Theory of phonon-assisted forbidden optical transitions in spin-gap systems

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(Received 21 October 2003; revised manuscript received 22 January 2004; published 9 July 2004)

We consider the absorption of light with emission of one $S_{tot}=1$ 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 $CuGeO_3$ and $SrCu_2(BO_3)_2$.

DOI: 10.1103/PhysRevB.70.024404 PACS number(s): 75.10.−b, 78.30.−j

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.[1] Later it was pointed out[2,3] 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[4] 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[4] 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[5] to explain far-infrared absorption. A variant is to replace the virtual electronic excitation by a virtual lattice distortion that modifies the magnetic exchange.[6] The intensities of such transitions can be calculated by writing effective operators for absorption or Raman scattering in terms of the spin operators.[4,7] 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 analyze 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 terahertz frequencies and may be made in large static or pulsed magnetic fields.[8] 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 polarizing 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 $S_{tot}=1$ excited state from the singlet $S_{tot}=0$ ground state. Many systems of interest are highly isotropic with respect to spin rotations, and transitions between the singlet $S_{tot}=0$ ground state of the spin liquid and the first triplet $S_{tot}=1$ 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, $CuGeO_3$ (Refs. 9–14) and NaV_2O_5,[15,16] to 2D system such as $SrCu_2(BO_3)_2$ (Refs. 17 and 18) and to the spin-1 chain compound, NENP.[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 *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[4] 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.[20] In the case of $CuGeO_3$ the suggestion that a staggered field would give rise to a magnetic dipole-transition[21] has been ruled out by the polarized experiments.[11] Furthermore the first-order corrections to the Hamiltonian in spin-orbit coupling lead to vanishing magnetic-dipole intensity owing to a

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lattice selection rule.[22] 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.[18] 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.[2,4] 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[7,23] 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 $SrCu_2(BO_3)_2$.[24]

In this paper we shall show that an effective operator of Dzyaloshinski-Moriya symmetry[26,27] acting on the spin degrees of freedom,

$$H_E = \sum_{i,a,\beta,\gamma} \mathbf{E}^{\beta}(t)\mathbf{A}_{\beta\gamma}(a)(\mathbf{S}_i \times \mathbf{S}_{i+a})^{\gamma} \tag{1}$$

can be used to explain the polarized experiments of $CuGeO_3$ and $SrCu_2(BO_3)_2$. Here $\mathbf{E}^{\beta}(t)$ is the component β 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 Sec. II. They couple the component β of the electric field with the component γ 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,[20] but centers of inversion at the middle of the Cu-Cu bonds in $CuGeO_3$ and $SrCu_2(BO_3)_2$ (Ref. 24) 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 Eq. (1). We therefore consider the phonons explicitly, and in Sec. 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_2O_5.[28] 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.[22] 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 (1) on the strongest bonds irrespective of whether the bond lacks an inversion center or not. In Sec. II, we give the selection rules and the order of magnitude of such electric-dipole transitions. We compare the experiments in $CuGeO_3$ and $SrCu_2(BO_3)_2$ in Sec. 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.[6] 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 superexchange arguments

$$H = \sum_{iad} \mathbf{S}_i \mathbf{J}(\{\mathbf{u}_{id}\})\mathbf{S}_{i+a} + H_{ph} - \mathbf{E}\cdot\mathbf{P}_{ph}, \tag{2}$$

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 time-dependent 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,

$$H_{sp} = \sum_{iad\alpha\beta} g_d^{\alpha} u_{id}^{\alpha} \mathbf{S}_i \cdot \mathbf{S}_{i+a} + d_d^{\alpha\beta} u_{id}^{\alpha} (\mathbf{S}_i \times \mathbf{S}_{i+a})^{\beta}, \tag{3}$$

where g_d^{α} 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 $\mathbf{u}_{id}$ 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 90° superexchange 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 linear in the displacements in the first order. This is the origin of the second term of Eq. (3) which involves a tensor $d_d^{\alpha\beta}$ since the displacements in one direction, α, generally produce a Dzyaloshinski-Moriya vector in another direction, β. Strictly speaking, $d_d^{\alpha\beta}$ also depends upon the bond i,a, but we do not

