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An Electron Spin Resonance Selection Rule for Spin-Gapped Systems

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The direct electron spin resonance (ESR) absorption between a singlet ground state and the triplet excited states of spin gap systems is investigated. Such an absorption, which is forbidden by the conservation of the total spin quantum number in isotropic Hamiltonians, is allowed by the Dzyaloshinskii-Moriya interaction. We show a selection rule in the presence of this interaction, using the exact numerical diagonalization of the finite cluster of the quasi-one-dimensional bond-alternating spin system. The selection rule is also modified into a suitable form in order to interpret recent experimental results on $CuGeO_3$ and NaV_2O_5.

KEYWORDS: spin gap, ESR, Dzyaloshinskii-Moriya interaction

The spin gap generated by strong quantum fluctuations in low-dimensional systems, such as the bond alternating chain, the spin 1-chain or spin ladders, continues to attract much interest, both experimental and theoretical. Electron spin resonance (ESR) experiments at very low temperatures provide very high-energy resolution measurements of the spin gap. Tuning an external magnetic field, the field-dependent energy of the excited triplet state is adjusted to the frequency of the electromagnetic propagating wave. A direct transition from the singlet ground state to the gapped triplet state may be observed. Such a direct transition would be, however, forbidden by the conservation law of the total spin quantum number for a perfectly isotropic but gapped spin system.

In recent ESR measurements for the spin-Peierls system $CuGeO_3$[1)] and the bond-alternating chain system NaV_2O_5,[2)] direct transitions from the ground state to the first excited triplet state have been detected. Since the observed intensity of the transition for $CuGeO_3$ was almost independent of the external magnetic field, Nojiri *et al.*[1)] concluded that the explanation may be provided by the Dzyaloshinskii-Moriya (DM) interaction, which had been suggested on the basis of electron paramagnetic resonance measurements.[3)] In contrast, another mechanism based on the effective staggered field due to alternating g-tensors,[4)] which had successfully explained the ESR absorption of the Haldane gap for the $S = 1$ antiferromagnetic chain $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, abbreviated NENP, should lead to a strong field dependence of the intensity. In addition, Kokado and Suzuki's phenomenological Hamiltonian including the DM interaction reproduced some of the results from the angle-dependent ESR measurement of $CuGeO_3$.[5)] These works motivated the derivation of a selection rule for direct ESR absorption in the presence of the DM interaction. In the present letter, we present such a general rule which emphasizes the role of the relative orientations of the external field, the *polarized* propagating magnetic field and the vector of the DM interaction. We also present a more suitable form for the experimental results, for which the electromagnetic wave is *not polarized*.

When the magnetic field of the wave $\boldsymbol{h}(t)$ is polarized along an axis α ($\alpha = x, y, z$), the intensity of ESR for quantum spin systems at zero temperature, assumed due to the magnetic dipole transitions, is determined by the matrix element

$$I^{\alpha} = |\langle g| \sum_j S_j^{\alpha} |e\rangle|^2, \tag{1}$$

where S_j^{α} is the α-component of the local spin operator at the j-th site, $|g\rangle$ and $|e\rangle$ denote the ground state and the excited state with the energy difference $E_e - E_g$ corresponding to the frequency ω of the electromagnetic wave. For an isotropic spin system, the dynamics conserves the total spin quantum number $S_{\rm total}$. Therefore, every component of the intensity (1) vanishes. In the presence of the DM interaction, however, $S_{\rm total}$ is no longer a good quantum number and some intensities may become finite. To investigate the effect of the DM interaction on the intensity, we first consider the problem of two coupled $S = 1/2$ spins with the Hamiltonian

$$\mathcal{H}_{(2)} = J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{D} \cdot (\boldsymbol{S}_1 \times \boldsymbol{S}_2) - \boldsymbol{H} \cdot (\boldsymbol{S}_1 + \boldsymbol{S}_2), \tag{2}$$

