Field-Induced Gap in $S = 1/2$ Antiferromagnetic Chains

Masaki Oshikawa[1] and Ian Affleck[1,2]
[1]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, V6T 1Z1, Canada*
[2]*Canadian Institute for Advanced Research, University of British Columbia, Vancouver, British Columbia, V6T 1Z1, Canada*
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In a recent neutron-scattering experiment on the quasi-one-dimensional $S = 1/2$ antiferromagnet Cu benzoate, a gap was induced by an applied magnetic field. We argue that the primary mechanism of the gap formation is an effective staggered field due to both the alternating g-tensor and the Dzyaloshinskii-Moriya interaction. We explain the dependence of the gap on the applied field, as well as identify several peaks in the structure factor $S(q, \omega)$. [S0031-9007(97)04220-8]

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Quantum spin chains have attracted much interest for a long time. This is partly because sophisticated theoretical analysis, such as exact solutions, can be applied to one-dimensional systems. Furthermore the effect of quantum fluctuations is more significant than in higher-dimensional systems, resulting in many interesting phenomena. On the other hand, progress in experimental techniques has increased the opportunity to observe physics of one-dimensional systems. In a recent high field neutron-scattering experiment [1] on Cu benzoate, which is a (quasi-)one-dimensional $S = 1/2$ antiferromagnet, the field-induced shift in the soft-mode momentum is observed for the first time. Although the shift of the momentum is consistent with previous theoretical analysis on the Heisenberg antiferromagnetic chain, the experiment also found an unexpected excitation gap induced by the applied field. The observed gap is proportional to $H_0^{0.65}$ where H_0 is the magnitude of the applied field. While the data are consistent with the power law with the same exponent 0.65 for three different directions of the applied field, the coefficient depends on the direction. The ratio of the coefficient is found to be $0.55 : 1.0 : 2.0$ for the field applied in a'', b, c'' axes, which are the principal axes of the effective exchange interaction. (For a detailed description of the compound, see Ref. [2].) The observed gap can be as large as $0.3J$ where J is the exchange coupling in the chain direction, at $H_0 = 7$ T where the average magnetization is 0.06 per site.

In this Letter, we discuss the mechanism of the field-induced gap observed in Cu benzoate. We argue that the primary mechanism is due to an effective staggered field. As pointed out by Dender *et al.* [1], an effective staggered field is generated by the alternating g-tensor. We found that the effective staggered field is also generated by the Dzyaloshinskii-Moriya (DM) interaction, and the latter is no less important than the former. Our theory successfully explains the experimental data, including the angle dependence of the gap. For quasi-one-dimensional compounds with alternating crystal axes, both effects are expected. Thus, our theory should apply to such compounds in general.

Since the interchain coupling is very weak in the compound, the gap formation should be understood primarily in a one-dimensional model. In this Letter, we restrict our discussion to one-dimensional models. As a first approximation, the system would be described as the standard isotropic Heisenberg antiferromagnet. Actually, the neutron-scattering data at zero magnetic field is consistent with the theoretical analysis based on the standard Heisenberg model with exchange coupling $J = 1.57$ meV. However, the standard Heisenberg model in an applied field remains gapless from zero magnetic field up to saturated magnetization [3]. Thus we have to consider some modification.

Even if we generalize the model Hamiltonian, the system remains gapless for generic values of the magnetization, as long as it has rotation symmetry about the direction of the magnetization (we call this axial symmetry hereafter). This can be seen from Abelian bosonization or the generalized Lieb-Schultz-Mattis theorem [4]. Since the gap is observed with a continuously changing magnetization, it must be related to a breaking of the axial symmetry. We bosonize, following the notation and conventions of Ref. [5], and take the direction of the magnetization as the quantization axis (z axis). The breaking of the axial symmetry allows the operator $e^{2\pi i R\tilde{\phi}}$, where $\tilde{\phi}$ is the dual field and R is the compactification radius. If this operator appears in the Hamiltonian with a nonvanishing coefficient, and it is relevant (in the renormalization-group sense), we expect an energy gap.

