Spin dynamics of $NiCl_2$-$4SC(NH_2)_2$ in the field-induced ordered phase

S. A. Zvyagin,[1] J. Wosnitza,[1] A. K. Kolezhuk,[2,*] V. S. Zapf,[3] M. Jaime,[3] A. Paduan-Filho,[4] V. N. Glazkov,[5] S. S. Sosin,[5] and A. I. Smirnov[5]

[1]*Dresden High Magnetic Field Laboratory (HLD), Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany*
[2]*Institut für Theoretische Physik C, RWTH Aachen, 52056 Aachen, Germany*
[3]*National High Magnetic Field Laboratory, Los Alamos National Laboratory, MS-E536, Los Alamos, New Mexico 87545, USA*
[4]*Instituto de Fisica, Universidade de Sao Paulo, 05315-970 Sao Paulo, Brazil*
[5]*P.L. Kapitza Institute for Physical Problems RAS, 117334 Moscow, Russia*

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$NiCl_2$-$4SC(NH_2)_2$ (known as DTN) is a spin-1 material with a strong single-ion anisotropy that is regarded as a new candidate for Bose–Einstein condensation (BEC) of spin degrees of freedom. We present a systematic study of the low-energy excitation spectrum of DTN in the field-induced magnetically ordered phase by means of high-field electron spin resonance measurements at temperatures down to 0.45 K. We argue that two gapped modes observed in the experiment can be consistently interpreted within a four-sublattice antiferromagnet model with a finite interaction between two tetragonal subsystems and unbroken axial symmetry. The latter is crucial for the interpretation of the field-induced ordering in DTN in terms of BEC.

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I. INTRODUCTION

Field-induced phase transitions in magnets have recently received a considerable amount of attention,[1–7] particularly in the context of the so-called Bose–Einstein condensation (BEC) of spin degrees of freedom. In accordance to the BEC scenario, for a uniform gas of identical particles, at some finite temperature T_c when the de Broglie wavelength becomes comparable to the average distance between the particles, a macroscopic fraction of the gas can be "condensed" into a single coherent quantum state and BEC occurs. It is worth mentioning that although there are some important arguments[8] about the interpretation of the field-induced transitions in magnets in terms of BEC (based on its original, canonical definition[9]), the application of this formalism to grand-canonical ensembles of quasiparticles in magnets appears to be widely accepted. An important property of BEC is the presence of $U(1)$ symmetry, which corresponds to the global rotational symmetry of the bosonic field phase. Below T_c, the $U(1)$ symmetry spontaneously gets broken, the wave function of the condensate gets coherent on a macroscopic scale and, as a consequence, a gapless Goldstone mode is acquired. The model of BEC in magnets assumes that the spin Hamiltonian is axially symmetric with respect to the magnetic field, requiring $U(1)$ rotational symmetry above T_c.

In accordance with mean-field BEC theory, the phase-diagram boundary for a three-dimensional magnet should obey a power-law dependence, $H-H_{c1}\sim T_c^{3/2}$, where H_{c1} is the first critical field as $T\to 0$. Importantly, critical exponents extracted from phase diagrams alone cannot be regarded as sufficient criteria for identifying field-induced transitions as BEC. For instance, the reopening of the energy gap in the excitation spectrum of $TlCuCl_3$ (which, based on the analysis of critical exponents, was regarded as the best realization of BEC of spin degrees of freedom in magnets[3]) in the field-induced ordered state[10] is a clear evidence for a broken uniaxial symmetry, which rules out the description of the magnetic ordering in this compound in terms of BEC.

$NiCl_2$-$4SC(NH_2)_2$ (known as DTN) is a gapped $S=1$ system with a single-ion anisotropy D dominating over the exchange coupling J (Refs. 6 and 7) and is a new candidate for BEC of spin degrees of freedom.[11] Although below $T_c\leqslant 1.2$ K DTN exhibits a field-induced antiferromagnetic (AF) ordering, with critical fields $B_{c1}=2.1$ T and $B_{c2}=12.6$ T and exponents corresponding to the BEC scenario,[7] the low-energy excitation spectrum in DTN (and, correspondingly, the microscopical picture of magnetic interactions) in the field-induced ordered state still remains an open question. In the present work, we have addressed these issues experimentally by means of electron spin resonance (ESR) measurements performed at temperatures down to 0.45 K. Two gapped modes were observed. Based on our detailed analysis, it is argued that the above excitation spectrum can be consistently interpreted within a four-sublattice AF model with an intact axial symmetry (at least on the energy scale down to 1.2 K, which corresponds to the lowest frequency used in our experiments, 25 GHz). The latter is of particular importance, being a necessary prerequisite for the interpretation of the AF ordering in DTN in terms of the BEC scenario.