where $\boldsymbol{D}$ is the vector of the DM interaction and $\boldsymbol{H}$ is the external magnetic field. Solving the problem of two spins, we calculate the intensities of the ESR transitions from the ground state to the excited states. For $\boldsymbol{H} = 0$ and $\boldsymbol{D} \parallel \boldsymbol{z}$, they are given by:

$$I^z = |\langle g, S^z = 0| \sum_j S_j^z |e, S^z = 0\rangle|^2 = 0 \tag{3}$$

$$I^x = |\langle g, S^z = 0| \sum_j S_j^x |e, S^z = \pm 1\rangle|^2 = \frac{1}{8}\left(\frac{D^z}{J}\right)^2. \tag{4}$$

For nonzero magnetic field, this leads to the following selection rule. Nonzero intensity appears only when the

$\boldsymbol{h}(t)$ has some component satisfying one of the following two conditions:
(i) $\boldsymbol{h}(t) \perp \boldsymbol{H} \parallel \boldsymbol{D}$: the intensity is independent of H.
(ii) $\boldsymbol{h}(t) \parallel \boldsymbol{H} \perp \boldsymbol{D}$: the intensities depend on $H \equiv |\boldsymbol{H}|$ and the intensity of the transition to the nondegenerate state ($S^z_{\rm total} = 0$ at $H = 0$), which vanishes at $H = 0$ increases as H^2 for small H. For the degenerate states ($S^z_{\rm total} = \pm 1$ at $H = 0$), the intensities decrease.
On the other hand, the intensity would still vanish if $\boldsymbol{h}(t) \parallel \boldsymbol{H} \parallel \boldsymbol{D}$ because of the rotational symmetry around these vectors. Since these rules depend only on the relative configuration of the vectors $\boldsymbol{h}(t)$, $\boldsymbol{H}$ and $\boldsymbol{D}$, and they are independent of the lattice structure, they are expected to be valid even in general bulk systems with a spin gap. (The H-independent intensity of rule (i) is generally justified by the conservation of $S^z_{\rm total}$.) We will justify them with the following numerical analysis on finite clusters of the quasi-one-dimensional bond-alternating spin system. In particular cases, special symmetries may lead to vanishing intensities at certain frequencies, in which case the gap observed in ESR may not coincide with that of neutron scattering.

In order to examine the above selection rules in many-spin systems, we consider a two-dimensional lattice of weakly coupled bond-alternating chains. $CuGeO_3$ is one example of such a lattice. The cluster is shown in Fig. 1, where the axes parallel and perpendicular to the chain correspond to the c- and b-axes of $CuGeO_3$, respectively. The Hamiltonian with an external magnetic field is given by

$$\mathcal{H}_0 = J\sum_{l,j}(1+(-1)^{l+j}\delta)\boldsymbol{S}_{l,j}\cdot\boldsymbol{S}_{l,j+1} + J_\perp\sum_{l,j}\boldsymbol{S}_{l,j}\cdot\boldsymbol{S}_{l+1,j} - \boldsymbol{H}\cdot\sum_{l,j}\boldsymbol{S}_{l,j}, \qquad (5)$$

where the index l specifies a chain. The parameters are fixed as $J = 1$, $\delta = 0.1$ and $J_\perp = 0.15$, realistic for $CuGeO_3$.[6] We consider the interchain and intrachain DM interactions (the direction of the vectors $\boldsymbol{D}$ is denoted z):

$$\mathcal{H}_{\rm DM,\perp} = \sum_{l,j}\boldsymbol{D}_{\perp l,j}.(\boldsymbol{S}_{l,j}\times\boldsymbol{S}_{l+1,j}), \qquad (6)$$

$$\mathcal{H}_{\rm DM,\parallel} = \sum_{l,j}\boldsymbol{D}_{\parallel l,j}.(\boldsymbol{S}_{l,j}\times\boldsymbol{S}_{l,j+1}). \qquad (7)$$

Using the numerical diagonalization based on the Lanczos algorithm, we obtain the eigenvalues and eigenvectors of the singlet ground state and the first excited triplet of the finite cluster described by the Hamiltonian (5) including the DM term. Under an external magnetic field, the triplet splits into three modes with energies Δ_+, Δ_0 and Δ_-. To estimate the ESR intensity for each singlet-triplet transition, we calculate the matrix elements (1) for each excitation mode, denoted by I^α_+, I^α_0 and I^α_-. The numerical calculation is performed for the 4×4-spins cluster shown in Fig. 1 with periodic boundary conditions in both directions.