write it explicitly. Note that this term is derived in a superexchange approach by taking into account the spin-orbit coupling in first order in perturbation theory in the lines of the original Moriya's paper.[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"

$$I(\omega) = |\langle f|\mathbf{E}\cdot\mathbf{P}_{ph}|0\rangle|^2 \delta(\omega-\omega_f), \tag{4}$$

$$\mathbf{P}_{ph} = \sum_{id} q_d \mathbf{u}_{id}, \tag{5}$$

where ω_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 the excited states

$$\langle f|\mathbf{E}\cdot\mathbf{P}_{ph}|0\rangle = \sum_n \frac{\langle f'|\mathbf{E}\cdot\mathbf{P}_{ph}|n\rangle\langle n|H_{sp}|0'\rangle}{\omega_0-\omega_n} + \sum_n \frac{\langle f'|H_{sp}|n\rangle\langle n|\mathbf{E}\cdot\mathbf{P}_{ph}|0'\rangle}{\omega_f-\omega_n}. \tag{6}$$

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

$$\langle f|\mathbf{E}\cdot\mathbf{P}_{ph}|0\rangle = \langle f'|\sum_{ia} \gamma\mathbf{S}_i\cdot\mathbf{S}_{i+a} + \boldsymbol{\delta}\cdot(\mathbf{S}_i\times\mathbf{S}_{i+a})|0'\rangle, \tag{7}$$

$$\gamma = \sum_s \frac{\Omega_s}{\omega_f^2-\Omega_s^2} g_s(\mathbf{D}_s\cdot\mathbf{E}), \tag{8}$$

$$\boldsymbol{\delta} = \sum_s \frac{\Omega_s}{\omega_f^2-\Omega_s^2} \mathbf{d}_s(\mathbf{D}_s\cdot\mathbf{E}), \tag{9}$$

where $\mathbf{D}_s=\Sigma_d q_d \boldsymbol{\lambda}_{dsq=0}$ 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 ω_f. $g_s=\Sigma_{d,\alpha} g_d^\alpha \lambda_{ds}^\alpha$ is the amplitude of the variation of the magnetic exchange energy due to the atomic distortions of the phonon s (λ_{ds}^α is the amplitude of the motion of the atom d, in the direction α due to the phonon s at $q=0$). Similarly, $d_s^\alpha = \Sigma_{\beta d} d_d^{\alpha\beta}\lambda_{ds}^\beta$ is the amplitude of the instantaneous Dzyaloshinski-Moriya vector due to the phonon s. The resulting γ and $\boldsymbol{\delta}$ depend on the bond considered. They would usually couple the nearest neighbors, but could be introduced for neighbors at larger distances if such superexchange 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. (1) with $\mathbf{A}_{\beta\gamma}=\partial\boldsymbol{\delta}^\gamma/\partial\mathbf{E}^\beta$.

The selection rules are as follows.

(i) $\mathbf{D}_s\cdot\mathbf{E}\neq 0$. The virtual phonon s creates distortions that carry an instantaneous electric dipole $\mathbf{D}_s$. In other words, the phonon s must be infrared active.

(ii) $g_s\neq 0$. 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.

$\mathbf{d}_s\neq 0$. 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 whose amplitude is given by $\mathbf{d}_s$. 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 $I_{ph,s}=(\mathbf{D}_s\cdot\mathbf{E})^2$. We can therefore rewrite the intensity of the $\Delta S_{tot}=1$ line as

$$I_e = \left[\frac{1}{2}\frac{\Omega_s\mathbf{d}_s}{\omega_f^2-\Omega_s^2}\right]^2 I_{ph,s}. \tag{10}$$

We denote by E the order of magnitude of the variation of the magnetic exchange energy due to the phonon and following Moriya,[27] we estimate $d_s\sim(\Delta g/g)E$. That gives

$$I_e \sim \left(\frac{\Delta g}{g}\right)^2\left[\frac{\Omega_s E}{\omega_f^2-\Omega_s^2}\right]^2 I_{ph,s}. \tag{11}$$