A simple possibility of axial symmetry breaking is the exchange anisotropy, including the dipole-dipole interaction. However, the magnitude of the anisotropy is of order of 1% of J [1,2]. From a bosonization analysis, which we do not discuss in detail in this Letter, we estimate the gap induced by the exchange anisotropy as $10^{-5}J$ at the field of 7 T. This is too small compared to the experimental value up to $0.3J$. Thus we must seek another mechanism.

Cu benzoate has alternating crystal axes, which gives an alternating g-tensor. Because of the alternating g-tensor, a uniform applied field produces an effective staggered field on the spin chain as pointed out in Ref. [1]. Moreover,

an additional contribution to the effective staggered field comes from the DM interaction, which is also present due to the alternating crystal axes. Both lead to a transverse staggered field; namely, the direction of the staggered field is (almost) orthogonal to the direction of the magnetization. As we will see, these two contributions to the staggered field are of the same order and both are important in analyzing the angle dependence of the gap.

According to Ref. [2], the local g-tensor for Cu ions is given by $g = \mathrm{diag}(2.08, 2.05, 2.36)$ in the local principal coordinates. Because of the alternating direction of the oxygen octahedra around the Cu ions, the principal axes of the g-tensor alternates along the chain. In the experiment, the field is applied in the principal directions (a'', b, c'') of the total exchange anisotropy. (For details, see Ref. [2].)

The g-tensor in a'', b, c'' bases [2] is given by

$$g = \begin{pmatrix} 2.115 & \pm 0.0190 & 0.0906 \\ \pm 0.0190 & 2.059 & \pm 0.0495 \\ 0.0906 & \pm 0.0495 & 2.316 \end{pmatrix}, \qquad (1)$$

where $\pm$ corresponds to the two inequivalent sites. For example, if we apply the magnetic field in c'' direction, the effective staggered field generated by g-tensor is $(0, 0.025, 0)H$ in $a''bc''$ coordinates. (The sign of the staggered field is defined by referring to the even sites.) For field applied in b'' and a'' directions, it is $(0.0095, 0, 0.025)H$ and $(0, 0.0095, 0)H$, respectively.

On the other hand, ignoring other than the nearest-neighbor interaction, DM interaction in the chain can be written as

$$H_{\mathrm{DM}} = \sum_j (-1)^j \vec{D} \cdot (\vec{S}_j \times \vec{S}_{j+1}). \qquad (2)$$

Note that the factor $(-1)^j$ is present, as required from the crystal structure [2,6]. When a magnetic field is applied, an effective staggered field is generated through the DM interaction. In fact, we can eliminate the DM interaction by a redefinition of the spin variables [7,8]. For simplicity, let us assume the $\vec{D}$ points in the z direction. Then, the Heisenberg Hamiltonian with a DM interaction is given by

$$H = \frac{1}{2} \sum_j [J S^+_{2j-1} S^-_{2j} + J^* S^+_{2j} S^-_{2j+1} + \mathrm{H.c.}] + J \sum_j [S^z_{2j-1} S^z_{2j} + S^z_{2j} S^z_{2j+1}], \qquad (3)$$

where $S^\pm = S^x \pm iS^y$ and $J = J + iD$. By the rotation about the z axis by an alternating angle

$$S^+_{2j} \to S^+_{2j} e^{i\alpha/2}, \qquad S^+_{2j-1} \to S^+_{2j-1} e^{-i\alpha/2}, \qquad (4)$$

where $\tan\alpha = D/J$, the Hamiltonian is transformed to

$$H = \frac{1}{2} |J| \sum_j [S^+_{2j-1} S^-_{2j} + S^+_{2j} S^-_{2j+1} + \mathrm{H.c.}] + J \sum_j [S^z_{2j-1} S^z_{2j} + S^z_{2j} S^z_{2j+1}]. \qquad (5)$$

Namely, the DM interaction is eliminated, resulting in an anisotropic exchange coupling. This anisotropy would be canceled by the exchange anisotropy before the redefinition of Eq. (4), under some assumptions [8]. In any case, the resulting anisotropy would be small for Cu benzoate and is neglected in the present Letter.