DTN is characterized by the $I4$ space group[12] with a body-centered tetragonal lattice that may be viewed as two interpenetrating tetragonal subsystems (hereafter TS). At $B\parallel c$, the spin dynamics can be described by the spin Hamiltonian

$$\mathcal{H}_0=\frac{1}{2}\sum_{\boldsymbol{n},\boldsymbol{\delta}} J_{\boldsymbol{\delta}}\boldsymbol{S}_{\boldsymbol{n}}\cdot\boldsymbol{S}_{\boldsymbol{n}+\boldsymbol{\delta}}+D\sum_{\boldsymbol{n}}(S_{\boldsymbol{n}}^z)^2-h\sum_{\boldsymbol{n}}S_{\boldsymbol{n}}^z+\mathcal{H}_{\rm int}, \quad (1)$$

where $\boldsymbol{S}_{\boldsymbol{n}}$ are spin-1 operators at site $\boldsymbol{n}$, the vectors $\boldsymbol{\delta}$ connect the site $\boldsymbol{n}$ to its nearest neighbors within the same subsystem, $h=g_c\mu_B B$ is the Zeeman term, and $\mathcal{H}_{\rm int}$ describes (yet unspecified) additional interactions. Assuming that the latter are much weaker than the interchain interaction within TS, the Hamiltonian parameters were estimated as $D=8.9$ K, $J_c=2.2$ K, $J_{a,b}=0.18$ K, and $g_c=2.26$.[13]

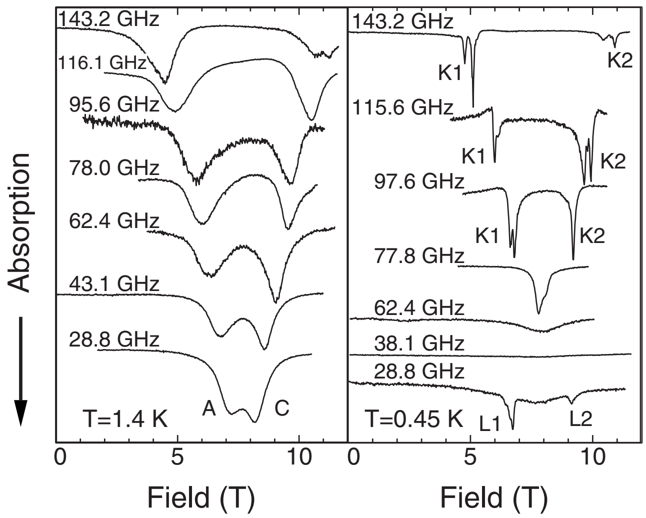

FIG. 1. Typical ESR spectra of DTN in the quantum-disordered phase taken at $T=1.4$ K (left) and in the ordered phase taken at $T=0.45$ K (right). The spectra are offset and rescaled for clarity.

II. EXPERIMENTAL RESULTS

The ESR measurements were done at the Kapitza Institute using a transmission-type ESR spectrometer equipped with a cylindrical multimode resonator and a ^{3}He cryostat. High-quality single-crystalline DTN samples from the same batch as in Ref. 13 were used. The magnetic field was applied along the tetragonal c axis.