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 $\Omega\sim 10$ meV, and the modulation can be as large as $E\sim 1$ meV.[29] 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 γ term). We denote their intensity by $I_e^{singlet}$. Then we have: $I_e^{triplet}\sim(\Delta g/g)^2 I_e^{singlet}$. It means that if the singlet bound state appears in the optical spectrum with an intensity $I_e^{singlet}$ 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 $\mathbf{H}\|\boldsymbol{\delta}(\|z)$, 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 $\boldsymbol{\delta}$, the wave function is a superposition of wave functions with different S^z,

$$\Psi^{\pm\prime} = \frac{1}{\sqrt{2}}|1,0\rangle \pm \left(\frac{H_\perp}{2|H_\perp|}|1,1\rangle + \frac{H_\perp^*}{2|H_\perp|}|1,-1\rangle\right), \quad (12)$$

$$\Psi^{0\prime} = \frac{1}{\sqrt{2}}\left(\frac{H_\perp^*}{|H_\perp|}|1,-1\rangle - \frac{H_\perp}{|H_\perp|}|1,1\rangle\right), \quad (13)$$

where the vector notation stands for $|S,S^z\rangle$. The transition is allowed to the states $\Psi^{\pm\prime}$ with quantum numbers $S^\perp = \pm 1$ and the mode whose 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 $CuGeO_3$.[10]

Magnetic versus electric-dipole transitions

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 we consider 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 favorable case (when no lattice selection rule forbids it), the matrix element is of the 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

$$I_M = |\langle f|g\mu_B \mathbf{h}\cdot\mathbf{S}_{tot}|0\rangle|^2 \sim [g\mu_B h]^2\left(\frac{\Delta g}{g}\right)^2, \quad (14)$$

$$I_E = |\langle f|\mathbf{D}\cdot\mathbf{E}|0\rangle|^2 \sim \left(\frac{\Delta g}{g}\right)^2\left(\frac{\Omega_s E}{\omega_f^2-\Omega_s^2}\right)^2(\mathbf{D}_s\cdot\mathbf{E})^2. \quad (15)$$

So that the ratio is

$$\frac{I_E}{I_M} \sim \left(\frac{\mathbf{D}_s\cdot\mathbf{E}}{g\mu_B H}\right)^2\left(\frac{\Omega_s E}{\omega_f^2-\Omega_s^2}\right)^2, \quad (16)$$

where $E=cH$, c is the speed of light. D is given by $D\sim e\lambda$ where $\lambda\sim\sqrt{\hbar^2/M\Omega}$ is the amplitude of the motion of the ion and e is its charge.

$$\frac{I_E}{I_M} \sim \left(\frac{ec\lambda}{g\mu_B}\right)^2\left(\frac{\Omega E}{\omega_f^2-\Omega^2}\right)^2 \sim 40 \quad (17)$$

with $M_{Cu}=63$ g/mol ($M_{at}\sim 10^{-25}$ kg), $\Omega=10$ meV, we find $\lambda\sim 0.1$ Å, $g\mu_B=120$ μeV/T. We take $\omega=5$ meV for the energy of the magnetic mode and $g=2$ meV for the spin-phonon coupling. This estimation may not be absolutely accurate 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.

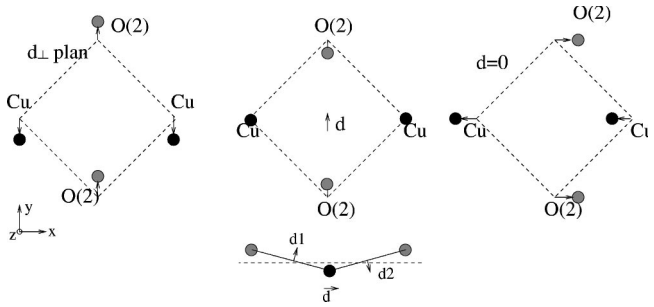

FIG. 1. Three examples of distortions of the Cu_2O_2 cluster with associated Dzyaloshinski-Moriya vectors. On the left, the motion along the y axis creates a Dzyaloshinski-Moriya interaction whose vector is along z [the mirror plane Cu_2O_2 and the one perpendicular which has the O(2) atoms]; on the 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 x axis is the c axis and the xy plane is the plane of the CuO_2 chains.

