Dzyaloshinski-Moriya Interaction in the 2D Spin Gap System $SrCu_2(BO_3)_2$

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The Dzyaloshinski-Moriya interaction partially lifts the magnetic frustration of the spin-1/2 oxide $SrCu_2(BO_3)_2$. It explains the *fine structure* of the excited triplet state and its unusual magnetic field dependence, as observed in previous ESR and new neutron inelastic scattering experiments. We claim that it is mainly responsible for the dispersion. We propose also a new mechanism for the observed ESR transitions forbidden by standard selection rules, which relies on an instantaneous Dzyaloshinski-Moriya interaction induced by spin-phonon couplings.

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Strontium copper borate [$SrCu_2(BO_3)_2$] is a new example of a magnetic oxide with a spin gap [1], with a ground state well described as simply a product of magnetic dimers in two dimensions on the bonds giving the strongest magnetic exchange [2]. The weaker exchanges are frustrated by the geometry and, as shown by Shastry and Sutherland [3], the ground state of the isotropic Hamiltonian is independent of the value of the weaker exchange, up to a critical value. The excitations, however, are not purely local and cannot be explicitly given. Recent experiments by ESR [4] and neutron inelastic scattering presented here show how, in fact, there are spin anisotropies needed for an accurate description of the dynamics. We show the corrections to the ground state are needed and, while small, are necessary to understand many physical properties. For example, at finite external magnetic field $SrCu_2(BO_3)_2$ appears to exhibit a number of finite magnetization plateaus [1,5], and the anisotropies determine the observability of plateaus in different field directions. Furthermore, $SrCu_2(BO_3)_2$ is believed to be close in parameter space to a quantum critical point whose nature is somewhat controversial, and while the anisotropies are small they may be essential to its nature.

For spin $\frac{1}{2}$ the leading anisotropic terms are of the Dzyaloshinski-Moriya form [6] and exchange anisotropy. The former is particularly relevant, since it may not be frustrated even if the isotropic exchange is. While a small Dzyaloshinski-Moriya interaction should not destroy a gap generated by larger isotropic interactions it modifies the pure locality of the ground state correlations and delocalizes the first triplet excitation. This is because it appears in lower order in perturbation theory than the frustrated isotropic interactions. In this Letter we predict the Dzyaloshinski-Moriya interactions that should be expected in $SrCu_2(BO_3)_2$ from the structure and show that they do indeed explain new features of the excitations observed with ESR and neutron inelastic scattering experiments.

Miyahara and Ueda [2] have introduced the frustrated Shastry-Sutherland model

$$H = J \sum_{\text{nn}} \mathbf{S}_i \mathbf{S}_j + J' \sum_{\text{nnn}} \mathbf{S}_i \mathbf{S}_j \qquad (1)$$

for $SrCu_2(BO_3)_2$, with $S = 1/2$ and where nn stands for nearest neighbor spins and nnn for next nearest neighbors. The lattice is shown in Fig. 1. $J = 85$ K and $J' = 54$ K are antiferromagnetic interactions estimated from the susceptibility and the gap [2]. The spectrum of spin excitations has several interesting features [7], in particular, the existence of singlet bound states [8]. Figure 2a summarizes the gaps to the first excited states, calculated by exact numerical diagonalization of the finite size system (20 spins). In addition to the triplet state (solid line) calculated in [2], the energies of the two lowest singlet states (dashed lines) are given as a function of J'/J. These roughly agree with recent calculation [9]: we find a ratio $J'/J \simeq 0.62$, comparing [10] the calculated ratio of

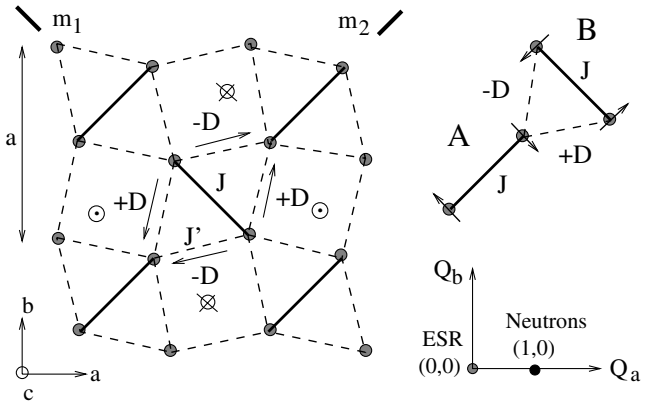

FIG. 1. Spin model including the Dzyaloshinski-Moriya interactions whose vectors are perpendicular to the plane. The arrows show the order of the spins in the expression $\mathbf{D} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$. At right, the unit cell of dimers A and B with the classical ground state with $J' = 0$, and definition of the reciprocal space.

