]

\[
I_E = |\langle f | \mathbf{D} \cdot \mathbf{E} | 0 \rangle|^2 \sim \left( \frac{\Delta g}{g} \right)^2 \left( \frac{\Omega E}{\omega_f - \Omega_s} \right)^2 (\mathbf{D} \cdot \mathbf{D})
\]

So that the ratio is:

\[
\frac{I_E}{I_M} \sim \left( \frac{\Omega E}{\omega_f - \Omega_s} \right)^2 \sim 40
\]

with \( M_{Cu} = 63g/\text{mol} \) (\( M_{at} \sim 10^{-25} \text{kg} \)), \( \Omega = 10\text{meV} \), we find \( \lambda \sim 0.1\text{A} \). \( g \mu_B = 120\mu\text{eV/T} \). We take \( \omega = 5\text{meV} \) for the energy of the magnetic mode and \( g = 2\text{meV} \) for the spin-phonon coupling. This estimation has to be taken with a pinch of salt because of the crude order of magnitude given above, but it shows that there is no particular reason to not consider the electric dipole transition due to dynamical Dzyaloshinski-Moriya interaction.

**III. APPLICATION TO CuGeO\(_3\) AND SrCu\(_2\)(BO\(_3\))\(_2\).**

We compare the selection rules derived above with the experimental observation in CuGeO\(_3\). Experimentally, the absorption has been observed in the configuration \( \mathbf{E} \perp c \) but an extinction has been reported for \( \mathbf{E} \parallel c \) even in the presence of a magnetic field.`
FIG. 1: Three examples of distortions of the Cu$_2$O$_2$ cluster with associated Dzyaloshinski-Moriya vectors. On the left, the motion along the $y$-axis creates a Dzyaloshinski-Moriya interaction whose vector is along $z$ (the mirror plane Cu$_2$O$_2$ and the one perpendicular which has the O(2) atoms); on the middle, the atoms move out of the plane and the Dzyaloshinski-Moriya vector is along $y$ (mirror plane $xz$ passing through the bond Cu–Cu); on the right, these distortions break the inversion center at the middle of the Cu–Cu bond. However, the two perpendicular mirror planes $xy$ and $xz$ imply that the Dzyaloshinski-Moriya interaction actually vanishes. For CuGeO$_3$, the $z$-axis is the $c$-axis and the $xy$ plane is the plane of the CuO$_2$ chains.

We now consider the electric dipole transitions in SrCu$_2$(BO$_3$)$_2$ in greater detail. The obvious advantage of this compound is that, neglecting anisotropies, it is described by the Shra-try-Sutherland Hamiltonian that possesses an exactly known ground state as a product of local singlets. Optical transitions have been observed between this ground state and each of the zero-field three-split triplet states (see Fig. 2) that have been described previously. The probability of a transition between the ground state $\Psi_0$ and an excited state $f$ is given by:

$$
(f|\sum_{nn} \gamma S_i S_j + \delta_{ij}(S_i \times S_j)|\Psi_0)
$$

(18)

We have restricted the operator $H_E$ to the nearest neighbor spins (nn) in order to find the largest effect. The first part of it does not change the total spin but may generate transitions to the first excited states if the system has some anisotropy. We have considered previously the existence of a Dzyaloshinski-Moriya interaction whose vector is perpendicular to the plane. We have shown that such first-order anisotropy does not give intensity within the assumption of magnetic dipole transitions. Here we start by considering the electric dipole transitions generated by the first part of the operator and in presence of the static Dzyaloshinski-Moriya interaction. Using a symmetry argument we show that this part actually vanishes.

FIG. 2: Excitation spectrum in SrCu$_2$(BO$_3$)$_2$ for two directions of the external magnetic field (from Ref. 33). Definitions of the intensities of the optical transitions are also given.
allows observation of the middle state, but not the lower one.\textsuperscript{15}

We now show that these observations are compatible with the dynamical Dzyaloshinski-Moriya interaction which leads to the second part of the effective operator \textsuperscript{1}. To explain these results we need to find the particular pattern of dynamical Dzyaloshinski-Moriya vectors and then the \( \delta_{ij} \). That crucially depends on the direction of the electric field of the wave, according to eq. \textsuperscript{19}. In the following, we will determine the \( \delta_{ij} \) but we restrict them to nearest neighbor interactions.