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 $\mathbf{E}\|c$,[11] even in the presence of a magnetic field.[14]

We have a natural interpretation of this fact: when $\mathbf{E}\|c$, the only contribution to $\boldsymbol{\delta}$ comes from the virtual phonons s that have $\mathbf{D}_s\|c$, or, in other words, the virtual phonons involved are those which are optically active in this configuration. The vector $\boldsymbol{\delta}$ is given by $\Sigma_\beta d_d^{\alpha\beta}\lambda^\beta_{ds,q=0}$ where $\lambda^\beta_{ds,q=0}$ are the displacements of the atoms, the same as those that appear at higher energy in the real phonon state s. In the configuration $\mathbf{E}\|c$, the atoms in the phonon state s roughly move along the c axis. In a crystal with many atoms per unit cell, this is not exactly true and the displacements will acquire other components (a full study of the phonons that have been theoretically predicted in Ref. 30 does not change the picture). Then, according to Fig. 1, the dynamical Dzyaloshinski-Moriya interaction is forbidden, $\mathbf{d}_s=0$, because of the mirror plane containing the atoms and the mirror plane perpendicular to the previous plane and containing the Cu atoms. Therefore, the intensity vanishes in this special configuration. In other configurations, however, there is no such symmetry arguments leading to a cancellation of the dynamical Dzyaloshinski-Moriya interaction, and an intensity is expected in agreement with the experiment performed in $CuGeO_3$.

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 Shastry-Sutherland[31] Hamiltonian that possesses an exactly known ground state as a product of local singlets.[32] Optical transitions have been observed between this ground state and each of the zero-field three-split triplet states[12,18]

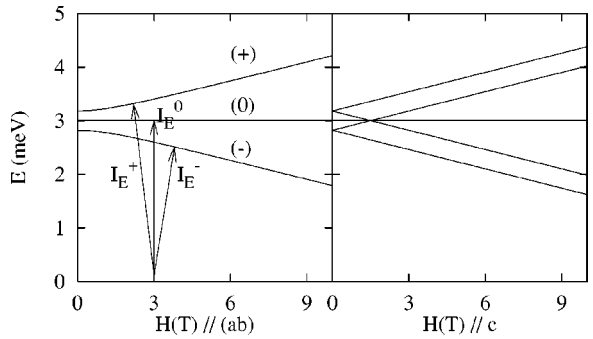

FIG. 2. Excitation spectrum in $SrCu_2(BO_3)_2$ for two directions of the external magnetic field (from Ref. 33). Definitions of the intensities of the optical transitions are also given.

(see Fig. 2) that have been described previously.[33] The probability of a transition between the ground state Ψ_0 and an excited state f is given by

$$\langle f|\sum_{nn} \gamma \mathbf{S}_i \cdot \mathbf{S}_j + \boldsymbol{\delta}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)|\Psi_0\rangle. \tag{18}$$

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.[33] 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 (18) and in presence of the static Dzyaloshinski-Moriya interaction. Using a symmetry argument we show that this part actually vanishes. S^z is a conserved quantity so that we only need to consider the matrix elements with an $S^z=0$ final state. The symmetry by the mirror plane perpendicular to the (ab) plane and passing through a dimer is a symmetry of the crystal. In this symmetry, the ground state and the operator $\Sigma_{nn}\gamma \mathbf{S}_i \cdot \mathbf{S}_j$ are both even. However, the triplet state $S^z=0$ adiabatically connected to the local triplet at $J'=0$ (the next-nearest-neighbor exchange) is odd. Then the matrix element vanishes. Additional spin anisotropy of the Dzyaloshinski-Moriya symmetry with extra in-plane components is present because of the small buckling of the crystal structure at low temperatures.[25] However, this (together with possible exchange anisotropies) would, in any case, respect the same mirror-plane symmetry. So the first term is not expected to give intensity, because of this special symmetry.