At, first the interchain DM interaction (6) is investigated. Since the particular pattern of $\boldsymbol{D}$-vectors, $D^z_{\perp l,j} = (-1)^l D^z_\perp$, leads to zero intensity for every polarization of the wave, we consider the sign-alternating one $D^z_{\perp l,j} = (-1)^{l+j}D^z_\perp$. In the presence of the DM interaction with $D^z_\perp = 0.1$, the ESR intensity is calculated under various external fields. To examine the selection rule (i), all the nonzero intensities are plotted versus the external field H^z which is parallel to $\boldsymbol{D}_\perp$ in Fig. 2(b). Figure 2(a) shows the H^z dependence of the three modes which still have the good quantum number $S^z_{\rm total}$. Note that the triplet is split even in zero field because of the DM interaction. Figure 2(b) shows that a finite intensity appears only when the polarized field has a magnetic component perpendicular to the DM vector and the external field. Since the magnetization along the external field is conserved in this case, the intensities are independent of H^z, as shown in Fig. 2(b). These results agree with rule (i).

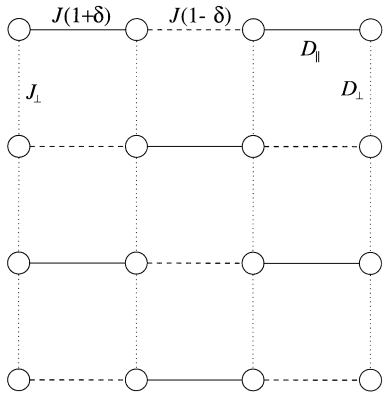

Fig. 1. Cluster of 16 spins with DM interaction, used in the exact numerical diagonalization. The lattice is taken to be similar to that of $CuGeO_3$.

The D^z dependence of the intensity is shown in Fig. 3(a). The $\ln(I^x_+)$-$\ln(D^z_\perp)$ plot in Fig. 3(b) is almost linear with a slope of 2. It indicates the relation

$$I^x = I^y \sim |D^z|^2, \qquad (8)$$

which is satisfied in the two-spin system discussed above. (We omitted the symbol $\perp$ for $D^z_\perp$ in eq. (8), because it is also held for the intrachain DM interaction.)

The results for the external field (H^x) perpendicular to the DM vector are shown in Figs. 4(a) and 4(b). Figure 4(b) shows that the intensities at the energies Δ_+ or Δ_- are finite only if the polarized field $\boldsymbol{h}(t)$ has one component along the external field. The intensity I^x_+ increases as H^x increases. These behaviors support the validity of rule (ii) even in many-spin systems.

Next, the DM coupling along the chain (7) is investigated. The intrachain DM interaction gives rise to some nonzero intensities in the case of a uniform sign, that is, $D^z_{\parallel l,j} = D^z_\parallel$. The results for such an intrachain DM interaction with $D^z_\parallel = 0.1$ are presented in Figs. 5 and 6, for the cases of $\boldsymbol{H} \parallel \boldsymbol{D}$ and $\boldsymbol{H} \perp \boldsymbol{D}$, respectively. These results reveal the same behaviors as the interchain DM interaction for all the wave polarizations, although the absolute value of the intensity is slightly larger. Thus, selection rules (i) and (ii) are revealed to be valid also for the DM coupling along the chain. These results suggests that the rules do not depend on where the DM interaction acts.