**Configuration** \( \mathbf{E}(t) \parallel (ab) \). Let us consider first the case of a wave-vector of the electromagnetic wave parallel to the \( c \)-axis, then the electric field lies in the \( ab \) plane. According to the first selection rule (i), only the virtual phonons which carry an electric dipole \( D_s \parallel (ab) \) may contribute to the sum \textsuperscript{19}. We basically assume that the main displacements of the atoms in such a virtual phonon mode are confined into the \( (ab) \) plane. We make the assumption that the main components of \( \lambda_{ds} \) are parallel to the electric field, so that we should be able to find the main components of the Dzyaloshinski-Moriya vectors \( \delta_{ij,s} \) (eq. \textsuperscript{19}). To estimate them (and then \( \delta_{ij} \)), we fix the atoms \( d \) at the distorted positions \( \lambda_{ds} \), and we then apply the Moriya’s rules which give the constraints on the Dzyaloshinski-Moriya vectors. In this case, the plane remains instantaneously an approximate mirror plane for the crystal structure. Subsequently, the instantaneous \( d \)-vector between the spins, generated by the distortions, should be perpendicular to this plane (parallel to the \( c \)-axis). The effective operator is therefore written:

\[
H_{E||(ab)} = \sum_{nn,A} \delta_{ij}^A (\mathbf{S}_i \times \mathbf{S}_j)^2 + \sum_{nn,B} \delta_{ij}^B (\mathbf{S}_i \times \mathbf{S}_j)\,\text{(19)}
\]

where \( z \) is here again the \( c \)-axis. We have introduced two different \( \delta_{ij}^A,B \) to take into account the existence of two dimers per unit-cell. Taking the same would not change the argument. In the following we take the notation \( \delta_{ij}^2 = [(\delta_{ij}^A)^2 + (\delta_{ij}^B)^2]/2 \). The operator \textsuperscript{19} does not break the symmetry by rotation around the \( c \)-axis. A transition to the \( S^2 = \pm 1 \) when the external magnetic field is parallel to the \( c \)-axis is still forbidden. Only the \( S^2 = 0 \) triplet mode (at the middle of the others\textsuperscript{33}) is allowed to appear in the spectrum (this is in agreement with the general symmetry argument given above since the electric field breaks the symmetry by mirror plane). This is in agreement with the experimental result at zero-field.\textsuperscript{33} We further predict that a magnetic field parallel to the \( c \)-axis does not change the picture and gives no intensity in the other branches. We can give an estimation of the intensity assuming an approximate wave-function for the excited state that we take from the strong dimerization limit. In this approximation, the excitation with \( S^2 = 0 \) is a purely local triplet on the dimer A or B. This gives an intensity:

\[
I_E(H_q) = |\langle \Psi^{A,0}_q | H_E | \Psi_0 \rangle|^2 + |\langle \Psi^{B,0}_q | H_E | \Psi_0 \rangle|^2 = \delta_{20}^2\Omega
\]

\[
I_E(H_0) = 0 \quad \text{(21)}
\]

We now consider the effect of a transverse magnetic field \( (H \perp c) \) on the intensities. A transverse magnetic field splits the modes into three branches (figure \textsuperscript{2} left). To evaluate the intensity of each branch, we first calculate the excited states in the approximation used above, taking into account the static Dzyaloshinski-Moriya interaction which is responsible for the zero-field splitting. Note that the other in-plane components do not play any role in the triplet spectrum at \( q = 0 \) so that only the perpendicular component appear in the following.

The eigenvalues are in fact twice degenerate. The eigenvectors are denoted by \( \psi^{(\pm,0)}_q \) and \( \psi^{(\pm,0)^T}_q \) with energies \( E^{(\pm,0)}_q \). We then calculate the matrix elements as a function of the transverse magnetic field:

\[
I_{E||(ab)}^{(\pm,0)}(H_L) \equiv |\langle \psi^{(\pm,0)}_q | H_E | \Psi_0 \rangle|^2 + |\langle \psi^{(\pm,0)^T}_q | H_E | \Psi_0 \rangle|^2 \quad \text{(22)}
\]