In $SrCu_2(BO_3)_2$, the transitions have been studied using polarized electromagnetic waves and exhibit very peculiar polarization properties: in the configuration $\mathbf{E}\|(ab)$, at zero field, only the state at 24.2 cm^{-1} [i.e., the $S^z=0$ state (the middle state)] appears in the spectrum, but an external in-plane magnetic field gives intensity in the two other modes (upper and lower modes).[18] Similarly when the magnetic field lies in the (ab) plane, only the upper state at 25.4 cm^{-1} (i.e., the $S^z=\pm 1$) appears at zero magnetic field while an in-plane magnetic field allows observation of the middle state, but not the lower one.[18]

We now show that these observations are compatible with the dynamical Dzyaloshinski-Moriya interaction which leads to the second part of the effective operator (1). To explain these results we need to find the particular pattern of *dynamical* Dzyaloshinski-Moriya vectors and then $\boldsymbol{\delta}_{ij}$. That crucially depends on the direction of the electric field of the wave, according to Eq. (9). In the following, we will determine $\boldsymbol{\delta}_{ij}$ but we restrict them to the nearest-neighbor interactions.

A. Configuration $\mathbf{E}(t)\|(ab)$

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 $D_s\|(ab)$ may contribute to the sum (9). 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 $\boldsymbol{\lambda}_{ds}$ are parallel to the electric field, so that we should be able to find the main components of the Dzyaloshinski-Moriya vectors $\mathbf{d}_{ij,s}$ [Eq. (9)]. To estimate them (and then $\boldsymbol{\delta}_{ij}$), we fix the atoms d at the distorted positions $\boldsymbol{\lambda}_{ds}$ 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

$$H_{E\|(ab)} = \sum_{nn,A} \delta_z^A (\mathbf{S}_i \times \mathbf{S}_j)^z + \sum_{nn,B} \delta_z^B (\mathbf{S}_i \times \mathbf{S}_j)^z, \tag{19}$$

where z is here again the c axis. We have introduced two different $\delta_z^{A,B}$ 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 $\delta_z^2=[(\delta_z^A)^2+(\delta_z^B)^2]/2$. The operator (19) does not break the symmetry by rotation around the c axis. A transition to the $S^z=\pm 1$ when the external magnetic field is parallel to the c axis is still forbidden. Only the $S^z=0$ triplet mode (at the middle of the others[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.[18] 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 $S^z=0$ is a purely local triplet on the dimer A or B. This gives intensities

$$I_E^0(H_\|) = |\langle \Psi_{q=0}^{A,0}|H_E|\Psi_0\rangle|^2 + |\langle \Psi_{q=0}^{B,0}|H_E|\Psi_0\rangle|^2 = \delta_z^2/2, \tag{20}$$

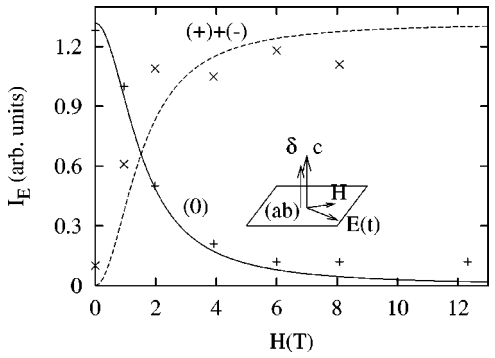

FIG. 3. Configuration $\mathbf{E}(t)\|(ab)\cdot\mathbf{H}\|(ab)$. Intensity of the optical transitions from the ground state to the first split triplet state in $SrCu_2(BO_3)_2$ in the electric-dipole approximation ($\boldsymbol{\delta}\|c$). $(+)+(-)$ is the sum of the intensity of the upper and lower 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. 18. Note the intensity of the $(+)+(-)$ mode is here twice as large as shown in the original experimental paper.[34].

$$I_E^{\pm}(H_{\|}) = 0. \tag{21}$$

We now consider the effect of a transverse magnetic field ($\mathbf{H}\perp c$) on the intensities. A transverse magnetic field splits the modes into three branches (Fig. 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 $q=0$,[25] so that only the perpendicular component appears in the following.