The examples of the ESR spectra taken at 1.4 K are shown in Fig. 1 (left), while the ESR temperature evolution is illustrated in Fig. 2. The corresponding frequency-field dependencies of magnetic excitations are presented in Fig. 3. Two ESR lines (denoted as A and C) have been observed at 1.4 K. Comparison with the data of Ref. 13 (filled gray circles, Fig. 3) reveals that mode A continues smoothly from

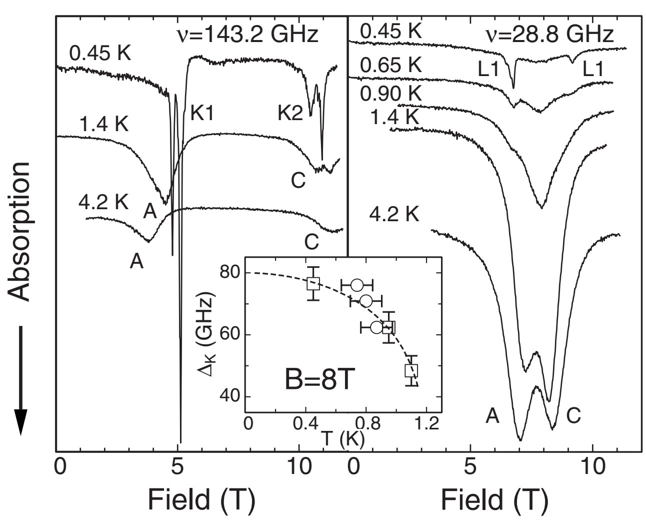

FIG. 2. Temperature evolution of ESR spectra taken at $\nu=143.2$ GHz (left) and 28.8 GHz (right); the absorption scale is retained at each frequency. The inset shows the temperature evolution of the energy gap Δ_K of the K mode, at a magnetic field of 8 T (the dashed line is a guide to the eyes).

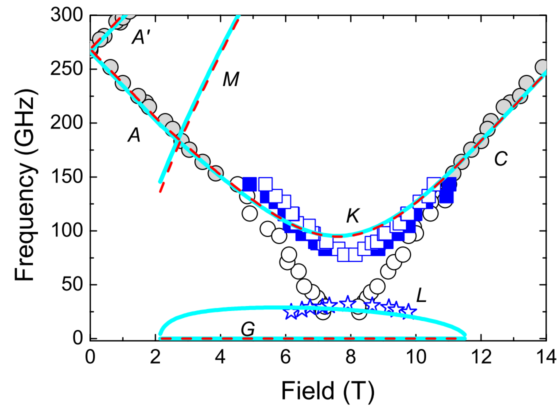

FIG. 3. (Color online) The frequency-field dependence of ESR in DTN measured at $T=1.4$ K (open circles) and 0.45 K (squares and stars). Filled gray circles denote the high frequency data ($T=1.6$ K) taken from Ref. 13. The dashed (red) lines correspond to results of calculations for the simplest axially symmetric two-sublattice AF model with parameters $g_c=2.26$, $D=9.4$ K, and $\tilde{J}_0=2.0$ K. The solid (cyan) lines correspond to results of model calculations assuming $d=0.02$ K (see text for details).

the ESR line in the low-field disordered phase, while mode C corresponds to single-magnon excitations in the high-field phase.

Several important features have been observed at lower temperatures. Upon cooling, modes A and C shift toward each other (Fig. 2). While at a temperature of 1.4 K they seem to cross at zero frequency in the vicinity of $B\sim 8$ T, in the low-temperature AF ordered phase, they are converted into a new gapped mode K. This mode exhibits a slight but distinct splitting, the origin of which will be discussed below (the corresponding frequency-field dependence of the resonances is denoted in Fig. 3 by pairs of open and closed squares). The temperature dependence of the gap Δ_K at $B=8$ T has been obtained by measuring the temperature of the maximum absorption at a fixed field (i.e., by the observation of so-called "temperature resonance") or by using a conventional ESR procedure, recording transmission vs magnetic field at different temperatures (circles and squares in Fig. 2, inset, correspondingly). The diminishing of Δ_K upon warming can be explained by the decrease of the order parameter. The low-temperature spectrum demonstrates one more set of resonances appearing at low frequencies (mode L, denoted by stars in Fig. 3). Unlike mode K, the integrated intensity of line L is 50–100 times smaller than that of modes outside the AF phase, e.g. modes A and C.