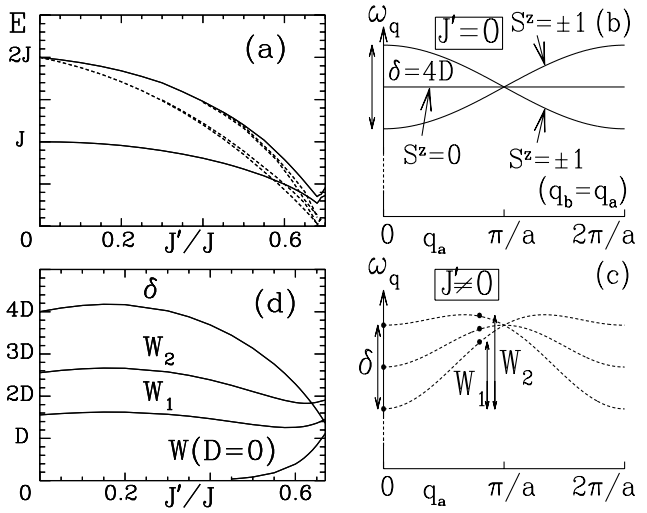

FIG. 2. (a) Gaps to the first excited states at $\mathbf{q} = 0$ for $D = 0$ (solid line triplets and dashed line singlets), calculated by exact numerical diagonalization. (b) The effect of the Dzyaloshinski-Moriya interaction on the first triplet for small J'. (c) For finite J', the exact diagonalization gives the energies of two reciprocal points (the dots). (d) Renormalization of the splitting δ and the bandwidths W_1 and W_2.

the energy of the Raman-active singlet (which is not the lowest singlet [9]) to the triplet excitation with the same ratio determined by experiment [7,8]. We find that the energy of the lowest singlet crosses the ground state at $(J'/J)_c \simeq 0.68$ (while the triplet state remains gapped), in agreement with the transition recently predicted [11], but no evidence for the reported $S = 1$ instability [9]. Below this value, the ground state of (1) is simply a product of localized singlets.

Anisotropic behavior of the first triplet energy, according to the direction of an external magnetic field, first appeared in ESR data [4], and cannot be explained by the fully isotropic model. We show that the Dzyaloshinski-Moriya coupling, which occurs in low-symmetry crystals, explains these features. In $SrCu_2(BO_3)_2$, an almost perfect center of inversion at the middle of the dimer bonds forbids the Dzyaloshinski-Moriya interactions between the two spins of a dimer. Each dimer is, however, separated from the neighboring dimer by a BO_3 triangle for which there is no center of inversion at the middle of the bond, allowing such an interaction between the spins of the nearest neighbor dimers. As the copper (**ab**) plane is approximately a mirror plane for the crystal structure the main components of **D** must be perpendicular to the plane [6], thus lying along the c axis. We neglect the other components, expected to be smaller. Furthermore, using mirror planes perpendicular to the copper plane and passing through the dimers (m_1 and m_2 in Fig. 1), we find an alternation of the **D** vector from bond to bond. Finally, the mapping of one dimer onto the next one fixes the whole pattern of **D** vectors (Fig. 1). We therefore predict an anisotropic term to the Hamiltonian:

$$H_{\mathrm{DM}} = \sum_{\mathrm{nnn}} \pm D\mathbf{e}_c(\mathbf{S}_i \times \mathbf{S}_j), \qquad (2)$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are spin operators which belong to next nearest neighbors and the sign $\pm$ depends on the bond (see Fig. 1). $\mathbf{e}_c$ is the unitary vector in the c direction. The magnitude can be estimated from Moriya's argument to be $D \sim \frac{\Delta g_c}{g_c} J'$, where $\Delta g_c \simeq 0.28$ has been measured by ESR [4] and $J' \simeq 54$ K [2]. This gives roughly $D \sim 0.5$ meV.

The Dzyaloshinski-Moriya interaction is not frustrated because of the alternation of its vector; classically, in the absence of the exchange interaction J', the spins of the neighboring dimers would be perpendicular. Quantum mechanically, the product of singlets on each dimer is no longer the exact ground state. To first order the ground state has corrections proportional to two triplets $\frac{D}{J}\prod_{a\neq(b,c)} s_a(t_b^{+1}t_c^{-1} - t_b^{-1}t_c^{+1})$. These corrections are, however, small and we checked by exact numerical diagonalization that the position of the critical point separating the two nonmagnetic ground states is not appreciably changed.