When an external magnetic field is present, the Zeeman term appears in the original Hamiltonian. For example, if we apply the magnetic field in the x direction, the Zeeman term is $H_{\mathrm{Zeeman}} = -H_0 \sum_j S^x_j$ where H_0 is the external field. After the redefinition (4), the Zeeman term gives

$$-H_0 \cos\frac{\alpha}{2} \sum_j S^x_j - H_0 \sin\frac{\alpha}{2} \sum_j (-1)^j S^y_j. \qquad (6)$$

Namely, the effective staggered field of strength $H_0 \sin(\alpha/2)$ is generated in the y direction. For general directions of the DM vector $\vec{D}$ and the external field $\vec{H}_0$, the direction of the effective staggered field is $\vec{H}_0 \times \vec{D}$. If $D \ll J$, then $\alpha \sim D/J$ and the staggered field is given by $\vec{H}_0 \times \vec{D}/2$.

In Cu benzoate, a staggered field is already present before the redefinition, due to the alternating g-tensor. The total effective staggered field is obtained by the redefinition of the Zeeman term (6) together with the alternating g-tensor. For a small alternating part of the g-tensor, the total effective staggered field is given by a sum of two effects. Both effects produce a transverse staggered field (orthogonal to the direction of the applied field), apart from the small longitudinal component due to the uniform part of the off-diagonal elements of the g-tensor. We neglect the longitudinal component of the staggered field, which is actually very small in Cu benzoate.

Thus we are led to consider a one-dimensional Heisenberg Hamiltonian with mutually perpendicular uniform field H and staggered field h

$$\hat{H} = \sum_i [J\vec{S}_i \cdot \vec{S}_{i+1} - HS^x_i + h(-1)^i S^z_i], \qquad (7)$$

with $H \gg h$. It is instructive to analyze the model (7) in the standard spin-wave theory approximation (lowest order $1/s$ expansion) [9], although some of the conclusions will be modified when we take into account one-dimensional quantum fluctuations more accurately. The classical ground state is a canted antiferromagnetic structure. The canting angle measured from the z axis, θ, determined by minimizing the classical energy is the solution of $2Js\sin 2\theta - H\cos\theta + h\sin\theta = 0$. Now considering fluctuations around this classical ground state to lowest order in $1/s$ gives two branches of spin waves, in the antiferromagnetic Brillouin zone ($|k| < \pi/2$) with energies

$$E_\pm(k) = \{[2Js\cos 2\theta + H\sin\theta + h\cos\theta \pm Js(1 - \cos 2\theta) \times \cos k]^2 - [Js(\cos 2\theta + 1)\cos k]^2\}^{1/2}. \qquad (8)$$

In the case $h = 0$, the minimum energies of two modes are $E_+ = H$ and $E_- = 0$ at $k = 0$. The $-$ Goldstone mode corresponds to a precession of the spins around the x axis. A nonzero staggered field h gives this mode a finite gap. To leading order in h but all orders in H this is given by

$$E_-(0) = \sqrt{4Jsh[1 + (H^2/8J^2s^2)]}[1 - (H/4Js)^2]^{1/4}. \tag{9}$$

Note the singular dependence on h but the weak dependence on H; $E_-(0)$ is essentially independent of H until $H \approx O(Js)$. Conversely, the upper mode $E_+(0)$ depends only weakly on h but strongly on H. In the case $h = 0$, the existence of the upper mode at energy H is more rigorously established [10] without the spin-wave approximation. The upper mode E_+ is presumably observed in the experiment: the peak at higher energy $\hbar\omega \sim 0.8$ meV in Fig. 3(c) of Ref. [1] is consistent with the upper mode energy $H = 7$ T ~ 0.8 meV. Taking into account 1D critical fluctuations, the power-law behavior of the lower gap $E_-(0) \propto h^{1/2}$ is changed to $h^{2/3}$, as we will discuss below. It is reasonable to expect the weak dependence of the lower gap on H to remain true.