The eigenvalues are in fact twice degenerate. The eigenvectors are denoted by $\Psi_{q=0}^{(\pm,0)}$ and $\Psi_{q=0}^{(\pm,0)'}$ with energies $E_q^{(\pm,0)}$. We then calculate the matrix elements as a function of the transverse magnetic field

$$I_{E\|(ab)}^{(\pm,0)}(H_{\perp}) \equiv |\langle\Psi_{q=0}^{(\pm,0)}|H_E|\Psi_0\rangle|^2 + |\langle\Psi_{q=0}^{(\mp,0)\prime}|H_E|\Psi_0\rangle|^2. \tag{22}$$

We find

$$I_E^0(H_{\perp}) = \frac{\delta_z^2}{2}\frac{1}{1+h^2}, \tag{23}$$

$$I_E^{\pm}(H_{\perp}) = \frac{\delta_z^2}{4}\frac{h^2}{1+h^2}, \tag{24}$$

where $h=g\mu_B H_{\perp}/2D$ 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 $I_E^0(H_{\perp})$ and $I_E^+(H_{\perp})+I_E^-(H_{\perp})$ are shown in Fig. 3 together with the experimental results of Ref. 18. We have used the nonrenormalized value of $D=0.09$ meV extracted from the energy spectrum[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 $I_E^0(H_{\perp})$ and $I_E^+(H_{\perp})$ for instance, they cross at a given field $H_{\perp}=2\sqrt{2}D/(g\mu_B)\sim 2.1$ T, which is in good agreement with the crossing of the fitted intensities in the original experimental article ($H_{\perp}=2.3$ T).[18] This is most probably coincidental since we are using the wave functions that are not renormalized by the interaction J'.

B. Configuration $\mathbf{E}(t)\|c$

We consider the case of an electric field perpendicular to the plane $\mathbf{E}(t)\|c$. Let us suppose that the atoms move out of plane. According to Fig. 1, 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

$$H_{E\|c} = \sum_{nn,A} \boldsymbol{\delta}'\cdot(\mathbf{S}_i\times\mathbf{S}_j) + \sum_{nn,B} \boldsymbol{\delta}'\cdot(\mathbf{S}_i\times\mathbf{S}_j), \tag{25}$$

where δ (respectively δ') is perpendicular to the Cu-Cu bond of the dimers A (respectively B), so parallel to y (respectively 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)

$$H_{E\|c}|\Psi_0\rangle = \frac{\delta}{2\sqrt{2}}(\Psi_{q=0}^{A,S^z=+1} + i\Psi_{q=0}^{B,S^z=+1}) - \frac{\delta}{2\sqrt{2}}(\Psi_{q=0}^{A,S^z=-1} - i\Psi_{q=0}^{B,S^z=-1}) \tag{26}$$

$$= \frac{\delta}{2}(\Psi_{q=0}^{+,S^z=+1} - \Psi_{q=0}^{-,S^z=-1}). \tag{27}$$

Note that $\Psi_{q=0}^{+,S^z=+1}$ and $\Psi_{q=0}^{-,S^z=-1}$ 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,[18] so that we conclude that $D>0$. Only a detailed superexchange calculation of D would be able to infer it. The matrix elements giving the intensities are given by

$$I_{E\|c}^{+,+1}(H_{\|}) \equiv |\langle\Psi_{q=0}^{+,S^z=+1}|H_{E\|c}|\Psi_0\rangle|^2 = \delta^2/4, \tag{28}$$

$$I_{E\|c}^{-,-1}(H_{\|}) \equiv |\langle\Psi_{q=0}^{-,S^z=-1}|H_{E\|c}|\Psi_0\rangle|^2 = \delta^2/4. \tag{29}$$