In order to calculate the effect of the Dzyaloshinski-Moriya interaction on the first triplet excitation, we start from small J' and from the exact ground state for $\mathbf{D} = \mathbf{0}$. At $J' = D = 0$, the first excited state is a localized triplet which is separated from the ground state by an energy gap J. Because of the frustration, a finite dispersion should appear only at the sixth order in J'/J [2]. In contrast, the Dzyaloshinski-Moriya interaction is not frustrated and the degeneracy of the localized triplets is lifted to first order in D. We consider the two inequivalent triplet states for the dimers A and B (Fig. 1). To linear order in J' and D, we can write the Hamiltonian for the sector of total spin $S^z = +1$ (respectively, -1) as a 2×2 matrix projected on the basis vectors: (i) All dimers are in singlets bar one, which is in the triplet state, spin $+1$ (respectively, -1). This triplet is on the sublattice of dimers A. (ii) The same with the triplet on the sublattice of dimers B. One obtains

$$\mathcal{H}^{S^z=\pm1} = \begin{pmatrix} J & \mp 2iDf(\mathbf{q}) \\ \pm 2iDf(\mathbf{q}) & J \end{pmatrix}, \qquad (3)$$

where $f(\mathbf{q}) = \cos(q_a a/2)\cos(q_b a/2)$. The dispersion of the two modes $\pm$ (each is twice degenerate with $S^z = \pm 1$) is therefore proportional to D: $\omega_{\mathbf{q}}^{\pm}(S^z = +1) = \omega_{\mathbf{q}}^{\pm}(S^z = -1) = J \pm 2D\cos(q_a a/2)\cos(q_b a/2)$. The Dzyaloshinski-Moriya interaction has no effect on the $S^z = 0$ component of the triplet, so that its energy remains equal to J [$\omega_{\mathbf{q}}(S^z = 0) = J$] (Fig. 2b).

In particular, at $\mathbf{q} = 0$, we have two upper (respectively, lower) modes $S^z = \pm 1$ with $\omega(S^z = \pm 1) = J + 2D$ [$\omega(S^z = \pm 1) = J - 2D$]. A magnetic field parallel to $z \parallel \mathbf{D} \parallel c$ splits these modes in four branches. This is in agreement with ESR when the magnetic field is parallel to the c axis (Fig. 3a). In such an experiment, however, an $S^z = 0$ state cannot be seen as the external magnetic field is tuned to adjust the energy of the state to the frequency of the propagating wave. We have, however, a clear prediction for the energy of the mode $S^z = 0$: it remains exactly at the middle of the four $\omega(S^z = 0) = J$. Such

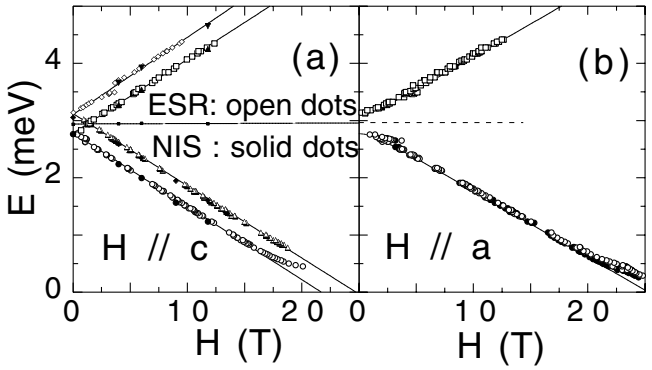

FIG. 3. The magnetic field dependence of the triplet energies: (a) $\mathbf{H} \parallel c$ and (b) $\mathbf{H} \parallel a$; ESR data from [4], the dashed line comes from [12]. The theory of the Dzyaloshinski-Moriya interaction explains these results (solid lines).

a crucial test can be made by neutron inelastic scattering experiments: we come back to this point next.

A transverse magnetic field leads to the diagonalization of a 6×6 matrix which reduces to two equal 3×3 matrices in the basis of the zero-field eigenstates. Therefore, the energies remain twice degenerate in a transverse magnetic field and are given by $\omega_{\mathbf{q}}^{\pm} = J \pm \sqrt{4D^2 f^2(\mathbf{q}) + (g_\perp \mu_B H_\perp)^2}$, $\omega_{\mathbf{q}}^0 = J$. This form also fits the ESR results in transverse magnetic field (Fig. 3b), apart from a small splitting in the high field regime which may be accounted for by the differences in the g tensors from the dimer A and B.