We derived general selection rules (i) and (ii) for a

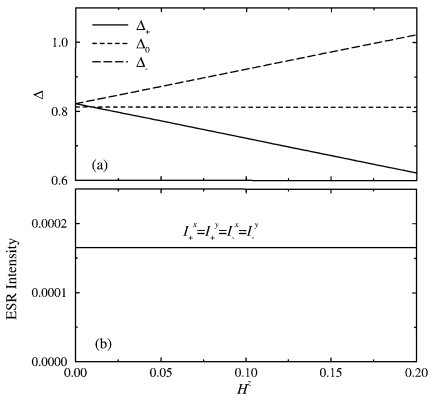

Fig. 2. (a) Energy gaps and (b) ESR intensities plotted versus the external magnetic field parallel to the interchain DM vector.

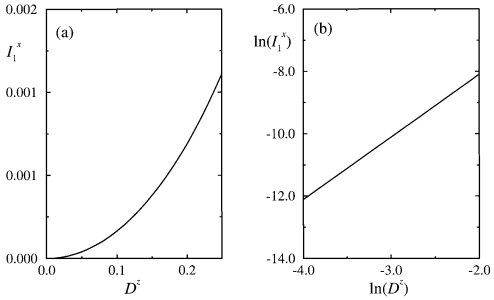

Fig. 3. (a) ESR intensity $I^x_+ = I^y_+ = I^x_- = I^y_-$ versus the amplitude of the DM vector D^z. (b) Plot of $\ln(I^x_+)$-$\ln(D^z)$. It suggests $I^x_+ \sim (D^z)^2$.

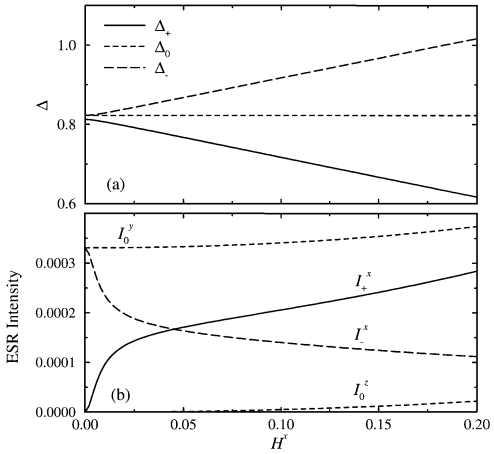

Fig. 4. (a) Energy gaps and (b) ESR intensities plotted versus the external magnetic field perpendicular to the interchain DM vector.

polarized electromagnetic wave. In the experiment on $CuGeO_3$, however, the wave was not polarized, and its wave vector $\boldsymbol{k}$ was oriented along different crystal axes. In order to compare with these experimental results, we would average the calculated ESR intensities over the two components of the magnetic field perpendicular to the wave vector $\boldsymbol{k}$. In the following, we discuss the modified rules for nonpolarized electromagnetic waves, in the Faraday or Voigt configurations.

(A) Faraday configuration: $\boldsymbol{k} \parallel \boldsymbol{H}$

Since the magnetic field $\boldsymbol{h}(t)$ perpendicular to $\boldsymbol{k}$ is always perpendicular to the external field, ESR absorption is

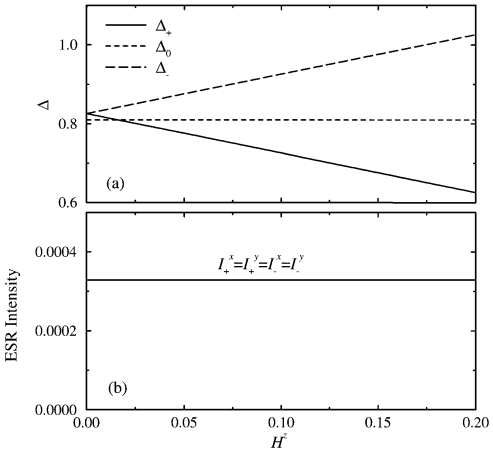

Fig. 5. (a) Energy gaps and (b) ESR intensities plotted versus the external magnetic field parallel to the intrachain DM vector.