The low-energy behavior of the system should be well described by Abelian bosonization. In the bosonization approach, the only effects of the uniform field H is shift of the Fermi momentum k_F (i.e., the soft-mode momentum) and the renormalization of the compactification radius R. The transverse staggered field is mapped to the operator $\cos(2\pi R\tilde{\phi})$. Thus, the effective low-energy theory for the model (7) is given by the sine-Gordon model with the Lagrangian density

$$\mathcal{L} = \frac{1}{2}(\partial_\mu\phi)^2 + \text{const} \times h\cos(2\pi R\tilde{\phi}). \tag{10}$$

The operator $\cos(2\pi R\tilde{\phi})$ has dimension πR^2, and is more relevant than the exchange anisotropy. Actually, it is the most relevant operator in the system. At zero field, the system is isotropic and $R = 1/\sqrt{2\pi}$; the dimension of the staggered field operator is $1/2$ [5]. The radius R is affected mainly by the uniform field. Its effect may be estimated from the Bethe ansatz solution for the Heisenberg model under a uniform field. The dimension of the operator $\cos(2\pi R\tilde{\phi})$ is reduced to $\pi R^2 = 0.41$ at $H \sim 0.52J$ (7 T for Cu benzoate). While the uniform field does affect the low-energy excitation, the effect is not drastic. This is consistent with the spin-wave calculation. We expect the H dependence of the soft-mode momentum to be only slightly modified by the staggered field since $h \ll H$ and hence the good agreement between theory and experiment noted in [1] remains.

A standard scaling argument shows that the gap Δ is proportional to $h^{1/(2-d)}$ where d is the dimension of the relevant operator and h is the total effective staggered field. If we neglect the effect of the uniform field H, $d = 1/2$, and thus $\Delta \sim h^{2/3} = h^{0.67}$. Precisely speaking, there is a log correction due to the presence of the marginal operator [11]: $\Delta \sim h^{2/3}|\ln h|^{1/6}$. The log correction is not significant in the present case. While the field-theory argument gives the exponent for the gap, it does not determine the magnitude. Thus, we studied numerically the excitation gap of the $S = 1/2$ Heisenberg antiferromagnetic chain under a staggered field (but with no uniform field), by Lanczos method up to 22 sites. The result is shown in Fig. 1. We found that, for small staggered field h, the lowest excitation gap to the total magnetization 1 sector behaves consistently with the field-theory prediction. We fixed the proportionality constant as

$$\Delta = 1.85(h/J)^{2/3}J|\ln(h/J)|^{1/6} \tag{11}$$

from the numerical result.

Since the effective staggered field h is proportional to the applied field H_0, the gap should be proportional to $H_0^{2/3}$. This is in a good agreement with the experiment [1] in which the gap is found to scale as $H_0^{0.65(3)}$ for three directions of the magnetic field. This supports our basic claim that the field-induced gap is due to the effective staggered field. If we include the change in R^2 due to the uniform field, the exponent changes to 0.63 at $H_0 = 7$ T. Taking an average, the agreement with the experiment is improved. Moreover, the sine-Gordon model (10) is integrable. The elementary excitations are given by soliton, antisoliton, and soliton-antisoliton bound states ("breathers"), and their exact mass ratios are available [12,13]. (For an introduction, see, for example, Ref. [14].) At the isotropic point $R = 1/\sqrt{2\pi}$, there are two kinds of breathers, and the mass of the lighter breather is degenerate with the soliton/antisoliton, forming a triplet. The mass ratio of the triplet and the singlet (heavier breather) is $1 : \sqrt{3}$. When the SU(2) symmetry is broken, the triplet is split and the mass ratio for light breather (antisoliton)soliton and heavy breather

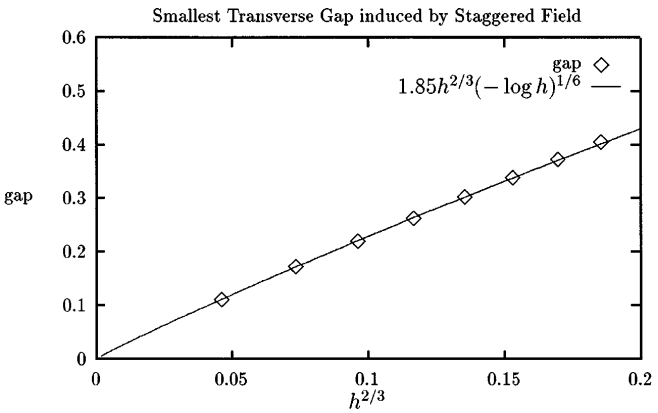

FIG. 1. The lowest excitation gap to $\sum S^z = 1$ sector in the Heisenberg antiferromagnetic chain, induced by the staggered field h. The gap is obtained by an extrapolation of finite-size gap by Lanczos method up to 22 sites. Both gap and h are measured in unit of the coupling constant J. The data are well fit by the field-theory prediction $h^{2/3}|\ln h|^{1/6}$, with a coefficient 1.85.

is $2\sin[\pi^2R^2/(4-2\pi R^2)] : 1 : 2\sin[\pi^2R^2/(2-\pi R^2)]$. For $H_0 = 7$ T, $\pi R^2 = 0.41$ and the ratio is $0.79 : 1 : 1.45$. This is close to the ratio of three peaks observed in Figs. 3(c) and 3(d) of Ref. [1], at 0.17, 0.22, and 0.34 meV ($0.77 : 1 : 1.55$).