III. DISCUSSION

The observation of the gapped mode L and splitting of mode K in a field range of 6–10 T clearly indicates the presence of additional interactions that are not accounted for in the simplest axially symmetric two-sublattice AF model [which would have the Goldstone mode as its lowest-energy excitation and a single mode K as the next excitation branch, as indicated by the dashed (red) lines in Fig. 3]. To gain further insight, we have studied several possible mechanisms that might cause gaps in the ESR excitation spectrum.

To do so, we have considered the model [Eq. (1)] with various additional interactions $\mathcal{H}_{\text{int}}$, using the mean-field approach outlined below. Assuming the wave function to be a product of single-spin coherent states parametrized by a pair of two-component real vectors $\boldsymbol{u}$, $\boldsymbol{v}$,

$$|\psi\rangle = s|t_0\rangle + \sum_{j=x,y}(u_j + iv_j)|t_j\rangle, \quad s=(1-u^2-v^2)^{1/2},$$

where the spin-1 states are $|0\rangle = |t_0\rangle$ and $|\pm\rangle = \mp\frac{1}{\sqrt{2}}(|t_x\rangle \pm i|t_y\rangle)$, one obtains the effective Lagrangian in the form $\mathcal{L}=\hbar\Sigma_{\mathbf{n}}(\boldsymbol{u_n}\cdot\partial_t\boldsymbol{v_n}-\boldsymbol{v_n}\cdot\partial_t\boldsymbol{u_n})-\langle\mathcal{H}\rangle$, with

$$\langle\mathcal{H}\rangle = \sum_{\boldsymbol{n}}\{D(u_{\boldsymbol{n}}^2+v_{\boldsymbol{n}}^2) - 2\boldsymbol{h}\cdot(\boldsymbol{u_n}\times\boldsymbol{v_n})\} + 2\sum_{\langle \boldsymbol{nn}'\rangle} J_{\boldsymbol{n}-\boldsymbol{n}'}\{(\boldsymbol{v_n}\cdot\boldsymbol{v_{n'}})(s_{\boldsymbol{n}}s_{\boldsymbol{n}'}+\boldsymbol{u_n}\cdot\boldsymbol{u_{n'}}) - (\boldsymbol{u_n}\cdot\boldsymbol{v_{n'}})(\boldsymbol{v_n}\cdot\boldsymbol{u_{n'}})\} + \langle\mathcal{H}_{\text{int}}\rangle, \tag{2}$$

where $\langle \boldsymbol{nn}'\rangle$ denotes summation over nearest neighbors within the corresponding TS. For weak fields, the static mean-field solution is $\boldsymbol{u},\boldsymbol{v}=0$. However, at $B>B_{c1}$, one obtains a nontrivial solution with finite $\boldsymbol{u}$ and $\boldsymbol{v}$ determined by the minimization of $\langle\mathcal{H}\rangle$, which describes the in-plane AF order and finite magnetization along the z axis. Linearizing around the static solution and solving the equations of motion, one can find the excitation energies $\varepsilon_{\boldsymbol{k}}$. Outside the AF phase, the ESR modes correspond to $\varepsilon_{\boldsymbol{k}=0}$, while inside the ordered phase, due to the folding of the Brillouin zone, one has the additional transitions at $\boldsymbol{Q}_B=(\pi/a,\pi/b,\pi/c)$ with energies $\varepsilon_{\boldsymbol{k}=\boldsymbol{Q}_B}$.