We find:

\[
I_{E}^{(0)}(H_L) = \frac{\delta_{zz}^2}{2} \frac{1}{1 + \hbar^2} \quad \text{(23)}
\]

\[
I_{E}^{(\pm)}(H_L) = \frac{\delta_{zz}^2}{4} \frac{\hbar^2}{1 + \hbar^2} \quad \text{(24)}
\]

where \( \hbar = g\mu_B H_L/2D \) is the transverse magnetic field in the units of the static Dzyaloshinski-Moriya interaction. A transverse field transfers intensity into the lower and upper modes. The two curves given by \( I_{E}^{(0)}(H_L) \) and \( I_{E}^{(\pm)}(H_L) \) in figure \textsuperscript{3} together with the experimental results of Ref. \textsuperscript{18}. We used the non-renormalized value of \( D = 0.09 \text{meV} \) extracted from the energy spectrum\textsuperscript{33} (all the calculations we performed here are in the limit \( J'/J \to 0 \), so that we use the value of \( D \) we would have extracted from such a calculation and not the renormalized value). Note that if we take \( I_{E}^{(0)}(H_L) \) and \( I_{E}^{(\pm)}(H_L) \) for instance, they cross at a given field \( H_L = 2\sqrt{2}D/(g\mu_B) \sim 2.1 T \), which is in good agreement with the crossing of the fitted intensities in the original experimental article \( (H_L = 2.37 T)\textsuperscript{18} \). This is most probably coincidental since we are using the wave-functions that are not renormalized by the interaction \( J' \).

**Configuration** \( \mathbf{E}(t) \parallel c \). We consider the case of an electric field perpendicular to the plane \( \mathbf{E}(t) \parallel c \). Let us suppose that the atoms move out of plane. According to the figure\textsuperscript{11} the dynamical Dzyaloshinski-Moriya interaction would be in plane and perpendicular to the Cu–Cu bond. The dimers are, however, perpendicular to one another. Therefore the dynamical Dzyaloshinski-Moriya vectors of adjacent dimers should be perpendicular as well. The effective electric operator is:
FIG. 3: Configuration $E(t) \parallel (ab)$, $H \parallel (ab)$. Intensity of the optical transitions from the ground state to the first split triplet state in SrCu$_2$(BO$_3$)$_2$ in the electric dipole approximation ($\delta \parallel c$). $(+)$ $+$ $(-)$ is the sum of the intensity of the upper and lower mode and $0$ is the middle mode. The theoretical curves are given by eqs. (23) and (24). There are no fitting parameters except an overall amplitude. The experimental data are from Ref. 13. Note the intensity of the $(+)+(-)$ mode is here twice as large as shown in the original experimental paper.  

$$H_E = \sum_{n,n,A} \delta_n (S_i \times S_j) + \sum_{n,n,A} \delta'_n (S_i \times S_j)$$  (25)

where $\delta$ (respectively $\delta'$) is perpendicular to the Cu-Cu bond of the dimers $A$ (resp. $B$), so parallel to $y$ (resp. $x$). Note that we take the same $|\delta|$ and $|\delta'|$. Strictly speaking there is no reason why they should be the same but taking into account the special direction of the field we can reasonably assume that the motions of the atoms which belong to adjacent dimers are similar at least for the low-energy phonons. Let us apply this operator on the ground state which is approximately a product of singlet states on the dimers (we thus neglect the effect the static Dzyaloshinski-Moriya interactions have on the ground state which would give small corrections to the result).

$$H_E|\Psi_0\rangle = \frac{\delta}{2 \sqrt{2}} \left( \Psi^{+,S_z=+1}_{q=0} + i \Psi^{+,\bar{S}_z=-1}_{q=0} \right)$$

$$- \frac{\delta}{2 \sqrt{2}} \left( \Psi^{+,S_z=1}_{q=0} - i \Psi^{+,\bar{S}_z=-1}_{q=0} \right)$$

$$= \frac{\delta}{2} \left( \Psi^{+,S_z=+1}_{q=0} - \Psi^{-,\bar{S}_z=-1}_{q=0} \right)$$  (26)

Note that $\Psi^{+,S_z=+1}_{q=0}$ and $\Psi^{-,\bar{S}_z=-1}_{q=0}$ are both eigenstates of the Hamiltonian restricted to triplet states with the same energy $J + 2D$. Depending on the sign of $D$, therefore, only the upper mode or the lower mode should appear in the spectrum. Experimentally, the upper mode has been found in such a polarized configuration so that we conclude that $D > 0$. Only a detailed super-exchange calculation of $D$ would be able to infer it. The matrix elements giving the intensities are given by:

$$I_{E||c}(H_{\parallel}) \equiv \langle \Psi^{+,S_z=+1}_{q=0} | H_E | \Psi_0 \rangle^2 = \frac{\delta^2}{4}$$  (28)

$$I_{E||c}(H_{\perp}) \equiv \langle \Psi^{-,S_z=-1}_{q=0} | H_E | \Psi_0 \rangle^2 = \frac{\delta^2}{4}$$  (29)

In zero external magnetic field, the two final states are degenerate so that the total intensity of the optical transitions is the sum of the two, i.e. $\delta^2/2$. In a magnetic field parallel to the $c$-axis ($z$-axis), the upper mode splits into two branches with equal intensity $\delta^2/4$.