In the experiment, the magnitude of the staggered field due to the alternating g-tensor depends on the direction of the applied field. The ratio is $0.019 : 0.053 : 0.049$ for field applied in a'', b, c'' directions. This can be understood in our theory, because the proportionality constant between h and H_0 depends on the field direction. If we only consider the staggered g-tensor effect, the ratio of the gap is $0.019^{2/3} : 0.053^{2/3} : 0.049^{2/3} \sim 1 : 2.0 : 1.9$. This does not explain the observed ratio of the gap $0.55 : 1 : 2.0$. In particular, the order of gap for b and c'' is reversed. Thus, it is necessary to include the effective staggered field due to the DM interaction, in order to explain the gap.

In general, the magnitude of $\vec{D}$ is argued to be of order of $(\Delta g/g)J$ where Δg is a shift of g factor in the crystal [6]. In Cu benzoate, $\Delta g/g \sim 0.1$. While a more precise estimate of $\vec{D}$ in Cu benzoate is unknown, it should be in ac plane (or equivalently $a''c''$ plane) from the crystal structure [2,6]. Thus $\vec{D}$ is specified by two parameters, for example, by $D = |\vec{D}|$ and the angle χ between $\vec{D}$ and a'' axis. We first determined $\vec{D}$ so that it reproduces the experimentally observed angle dependence of the gap $a'' : b : c'' = 0.55 : 1 : 2.0$. We found two solutions: $(\chi, D) = (0.22, 0.034J)$ and $(-0.0066, 0.10J)$. (χ is in radians.) Both directions are close to a'' axis (or a' axis) as claimed in Ref. [2]. Moreover, both values of D are consistent with the general estimate $D \sim (\Delta g/g)J \sim 0.1J$. Thus, it has been shown that a reasonable magnitude of the DM interaction can give the angle dependence observed in the experiment.

We can also estimate the magnitude of the gap from our theory, using (11). For the former solution $(\chi, D) = (0.22, 0.034J)$, the gap for $H_0 = 7$ T applied in the b direction is $0.096J$. For the latter solution $(\chi, D) = (-0.0066, 0.10J)$, the gap for the same field is $0.15J$. Both give a correct order of magnitude compared to the experimental value ~ 0.2 meV $= 0.13J$ in Ref. [1]. More quantitative comparison would require further analysis of the specific heat data, since aspects of the treatment in Ref. [1] could be questioned. They fit the low-temperature specific heat by six independent massive bosons with the same gap Δ, but the sine-Gordon theory predicts four elementary excitations with different masses, as discussed. While their estimate presumably gives a correct order of magnitude, the precise value would be changed by a refined analysis. Experiments with other field directions would provide a further check of our theory.

Finally, we comment on other consequences of our theory. From a scaling argument, the staggered magnetization behaves as $H_0^{1/3}$. The direction of the staggered magnetization is given by the effective staggered field. Thus our theory could be tested if the staggered magnetization is measured. Moreover, by the redefinition (4), the physical spin operator corresponds to a rotated spin operator in the Heisenberg antiferromagnet without the DM interaction. While it has no drastic effect on the neutron-scattering experiment, it affects the susceptibility measurement dramatically. The observed susceptibility $\chi_{\rm exp}$ is given by a linear combination of the uniform susceptibility χ_u and the staggered one χ_s of the Heisenberg model. Since the latter diverges at low temperature, $\chi_{\rm exp}$ would also diverge at low temperature. This could explain the enhancement of the susceptibility observed in Ref. [15], though a quantitative theory would require inclusion of interchain interactions. Further discussions, including details of the arguments in the present Letter, will be given in a future publication.

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