First, we have considered the possibility of axial symmetry breaking, caused either by rhombic in-plane anisotropy or by the Dzyaloshinskii–Moriya (DM) interaction inside a TS, with the DM vector $\boldsymbol{d}$ deviating from the anisotropy c axis (note that DM is generally allowed in DTN due to the absence of inversion symmetry[14]). In both cases, the axial symmetry breakdown would open a gap in the excitation spectrum, "lifting" the Goldstone mode. Even so, this mode corresponds to a coherent collective excitation of the magnon condensate below T_c and thus would be expected to be particularly strong in comparison with ESR excitations in the disordered phase. As mentioned, the gapped mode L observed in our experiments is much less intense than ESR absorptions above T_c, raising questions about the above scenarios. In addition, the rhombic in-plane anisotropy would necessarily cause splitting of the doublet at $B=0$ (roughly of the same strength as the maximum energy of the L mode), which was not observed in the experiment. It is worth mentioning that the DM term is cubic in $\boldsymbol{u}$, $\boldsymbol{v}$, so it does not contribute to the quadratic spectrum at $B<B_{c1}$ and thus does not produce mode splitting at $B=0$. However, a finite in-plane component of $\boldsymbol{d}$ (e.g., d_y) contributes to the energy as $W_{DM}=\frac{1}{2}\Sigma_{\boldsymbol{n}\delta}\eta_{\boldsymbol{n}}d_y(\boldsymbol{S_n}\times\boldsymbol{S}_{\boldsymbol{n}+\delta})_y$, where $\eta_{\boldsymbol{n}}=\pm1$ for sites $\boldsymbol{n}$ belonging to the different magnetic sublattices (inside the same TS). Close to the fully spin-polarized state, this contribution provides an energy gain linear in the AF order parameter, while the corresponding Zeeman energy loss is quadratic, so AF order is favored for arbitrarily large B. Consequently (and this is of particular importance for our analysis), such a symmetry-breaking DM term would lead to the absence of the second critical field B_{c2}, which is incompatible with the results of Refs. 6 and 7.

Here, we argue that a natural explanation of all available experimental results is possible if we take into account a weak isotropic corner-center interaction of magnetic ions in the body-centered tetragonal lattice, i.e., an interaction between TS that preserves the axial symmetry. In case of such interactions in addition to conventional (relativistic) modes, modes with antiphase oscillations of two interacting AF sublattices (exchange modes) should be present. Having much weaker coupling to the microwave field,[15] exchange modes should be less intensive than relativistic modes. In accordance to our observations, the gapped mode L would then be an exchange mode, coexisting with the lowest-energy relativistic mode.

The physically simplest scenario would correspond to the isotropic "corner-center" exchange. However, the theoretical analysis of such a model is very difficult; if, as indicated by previous studies,[13] the exchange interaction within each TS is AF, then the system is highly frustrated and its mean-field ground state at $B>B_{c1}$ is infinitely degenerate. This degeneracy may be lifted by quantum fluctuations or by additional interactions. For that reason, we would like to illustrate the effect of corner-center coupling by assuming a finite DM interaction between the TS, which already lifts the degeneracy at the mean-field level,

$$\mathcal{H}_{\text{int}} = \sum_{\boldsymbol{nn}'}\eta_{\boldsymbol{n}}\eta_{\boldsymbol{n}'}\boldsymbol{d}\cdot(\boldsymbol{S}_{A,\boldsymbol{n}}\times\boldsymbol{S}_{B,\boldsymbol{n}'}), \tag{3}$$

where the DM vector $\boldsymbol{d}$ is along the c axis and A, B denote the two TSs. Such interaction favors a 90° angle between the AF order parameters of the subsystems. The static mean-field solution at $B>B_{c1}$ is then

$$\begin{pmatrix}\boldsymbol{u}_{A,\boldsymbol{n}} & \boldsymbol{u}_{B,\boldsymbol{n}}\\ \boldsymbol{v}_{A,\boldsymbol{n}} & \boldsymbol{v}_{B,\boldsymbol{n}}\end{pmatrix} = \eta_{\boldsymbol{n}}\begin{pmatrix}u_0\hat{\boldsymbol{x}} & u_0\hat{\boldsymbol{y}}\\ v_0\hat{\boldsymbol{y}} & v_0\hat{\boldsymbol{x}}\end{pmatrix}, \tag{4}$$

and the excitation energies $\varepsilon_{\boldsymbol{k}}$ are obtained from the secular equation $\det(R)=0$, with

$$R=\begin{bmatrix} F & U\\ U^{\dagger} & F\end{bmatrix},$$

where

$$F=\begin{bmatrix} -D+W_1 & 0 & i\varepsilon_{\boldsymbol{k}} & -h+W_4\\ 0 & -D+W_3 & H+W_2 & i\varepsilon_{\boldsymbol{k}}\\ -i\varepsilon_{\boldsymbol{k}} & h+W_2 & -D+W_5 & 0\\ -H+W_4 & -i\varepsilon_{\boldsymbol{k}} & 0 & -D+W_6\end{bmatrix}.$$