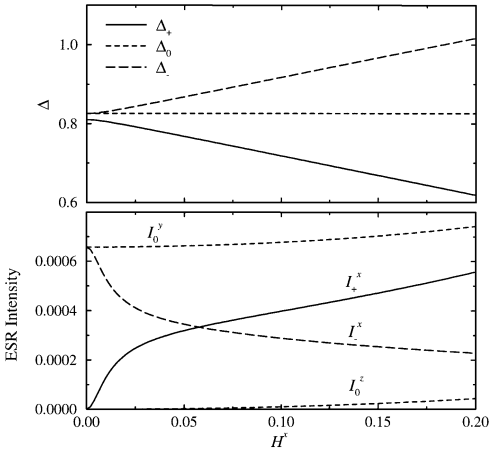

Fig. 6. (a) Energy gaps and (b) ESR intensities plotted versus the external magnetic field perpendicular to the intrachain DM vector.

allowed only if the rule (i) is satisfied. The intensity should then be independent of the external field. It is expected to be largest for $\boldsymbol{H} \parallel \boldsymbol{D}$ and zero for $\boldsymbol{H} \perp \boldsymbol{D}$. Based on the eq. (8), the measured intensities for the cases where the external field is successively along a-, b- and c-axes, would enable us to determine the direction of the vector $\boldsymbol{D}$ in the following way. The intensity at the energy Δ_+ for $\boldsymbol{H} \parallel \alpha$ in the Faraday configuration is noted $I^{\alpha}_{(\mathrm{F})}$, so that the components of $\boldsymbol{D}$ should be determined by

$$I^a_{(\mathrm{F})} : I^b_{(\mathrm{F})} : I^c_{(\mathrm{F})} = (D^a)^2 : (D^b)^2 : (D^c)^2. \qquad (9)$$

(B) Voigt configuration: $\boldsymbol{k} \perp \boldsymbol{H}$

Since $\boldsymbol{h}(t)$, which is perpendicular to $\boldsymbol{k}$, has components parallel and perpendicular to $\boldsymbol{H}$, both rules (i) and (ii) can be realized. We discuss the two possibilities separately.

(α)$\boldsymbol{H} \parallel \boldsymbol{D}$ (rule (i)): every intensity is independent of the external field and the intensities at the energies Δ_+ and Δ_- are half that of the Faraday configuration with $\boldsymbol{H} \parallel \mathbf{D}$.

(β)$\boldsymbol{H} \perp \boldsymbol{D}$ (rule (ii)): the ESR intensities at the energies Δ_+ and Δ_- depend on the external field.

In a vanishing external magnetic field, symmetry arguments based on the rotation of the spin operators[7] can be given. In particular, we explain the vanishing intensity found for a transverse alternating DM interaction as well as the D^2 dependence of the intensity for the others.

First, consider the alternating transverse DM interaction $D^z_{\perp l,j} = (-1)^l D^z_\perp$. Following Oshikawa and Affleck,[8] we introduce rotated spin operators $S'^{\pm}_{l,j} = \mathrm{e}^{\mathrm{i}\pm(-1)^l\theta/2}S^{\pm}_{l,j}$, $S'^z_{l,j} = S^z_{l,j}$ with $\tan\theta = D^z_\perp/J_\perp$. This exactly maps the Hamiltonian onto an XXZ model with alternating coupling for S' operators for which we can neglect the small second-order anisotropy. Transforming the Zeeman coupling gives rise to a staggered magnetic field $\boldsymbol{h}^{stagg}(t)$ for rotated operators.[8] The intensity of the transition is given for the rotated variables as

$$I^x = |\langle g'|\cos(\frac{\theta}{2})\sum_{l,j} S^{x'}_{l,j} + \sin(\frac{\theta}{2})\sum_{l,j}(-1)^l S^{y'}_{l,j}|e'\rangle|^2. \tag{10}$$