These expressions are first order in J'/J (although corrections like DJ'/J^2 may appear), which is not accurate for $SrCu_2(BO_3)_2$ ($J'/J \simeq 0.62$). We performed exact numerical diagonalization to see how these results survive in the strong coupling limit. We know, for instance, that the gap between the ground state and the first triplet state is renormalized to order $(J'/J)^2$ [2]. In addition, we find, for $D = 0$, a finite bandwidth W for the triplet dispersion. This bandwidth is smaller than that found previously from a perturbative treatment [13]. We interpret this difference as a breakdown of the perturbative series close to the quantum critical point. When $D \neq 0$, we calculated again the splitting δ between lower and upper modes at $\mathbf{q} = 0$. The result $\delta(J'/J \to 0) = 4D$ is renormalized by finite J' (Fig. 2d). Taking the relevant parameters, we find $\delta(J'/J = 0.62) \simeq 2.0D$. On the other hand, the dispersion is changed from that calculated in the limit of small J': the energy of the $S^z = 0$ mode acquires a small dispersion $W(D = 0)$ (Figs. 2c and 2d), though smaller than the $S^z = \pm 1$ dispersions.

In order to test the prediction of the energy of the $S^z = 0$ mode, we compare it to neutron inelastic scattering measurements in the presence of a magnetic field, up to $H = 12$ T. They have been realized on the three-axes spectrometer CRG/CEA-IN12 installed on a cold neutron guide at the Institut Laue Langevin. The final wave vector was kept fixed at $k_f = 1.55A^{-1}$. A vertical curved pyrolytic graphite PG(002) monochromator and a horizontally curved PG(002) analyzer were used and a cooled beryllium filter was placed after the sample to eliminate higher-order contamination. The collimations were 40′-open-open. A single crystal of about $15 \times 6 \times 6$ mm^3 was installed in a cryomagnet with the $\mathbf{c}$ axis aligned along the vertical field. In the following, we refer to the $(\mathbf{a}^*\mathbf{b}^*)$ reciprocal plane defined in [7] (Fig. 1). In reciprocal lattice units, the wave vector components are defined as $Q_{a,b} = q_{a,b}a/(2\pi)$, where a is the lattice parameter. Examples of energy scans obtained at $\mathbf{Q} = (1, 0, 0)$ for $H = 0$ and $H = 6T$ are shown in Fig. 4. In Fig. 4a, we observe a broad single peak at $E \simeq 3$ meV, corresponding to the lowest triplet excitation branch (the signal above $\simeq$4.4 meV corresponds to a higher triplet [7] as well as the dashed line in Fig. 4b). For $H = 0$, it is of note that the 3 meV mode is appreciably broader than the energy resolution ($\simeq$0.2 meV at full width at half maximum). In Fig. 4b, the application of H shows a Zeeman splitting of this mode in five distinct lines. The five peaks become resolution limited. Their energies are shown in Fig. 3a.

The energies of the $S^z = \pm 1$ excitations at $\mathbf{Q} = (1, 0, 0)$ (solid dots) agree with the ESR field-dependent branches [$\mathbf{Q} = (0, 0, 0)$], confirming the translational symmetry of the model. In addition, we find the energy of the $S^z = 0$ mode of the triplet (solid squares) which cannot be seen by ESR. It lies exactly at the middle of the four other branches, as predicted above. Furthermore, the observed intensities of the $S^z = \pm 1$ peaks are all equal and roughly $1/4$ of that of the $S^z = 0$ peak (Fig. 4b). We calculate the spin correlation function transverse to the scattering wave vector which gives the intensities. Because of the purely imaginary off-diagonal elements in the matrix (3), the upper ($S^z = \pm 1$) and lower ($S^z = \pm 1$) have the same intensity at zero field. Both are split in longitudinal field into two modes of half the zero-field intensity. Similarly, for the $S^z = 0$ sector, there are, in fact, two degenerate modes at zero field which remain degenerate at finite field with the original weight. Each weight is twice that of $S^z = +1$ since only spin correlation functions transverse to the momentum transfer contribute to the intensities. The intensity factor $1/4$ then follows. The agreement with experiment suggests that the

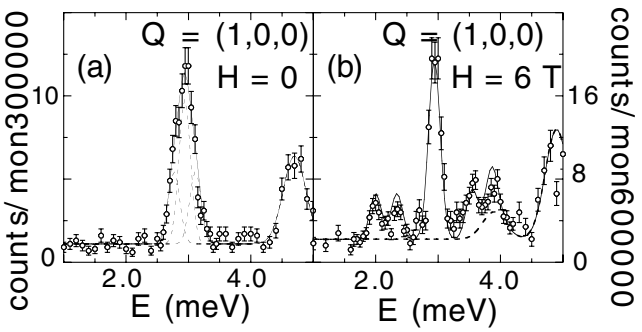

FIG. 4. Scans in the neutron experiment at $\mathbf{Q} = (1, 0, 0)$: (a) the broad signal comes from three superimposed modes (dashed lines) and (b) Zeeman splitting of the modes.

ratio of intensities is a good test of a mechanism based on couplings of Dzyaloshinski-Moriya symmetry, even in the regime of large J'/J.

