Antiferromagnetic Resonance in a Spin-Gap Magnet with Strong Single-Ion Anisotropy

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Quasi-one-dimensional magnet NiCl$_2$·4SC(NH$_2$)$_2$ denoted as DTN remains disordered in zero magnetic field down to $T = 0$; the $S_x = 0$ ground state is separated from $S_z = \pm 1$ excitations by a gap caused by strong single-ion easy-plane anisotropy acting on the Ni$^{2+}$ ions. When a magnetic field is applied along the principal axis of anisotropy, the gap closes in a field above $B_0 = 2.18$ T and the field-induced antiferromagnetic order arises. There are two excitation branches in this field-induced phase, one of which should be the Goldstone mode. Recent studies of the excitation spectrum in the field-induced ordered phase of the DTN magnet (T. Soldatov et al., Phys. Rev. B 101, 104410 (2020)) have revealed that the Goldstone mode acquires a gap in the excitation spectrum of the field-induced phase at small deviation of the applied magnetic field from the tetragonal axis of the crystal. In this work, a simple description of both magnetic resonance branches in the ordered phase of a quasi-one-dimensional quantum $S = 1$ magnet with strong single-ion anisotropy is proposed. This approach is based on a combination of an effective strong coupling model for an anisotropic spin chain and the classical antiferromagnetic resonance theory. This description reproduces the experimental results semi-quantitatively without additional parameters.

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The NiCl$_2$·4SC(NH$_2$)$_2$ (DTN) metal-organic compound is a collective paramagnet with a gap excitation spectrum (a spin-gap magnet). Magnetic Ni$^{2+}$ ions ($S = 1$) form one-dimensional chains in this compound located along the fourfold axis of the tetragonal crystal [1, 2]. Unlike Haldane magnets, DTN has a very strong single-ion anisotropy owing to which the $S_x = 0$ ground state of the ion in zero field is substantially separated from the excited $S_z = \pm 1$ doublet. The Heisenberg exchange interaction between ions, which is weak in comparison with the single-ion anisotropy, leaves the ground state non-magnetic and makes excited $S_z = \pm 1$ states delocalized. When a magnetic field is applied, the energy of one of the excited states decreases and a field-induced antiferromagnetic order appears in a certain field because of the presence of weak interchain interactions [3, 4].

The transition of spin-gap magnets to the field-induced antiferromagnetic state is widely discussed in the context of Bose–Einstein condensation of magnons [5, 6]. One of the expected properties of the field-induced ordered phase is the existence of a gapless Goldstone excitation mode in the ordered phase. This prediction is based on the conservation of axial symmetry in a field above the gap closure field, which is often not observed in real magnets because of low crystal symmetry. The tetragonal symmetry of DTN crystals makes them one of the most suitable objects for testing this prediction.

The dynamics of low-energy excitations in DTN was studied using magnetic resonance spectroscopy [7–9]. It was found experimentally in the recent work by Soldatov et al. [9] that the gapless Goldstone mode acquires a finite frequency at a small tilt (up to 5°) of the field from the fourfold axis. The magnetic resonance frequencies in the field-induced ordered DTN phase were calculated theoretically using various approaches in [8, 10], but these descriptions did not give compact analytical expressions for the magnetic resonance frequencies and did not determine the form of their dependence on the exchange interaction and single-ion anisotropy parameters. In this work, an interpretation of the magnetic resonance frequencies in the field-induced antiferromagnetically ordered phase of the $S = 1$ quantum magnet DTN is proposed in terms of the combination of the effective model obtained in the strong coupling limit and the classical theory of antiferromagnetic resonance, which makes it possible to trace the characteristic dependence of the magnetic resonance frequencies on the parameters of the microscopic model, as well as to explain quantitatively the effects observed in a tilted field orientation and their dependence on the magnetic field.
The spin Hamiltonian for a chain of spins in DTN can be written as
\[
\mathcal{H}_{\text{chain}} = \sum_i \left( D S_i^2 + J S_i S_{i+1} - g \mu_B B S_i \right) \tag{1}
\]
with the parameters \( D = 8.9 \) K and \( J = 2.2 \) K; the strongest of the interchain exchange integrals is about an order of magnitude smaller (0.18 K), and the \( g \)-factor for the field applied along the tetragonal axis is \( g = 2.26 \) [7].

The dispersion of spin excitations for \( D \gg J \) can be found within perturbation theory for \( B \parallel Z \) in fields lower than the gap closure field. In [11], the zero field excitation spectrum is calculated up to the third order in the parameter \( J/D \) for \( S = 1 \) (a similar result was obtained for an arbitrary spin [12]), and the magnetic field can be easily taken into account since \( S_z \) remains a good quantum number. The spectrum of single-particle excitations is found exactly for fields higher than the saturation field (the calculations with allowance for interchain interactions for DTN are given in [7]).