In zero external magnetic field, the two final states are degenerate so that the total intensity of the optical transitions is

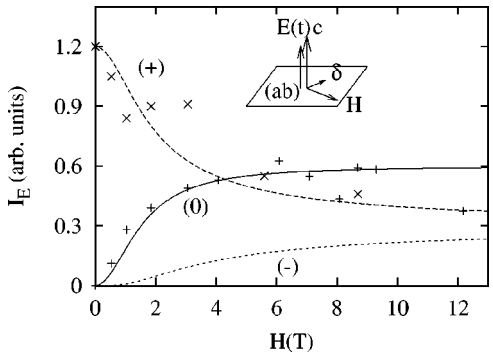

FIG. 4. Configuration $\mathbf{E}(t)\|c\cdot\mathbf{H}\|(ab)$. Intensity of the optical transitions from the ground state to the first split triplet state in $SrCu_2(BO_3)_2$ in the electric-dipole approximation ($\boldsymbol{\delta}\perp c$). (+), (−), and (0) are, respectively, the upper, lower, and middle mode. The theoretical curves are given by Eqs. (32) and (32). There are no fitting parameters except an overall amplitude. The experimental data are from Ref. 18.

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 $\Psi_{q=0}^{(\pm,0)}$ and $\Psi_{q=0}^{(\mp,0)\prime}$ are twice degenerate, so we calculate

$$I_{E\|c}^{(\pm,0)}(H_\perp) \equiv |\langle\Psi_{q=0}^{(\pm,0)}|H_E|\Psi_0\rangle|^2 + |\langle\Psi_{q=0}^{(\mp,0)\prime}|H_E|\Psi_0\rangle|^2. \tag{30}$$

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

$$I_{E\|c}^{\pm}(H_\perp) = \frac{\delta^2}{8}\frac{h^4}{[1+h^2][\pm\sqrt{1+h^2}-1]^2}, \tag{31}$$

$$I_{E\|c}^{0}(H_\perp) = \frac{\delta^2}{4}\frac{h^2}{1+h^2}, \tag{32}$$

where $h=g\mu_B H_\perp/2D$. The corresponding curves are given in Fig. 4. Note that the crossing between I_E^+ and I_E^0 occurs at $g\mu_B H_\perp = 4\sqrt{2}D$, therefore at a field two times larger than in the configuration $\mathbf{E}\|(ab)$. The agreement with the experiment is very good since such a balance of the intensities has been observed.[18] The lower mode does not actually appear in the spectrum experimentally and this is compatible with the low intensity we found. If we take the nonrenormalized value of $D=0.09$ meV, the crossing of the intensities occur at $H_\perp = 4.6$ T which is in good agreement with the experimental value ($\sim$6 T), as well as the overall behavior of the curves.

In this paper we have restricted ourselves to the intensities at zero temperature. Experimentally[18] the intensities decrease as the temperature is raised and above 10 K can no longer be detected. While a full treatment of temperature effects would involve thermal population factors of the phonons and all magnetic excitations, the primary cause of this extinction is most likely to be the thermal excitations of magnetic excitations. These excitations, which decrease the weight of the singlet ground state in the expression for the intensity, are of lower energy than the lowest optical phonons.

IV. CONCLUSIONS

In this paper, we have considered optical transitions with emission of one magnetic excitation, $\Delta S_{tot}=1$. 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 polarizations 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 polarized 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 a function of the external magnetic field. Further optical data should be analyzed 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 scattering experiments at finite momentum transfer, and a way of studying four-spin correlation functions involving some sort of local chiralities.

ACKNOWLEDGMENTS

We would like to thank T. Rõõm for correspondence and for providing us with his experimental results, J.-P. Boucher, H. Nojiri, and T. Sakai for stimulating discussions. O.C. acknowledges financial support from the ILL, from the Indo-French Grant No. IFCPAR/2404.1, and from the Australian Research Council.

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