Since the spectra are well fitted for both directions, we can extract the coupling D from the zero-field splitting $\delta = 0.352 \pm 0.008$ meV. Using the numerical result $\delta \simeq 2.0D$ (Fig. 2d), this gives $D \simeq 0.18$ meV, consistent with the approximate value from Moriya's formula, as given earlier. We obtain the gap (which is no longer simply J but the function shown in Fig. 2a) and the g factors in both directions: $g_{\parallel} = 2.24 \pm 0.09$ and $g_{\perp} = 2.00 \pm 0.09$.

We then discuss the origin of the finite intensities in ESR [4] and infrared absorption [12]. No magnetic transition can be induced from a purely singlet ground state. Spin-orbit couplings generate anisotropies that may permit transitions from the ground state to the original triplet excited states. First, note that Dzyaloshinski-Moriya interactions are not sufficient to explain the observed transitions. Indeed, the magnetic operator $H_M = h \sum_i S_i^+$ is odd under the symmetry transformation: the reflection using the mirror plane m_1 and the rotation of π around the dimer bond. The ground state and the triplet state are, however, even under this transformation. The matrix element therefore vanishes, leading to zero intensity. Second, the exchange anisotropy only (both in J and J') leaves the ground state as the product of singlets, leading again to zero intensity. With both Dzyaloshinski-Moriya and exchange anisotropy, the transition can exist but should be very small, of the order of λ^6, where λ is the spin-orbit coupling. Note also that an exchange anisotropy of order D^2/J always occurs with a Dzyaloshinski-Moriya coupling [6], but unlike the unfrustrated case [14], here it does not eliminate the splitting which is linear in D. Third, we have mentioned that the anisotropy of the g tensors may be responsible for the very small splitting of the modes in high field. A staggered field between dimers (due to perpendicular orientations of oxygen ions surrounding copper ions) is written $H_M = h\Delta g(\sum_{i\in A} S_i^+ - \sum_{i\in B} S_i^+)$. This term is odd in the transformation introduced above and transitions are thus forbidden for the same reasons. An intradimer staggered field should be very small giving an intensity we estimate as $\lambda^2\alpha^2$, where α — a few degrees — is the tilting angle of the crystal structure [15].

Consider now *electric dipole transitions* between magnetic states. We restrict ourselves here to a phonon-assisted mechanism. A purely electronic mechanism may, in fact, also apply [16]. Treating the spin-phonon interactions perturbatively leads to an effective matrix element between pure magnetic states $|\langle f|H_E|i\rangle|^2$, where the effective operator H_E has now a correction of spin-orbit origin [17]: $H_E = \sum_{\mathrm{nn}} \boldsymbol{\gamma}\mathbf{S}_i \cdot \mathbf{S}_j + \boldsymbol{\eta} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$. The first term comes from a transition via a virtual phonon as an intermediate state. The second term, which comes from the spin-orbit coupling should be $|\eta| \sim \lambda\gamma$, with a direction that depends on details of the phonons. This mechanism gives an intensity proportional to η^2, suggesting that the observed transitions may be electric dipole. Further polarized experiments can test this: if the intensity of the transition changes in rotating the crystal around the magnetic (respectively, electric) field of the wave, the transition would be demonstrated explicitly to be electric dipole (respectively, magnetic).

We have shown that the *static* Dzyaloshinski-Moriya interaction explains the magnetic field behavior of the first triplet excitation (Fig. 3) and gives a dispersion (Fig. 2), because it is not frustrated. We extracted its value from the zero-field splitting, taking into account a finite J': $D = 0.18$ meV. Since the direction of the main anisotropy is given by $\mathbf{D} \parallel c$, we expect clear magnetization plateaus only when the magnetic field is applied along the c axis. This is consistent with current results [5]. The static interaction does not, however, explain the finite intensity for the ESR transitions. We presented an alternative mechanism using a *dynamical* Dzyaloshinski-Moriya interaction.

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