Critical fields are the fields in which the excitation energy vanishes at the minimum of the spectrum at \( k a = \pi [7, 13] \):
\[
g \mu_B B_{c1} = D - 2J + \frac{J^2}{D} + \frac{J^3}{2D^2}, \tag{2}
g \mu_B B_{c2} = D + 4J. \tag{3}
\]

The fields \( B_{c1} \) and \( B_{c2} \) are close to each other in the limit \( D \gg J \). In this case, the spin chain in the interval of \( B_{c1} < B < B_{c2} \) can be considered within projection on two close single-ion levels with \( S_z = 0 \) and 1. Such a two-level system can be formally described by the pseudospin \( t = 1/2 \), matching \( t_z = -1/2 \) with \( S_z = 0 \) and \( t_z = 1/2 \) with \( S_z = 1 \) [13]. The spin operator transformation rules have the form
\[
S_z = t_z + 1/2, \tag{4}
S^+ = \sqrt{2} t^+. \tag{5}
\]

After this substitution, the Hamiltonian (1) is transformed at the field \( B \parallel Z \) with the accuracy linear in \( J/D \) as
\[
\mathcal{H} = 2J \sum_i \left( t_{x,i} t_{x,i+1} + t_{y,i} t_{y,i+1} + \frac{1}{2} t_{z,i} t_{z,i+1} \right) + (J + D - g \mu_B B) \sum_i t_{z,i} + N \left( \frac{2J + D - g \mu_B B}{2} \right). \tag{6}
\]

Thus, the problem was reduced to a homogeneous \( S = 1/2 \) spin chain with the strong \( XY \) anisotropy of the spin–spin interaction in the effective magnetic field \( B_{\text{eff}} = B - (J + D)/(g \mu_B) \). The effective field is zero in the field \( B_0 = (J + D)/(g \mu_B) \), which is equal to the half-sum of the critical fields in the first-order perturbation theory. It is also noteworthy that EPR-active transitions observed at \( B < B_{c1} \) in the limit \( D \gg J \) have the frequencies \( hf = \left( D + 2J + \frac{J^2}{D} - \frac{J^3}{2D^2} \pm g \mu_B B \right) \) at \( k = 0 \) and the lower branch in the paramagnetic phase in the approximation \( D \gg J \) vanishes in the field \( B_{0}^{(\text{PM})} = \left( D + 2J + \frac{J^2}{D} - \frac{J^3}{2D^2} \right) / (g \mu_B) \), which is close to \( B_0 \) but not does not coincide with it. Analogously, the extrapolation of the high-field EPR mode (\( k = 0 \)) to zero at \( B > B_{c2} \), \( hf = g \mu_B B - D \), vanishes in the field \( B_{0}^{(\text{HF})} = D / (g \mu_B) \) [7], which differs from \( B_0 \) and \( B_{c2} \).

A similar transformation also reduces the interchain exchange interaction to the form of the interaction with \( XY \) anisotropy. Then, a three-dimensional ordered antiferromagnet with strong easy-plane anisotropy in zero effective field equivalent to the original problem is obtained in the field \( B_0 \) at \( T = 0 \).

An equivalent problem of an easy-plane antiferromagnet in the field \( B_{0} = B - B_0 \) applied along the \( Z \) axis is obtained when the applied field deviates from \( B_0 \). In this case, the fields \( B_{c1} \) and \( B_{c2} \) symmetrically located with respect to \( B_0 \) are the saturation fields for the equivalent model. The eigenfrequencies (antiferromagnetic resonance frequencies) for the easy-plane antiferromagnet with strong anisotropy can be calculated within the sublattice model [14, 15]: one eigenfrequency remains zero, and the other depends on the field in the gapped manner \( f = \sqrt{(\gamma B_{\text{eff}}^2)^2 + \Delta^2} \), where \( \gamma = g \mu_B / h \) is the gyromagnetic ratio. The first mode corresponds to the expected Goldstone mode, and the second mode corresponds to the frequency of the spectral branch with a gap of 78 GHz at \( T = 0.45 \) K observed in [8, 9].

Within the sublattice model, neglecting weak interchain interactions, the gap \( \Delta \) can be derived from the \( XY \) anisotropy of the effective model (6) and the order parameter [13–15]:
\[
\Delta = \gamma \sqrt{2H_A H_E}. \tag{7}
\]
Here, \( H_A = J \mu / (g \mu_B^2) \) and \( H_E = 4J \mu / (g \mu_B^2) \) are the anisotropy and exchange fields, respectively, where \( \mu \) is the average sublattice magnetization. Hence, \( \Delta = 2\sqrt{2}(J/h)\langle t_z \rangle \), where \( \langle t_z \rangle \) is the mean pseudospin projection on the \( XY \) plane. The substitution of the relation between the spin and pseudospin in the form of Eq. (5) into the last expression for the gap gives the following expression for the gap in terms of the transverse component of the real spin:
\[
\Delta = \frac{2J}{h} \langle S_\perp \rangle. \tag{8}
\]
Thus, the gap \( \Delta \) for the upper magnetic resonance branch in the ordered phase is mainly determined by the intrachain exchange integral \( J \), while the position
of the minimum of this branch is mainly determined by the single-ion anisotropy constant $D$.