The matrix U describes the intersubsystem interaction,

$$U = 4\tilde{d}_k \begin{bmatrix} -s_0^2 & 0 & 0 & 0 \\ 0 & s_0^2 - 2v_0^2 + v_0^4/s_0^2 & -u_0v_0(1 - v_0^2/s_0^2) & 0 \\ 0 & -u_0v_0(1 - v_0^2/s_0^2) & u_0^2v_0^2/s_0^2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

and the following shorthand notations have been used:

$$W_1 = -4s_0^2\tilde{J}_k + W_6, \quad W_2 = u_0v_0(\tilde{f}_k - \tilde{g}_k),$$

$$W_3 = 4\tilde{J}_k(2u_0^2 - 1) + v_0^2(3\tilde{f}_k - \tilde{g}_k), \quad W_4 = 4u_0v_0\tilde{J}_0,$$

$$W_5 = +v_0^2\tilde{f}_{\boldsymbol{k}} - u_0^2\tilde{g}_{\boldsymbol{k}}, \quad W_6 = -4v_0^2(\tilde{J}_0 + \tilde{d}_0),$$

with $\tilde{J}_{\boldsymbol{k}} = \Sigma_{\boldsymbol{\lambda}=\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}} J_{\boldsymbol{e}} \cos(\boldsymbol{k}\cdot\boldsymbol{\lambda})$, $\tilde{d}_0 = 4d$, and

$$\tilde{d}_{\boldsymbol{k}} \equiv (\tilde{d}_0/8) \prod_{\boldsymbol{\lambda}=\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}} [1 - \exp(i\boldsymbol{k}\cdot\boldsymbol{\lambda})],$$

$$\tilde{f}_{\boldsymbol{k}} = 4(\tilde{J}_{\boldsymbol{k}} - \tilde{J}_0 - \tilde{d}_0), \quad \tilde{g}_{\boldsymbol{k}} = (4v_0^2/s_0^2)(\tilde{J}_{\boldsymbol{k}} + \tilde{J}_0 + \tilde{d}_0).$$

The results of model calculations using $g_c = 2.26$, $D = 9.4$ K, $\tilde{J}_0 = 2.0$ K, and $d = 0.02$ K are shown in Fig. 3 by solid (cyan) lines. Due to a finite interaction between the two TSs (the term d), the low-energy mode is split into a doublet with a gapped upper component and a zero frequency lower component. One can see that the model qualitatively describes frequency-field dependencies of all observed ESR modes assuming the existence of a gapless Goldstone mode G, which cannot be detected experimentally. It is important to mention that it was not possible to fit the frequency-field dependence of magnetic excitations in DTN in the AF phase using the set of parameters obtained in Ref. 13, although they are very close to those used in our calculations. This discrepancy mainly stems from neglecting quantum fluctuations in the mean-field-theory approach used in this Brief Report. In the above calculation, the mode K (determined by $\varepsilon_{\boldsymbol{k}=0}$) comes out doubly degenerate, which is an artifact of the model assumption on purely DM inter-TS interaction, making the interaction matrix U vanish at $\boldsymbol{k} = 0$. Any finite symmetric exchange interaction between the TS will be sufficient to lift this degeneracy and thus will explain the observed slight splitting of the K mode. The theory also predicts the existence of a third ESR mode M in the AF phase (Fig. 3), which corresponds to the second magnon branch at $\boldsymbol{k} = \boldsymbol{Q}_B$; this mode could not be observed in the present study due to the limited frequency range.

In summary, high-field ESR studies of magnetic excitations in the field-induced ordered phase of DTN have been performed at frequencies down to 25 GHz. Two gapped modes were observed in the ESR spectrum. Our experimental observations can be consistently interpreted within the four-sublattice AF model with an intact axial symmetry, which is of crucial importance for the interpretation of the field-induced ordering in DTN in terms of BEC of spin degrees of freedom.

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*On leave from Institute of Magnetism, National Academy of Scineces and Ministry of Education, 03142 Kiev, Ukraine.

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