The first term, involving the total spin operator, still gives a vanishing contribution because the rotated Hamiltonian is isotropic. The second term comes from the field that is staggered in the transverse direction. It therefore has $q_\perp = \pi$ symmetry. On the other hand, the lowest-lying excitation and the ground state have $q_\perp = 0$ symmetry for an antiferromagnetic transverse interaction for the lattice of Fig. 1.[6] This is why the transition from the ground state to the first gapped excited state is still forbidden with this DM anisotropy. A transition to the triplet excited state $q_\perp = \pi$ with higher energy is, however, allowed with an intensity factor $\sin^2(\theta/2) = (D^z_\perp/2J_\perp)^2$ in the small D limit.[9]

Second, consider the case of a constant DM interaction $D^z_{\parallel l,j} = D^z_\parallel$. A rotation to the new set of operators $S'^{\pm}_{l,j} = \mathrm{e}^{\mathrm{i}\pm\theta j}S^{\pm}_{l,j}$, $S'^z_{l,j} = S^z_{l,j}$ (with $\tan\theta = D^z_\parallel/J$) also maps the Hamiltonian onto a bond-alternating XXZ model. In the rotated frame, the magnetic field $\boldsymbol{h}(t)$, however, transforms into a field which rotates in space with a periodicity $2\pi/\theta$. The intensity is then:

$$I^x = |\langle g'|\sum_{l,j}\cos(\theta j)S^{x'}_{l,j} + \sin(\theta j)S^{y'}_{l,j}|e'\rangle|^2. \tag{11}$$

Therefore, the intensity of the ESR transition at $q = 0$ induced by uniform DM interaction equals the intensity at small $q = \theta$ calculated for a model without DM interaction. For small q, the intensity should behave as $I \sim q^2$ (the matrix element should be analytic for a spin-gapped system), so that $I^{x,y} \sim \theta^2 = (D^z_\parallel/J)^2$, in agreement with the relation found numerically.

Finally, we briefly discuss the experimental results of $CuGeO_3$ on the basis of the above selection rules. We assume that the forbidden absorption observed is induced by a DM interaction and see what are the consequences. Considering only the absorption at the energy Δ_+, the measurement in the Faraday configuration revealed that $I^c_{(\mathrm{F})}$ is the largest one. Relation (9) thus indicates that $\boldsymbol{D}$ is along the c-axis. The interchain DM interaction with $\boldsymbol{D}_\perp$ along the c-axis is in fact the most realistic situation with regards to the crystallographic structure of $CuGeO_3$. The sign configuration $D^c_{\perp l,j} = (-1)^l D^c_\perp$ is, however, expected,[9,10] but it leads to zero intensity for every polarization, as proven by the symmetry argument, and cannot explain the transition observed. The other patterns for interchain $D^c_{\perp l,j} = (-1)^{l+j}D^c_\perp$ or intrachain $D^c_{\parallel l,j} = D^c_\parallel$ give intensities (the observed intensities would then indicate an extra small component of $\boldsymbol{D}$ along the a-axis), but we cannot conclude from these measurements alone whether they exist or whether we need other interactions such as exchange anisotropies or alternation of the g-tensor to explain the ESR absorptions. In particular, the measured intensities in the Voigt configuration cannot be compared with the above rules, because the external field dependence has not been measured yet. The observation of increasing intensity with the external field would be good evidence of the contribution of the DM interaction to the absorption. Here, we can make the following observation for the case of NaV_2O_5: An absorption at the energy gap with no strong field dependence has been observed in the Faraday configuration[2] for an external field along the a-axis. If we assume that it is mainly due to DM interaction, the above rule (A) would tell us that the DM vector is along the a-axis, in agreement with the crystallographic structure of V-O-V bonds along the chains.

In summary, we presented two selection rules (i) and (ii) for the ESR polarized absorption for a spin-gap system in the presence of the DM interaction. For certain frequencies there may be additional selection rules, depending on the spatial variations of the DM interactions. We also modified the rules for a nonpolarized electromagnetic wave for comparison with recent experiments. It was found that the intensity depends on the external field in some of the Voigt configurations.

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