The temperature dependence of the gap $\Delta$ was studied in [8]. These data can be used to reconstruct the temperature dependence of the order parameter at a field of 8 T (Fig. 1). The result obtained is qualitatively consistent: the determined order parameter values are $\langle S_z \rangle < 1$.

The case where the magnetic field is tilted from the $Z$ axis by a small angle $\Theta$ towards the $X$ axis is now considered. The field-induced antiferromagnetically ordered state does not disappear at small tilt angles of the field from the $Z$ axis, although the critical fields change slightly [16]. The transformation to pseudospin operators reduces the Zeeman part of the Hamiltonian (6) up to the term linear in $\Theta$ to the form

$$\mathcal{H}_Z = -g\mu_B B_{\text{eff}} \sum_i z_{i}^2 - \sqrt{2} g\mu_B B\Theta \sum_i f_{z,ir}.$$  

(9)

Thus, an additional contribution determined by the total external field applied in the easy plane arises. This contribution is assuming small: $g\mu_B B\Theta = D\Theta \ll J \ll D$.

If the external field is $B_0$, there is no effective field component along the symmetry axis, and an equivalent problem of an easy plane antiferromagnet in a field applied in a plane arises. The eigenfrequencies of such an antiferromagnet [14, 15] are $f_1 = \gamma B$ and $f_2 = \Delta$. Thus, the frequency of the lower branch of the magnetic resonance spectrum arising in the field $B_0 = (B_{c1} + B_{c2})/2$ is quantitatively given by the expression

$$f_1(\Theta) = \sqrt{2}\gamma B_0 \Theta.$$  

(10)

It should be emphasized that, unlike the interpretation of the gap in the upper magnetic resonance branch, this result is independent of the field-induced order parameter.

When the amplitude of the external field deviates from $B_0$, the effective field is tilted in the $XZ$ plane: $B_{\text{eff}} = \sqrt{2}B\Theta; (B - B_0)$, and one can use the known expression [14]

$$\frac{(\gamma B_{\text{eff},x})^2}{f^2} + \frac{(\gamma B_{\text{eff},z})^2}{f^2 - \Delta^2} = 1.$$  

(11)

Hence, the square of the magnetic resonance frequencies are given by the expression

$$f_1^2 = \frac{1}{2} \left[ \Delta^2 + 2(\gamma B\Theta)^2 + \gamma^2(B - B_0)^2 \right] \pm \sqrt{\left[ \Delta^2 + 2(\gamma B\Theta)^2 + \gamma^2(B - B_0)^2 \right]^2 - 8\gamma^2(\gamma B\Theta)^2}.$$  

(12)

In the proposed model, the classical mean-field approximation for a two-sublattice antiferromagnet is in fact used to describe ordering. In this approximation, the magnetization of the antiferromagnet should depend linearly on the field up to the saturation field. Because of the strong one-dimensionality of DTN, the magnetization changes nonlinearly when approaching critical fields [4, 6, 7], and deviations from the linear dependence appear asymmetrically with increasing and decreasing field. Such an asymmetry of the properties of a real magnet in comparison with the model predictions is associated with the limited accuracy of the approximation linear in $J/D$. Thus, the proposed model is applicable only in the immediate vicinity of the field $B_0$, which can be estimated as the field region in which the field dependence of the magnetization [7] is linear: this is the field range from 4 to 10 T. To expand the region of applicability of the model, it is necessary to simultaneously take into account the higher orders of $J/D$ when transforming to the pseudospin representation and the one-dimensionality of the DTN spin subsystem. However, it can be predicted that the frequency of the lower branch vanishes at the critical fields $B_{c1}$ and $B_{c2}$, which are the saturation fields of the equivalent model.

The model curves are shown in Fig. 2 in comparison with experimental data from [9]. The model curves were obtained with the parameters $D = 8.9$ K, $J = 2.2$ K, $g = 2.26$ ($\gamma = 31.6$ GHz/T) [7], for which $B_{c1} = 7.3$ T (the half-sum of the experimental $B_{c1}$ and $B_{c2}$ values is 7.4 T) and the experimentally measured
value \( \Delta = 78 \text{ GHz} \) \cite{8, 9}, without additional fitting parameters. The model curves were calculated for the field tilt angles of 0°, 1°, 3°, and 6° indicated for the experimental data in \cite{9}; these angles are determined in the experiment with an accuracy of about 1°–2°. It can be seen that there is good agreement between the model and experimental data.

To summarize, an illustrative model has been obtained to describe the antiferromagnetic resonance frequencies in the quasi-one-dimensional magnet NiCl\(_2 \cdot 4\text{SC(NH}_2\text{)}_2\) with strong easy plane anisotropy, including the case of the magnetic field slightly tilted with respect to the symmetry axis.

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