Furthermore, we calculate the intensities as a function of a transverse magnetic field. The excited states $\Psi^{(\pm,0)}_{q=0}$ and $\Psi^{(\mp,0)}_{q=0}$ are twice degenerate, so we calculate:

$$I^{(\pm,0)}_{E||c}(H_{\parallel}) = \langle \Psi^{(\pm,0)}_{q=0} | H_E | \Psi_0 \rangle^2 + \langle \Psi^{(\mp,0)}_{q=0} | H_E | \Psi_0 \rangle^2$$  (30)

We find the following expressions for the intensity of the upper $(+)$, lower $(-)$ and middle $0$ states:

$$I_{E||c}(H_{\parallel}) = \frac{\delta^2}{4} \frac{h^2}{[1 + h^2]^2}$$  (31)

$$I_{E||c}(H_{\perp}) = \frac{\delta^2}{4} \frac{h^2}{1 + h^2}$$  (32)

where $h = g\mu_B H_{\perp}/2D$. The corresponding curves are given in the figure. Note that the crossing between $I_E^{(\pm,0)}$ and $I_E^{(\mp,0)}$ occurs at $g\mu_B H_{\perp} = 4\sqrt{2}D$, therefore at a field two times larger than in the configuration $E \parallel (ab)$. The agreement with the experiment is very good since such a balance of the intensities has been observed. The lower mode does not actually appears in the spectrum experimentally and this is compatible with the low intensity we found. If we take the non-renormalized value of $D = 0.09$meV, the crossing of the intensities occur at $H_{\perp} = 4.6T$ which is in good agreement with the experimental value ($\sim 6T$), as well as the overall behavior of the curves.

IV. CONCLUSIONS

In this paper, we have considered optical transitions with emission of one magnetic excitation, $\Delta S_{\text{tot}} = 1$. We give a mechanism in terms of phonon-assisted transitions in which a virtual phonon is involved. The selection rules of such processes were made explicit: in brief we need a coupling to an infrared active phonon that breaks, at least instantaneously, the symmetry of inversion between magnetically coupled ions. The intensity of such a process has been estimated and we argue that it should be larger than a magnetic-dipole transition, at least in systems in which spin-phonon couplings are appreciable. It
provides an alternative to purely electronic transitions that are not allowed when an inversion center is present.

We note that we have considered uniquely the consequences of phonon assisted optical transitions in the context of single-phonon experiments, i.e. ESR and absorption. The same mechanism can lead to processes in Raman scattering allowing single magnon creation, with similar selection rules concerning centers of inversion in the lattice. The effective operators will have similar symmetry but are not identical, involving the polarisations of both incoming and outgoing photons. Experimentally there are extra contributions linear in both spin operators and spin-orbit couplings that are not present in the single photon case. While for the spectroscopy of single magnons in the materials studied, Raman scattering should be useful, single photon experiments may permit more direct comparison with microscopic estimates of intensities.

In the final section we have studied the two specific case of CuGeO$_3$ and SrCu$_2$(BO$_3$)$_2$ for which polarised experiments are available. We have shown that predictions of the phonon-assisted theory agrees well both with observed extinctions and also, for the case of SrCu$_2$(BO$_3$)$_2$ where detailed results are available, with the dependence of intensities as function of the external magnetic field. Further optical data should be analysed in terms of an effective operator of the Dzyaloshinski-Moriya symmetry for the matrix elements in the electric dipole approximation. Potentially such optical experiments can provide a means of probing microscopically the spin-phonon coupling which may be relevant to other experiments, for example neutron inelastic microscopically the spin-phonon coupling which may be relevant to other experiments, or of looking at the local chiralities.

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Note that there is a small buckling in the crystal structure of SrCu$_2$(BO$_3$)$_2$ in the low temperature phase that actually removes the inversion center. Nevertheless the buckling is very small. Therefore while the corresponding operator would not vanish exactly, it will be strongly reduced. The consequences on static Dzyaloshinski-Moriya interactions have been discussed in Ref. 25. Recently effects of the extra components of the Dzyaloshinski-Moriya generated on the magnetic-dipole induced transitions have been considered in S. Miyashita, A. Ogasahra J. Phys. Soc. Japan 72, 2350 (2003).

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