Magnetic and thermodynamic properties of $Ni(C_{10}H_8N_2)_2Ni(CN)_4 \cdot H_2O$: A $S=1$ Heisenberg antiferromagnetic chain with strong in-plane anisotropy and subcritical exchange coupling

M. Orendáč, E. Čižmár, A. Orendáčová, J. Černák, and A. Feher
Faculty of Science, P. J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia

M. W. Meisel
Department of Physics and Center for Ultralow Temperature Research, University of Florida, P.O. Box 118 440, Gainesville, Florida 32611-8440

K. A. Abboud
Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200

S. Zvyagin
Institute for Low Temperature Physics and Engineering, 47 Lenin Avenue, 310164 Kharkov, Ukraine and Physikalisches Institut der J. W. Goethe Universität, Robert-Mayer-Strasse 2-4, 60054 Frankfurt, Germany

M. Sieling, T. Rieth, and B. Lüthi
Physikalisches Institut der J. W. Goethe Universität, Robert-Mayer-Strasse 2-4, 60054 Frankfurt, Germany
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The results of experimental studies of the magnetic and thermodynamic quantities and ESR data of a magnetic chain compound $Ni(C_{10}H_8N_2)_2Ni(CN)_4 \cdot H_2O$ are reported. The system is identified as an $S=1$ planar Heisenberg antiferromagnetic chain with subcritical exchange coupling and strong in-plane anisotropy. The influence of in-plane anisotropy is discussed with respect to the validity of a theoretical model proposed for $S=1$ Heisenberg chains with strong planar anisotropy. The analysis suggests that in-plane anisotropy should be considered in any attempt to find a compound potentially located at the boundary between the Haldane and large-D phases.

Antiferromagnetic quantum spin chains have been the subject of intense theoretical and experimental studies since Haldane's prediction about the difference between the integer and half-integer spin chains.[1] Integer spin chains were predicted to possess an energy gap which persists in the presence of a weak easy-plane anisotropy D, but is expected to vanish at a critical value of the anisotropy constant $D_c=J$, where J is an exchange coupling constant.[2] Nevertheless, a gap of a different nature reappears above the critical value and is present in both antiferromagnetic and ferromagnetic chains. For systems with strong planar anisotropy (the so-called large-D phase), the concept of (anti)excitons as the elementary excitations from the singlet-ground state was proposed in the framework of a strong-coupling theory.[3] The exciton dispersions proved useful for the calculation of the specific heat at very low temperatures within a dilute-exciton approximation. This result was applied for the analysis of the specific heat of $Ni(C_2H_8N_2)_2Ni(CN)_4$ (hereafter abbreviated as NENC).[4] These results stimulated the extension of the theoretical model to provide predictions which would go beyond the low temperature region and would involve the effect of external magnetic field and in-plane anisotropy E, which is typically present in real systems.[5] The corresponding theoretical predictions were in turn used for the reanalysis of NENC specific heat and susceptibility data which reinforced the identification of NENC as an $S=1$ Heisenberg antiferromagnetic chain with strong planar and weak in-plane anisotropy.[6] In this report, we discuss the influence of in-plane anisotropy on the magnetic properties of large-D systems which may be located in the vicinity of the boundary between the Haldane and large-D phases. To this end, we studied the ESR spectrum, specific heat, susceptibility, and magnetization of $Ni(C_{10}H_8N_2)_2Ni(CN)_4 \cdot H_2O$ (hereafter abbreviated as NBYC) which we identify as an $S=1$ Heisenberg antiferromagnetic chain with strong in-plane anisotropy ($E>|J|$). The analysis of the experimental results suggests that the low temperature ($T \approx |J|/k_B$) predictions of the aforementioned strong-coupling model rapidly deteriorate with increasing E/D ratio.

The material NBYC crystallizes in the orthorhombic space group $Pbcn$ with cell parameters $a=14.067(1)$ Å, $b=10.1759(7)$ Å, $c=15.755(1)$ Å. The structure (see Fig. 1) consists of infinite zigzag chains containing two kinds of Ni^{2+} ions. The Ni^{2+} ion in the $[Ni(CN)_4]^{2-}$ anion is square planar coordinated and thus diamagnetic. The Ni^{2+} ion in the $[Ni(C_{10}H_8N_2)_2]^{2+}$ cation is paramagnetic and is located in the center of the distorted octahedron. Since the distance between the magnetic Ni^{2+} ions is about 10 Å, the direct exchange interaction will be of a minor importance. Nevertheless, reminiscent of the structure of NENC, superexchange can occur via the bridging units of $-CN-Ni(CN)_2-NC-$. It should be noted, that the exchange bridge is straight and consists of five nonmagnetic atoms, therefore, according to Goodenough-Kanamori rules, weak antiferromagnetic coupling can be expected. Although the separation between the chains is comparable to the distances

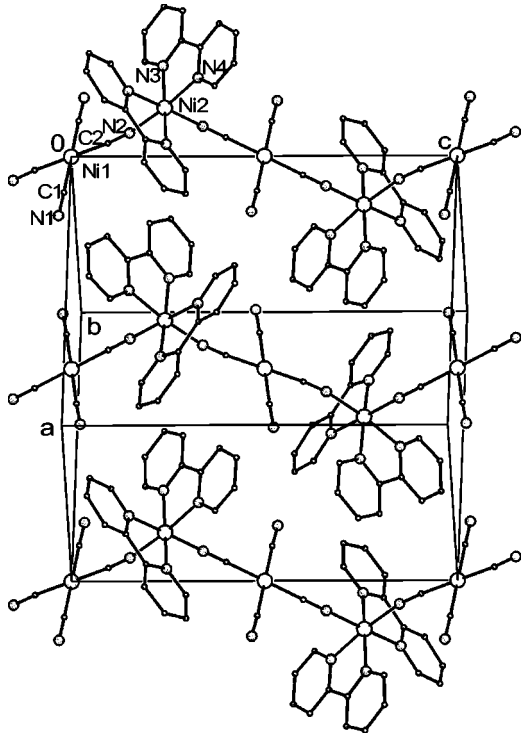

FIG. 1. Crystal structure of NBYC. Diamagnetic nickel atoms (Ni1) are coordinated by four cyano groups, while paramagnetic nickel ions (Ni2) are located in the center of slightly deformed nitrogen octahedron, (a)–(c) represent cell axes.

between the paramagnetic ions within the chain, more complicated interchain superexchange paths are expected to allow the formation of well-isolated magnetic linear chains in this compound. A detailed characterization of the NBYC structure will be reported elsewhere.[7]

The specific heat of two powdered samples (345 mg and 1.05 g) was studied in the temperature range from 100 mK to 6 K using the dual-slope method[8] in a commercial dilution refrigerator. To cover the whole temperature interval, a RuO_2 thermometer was used for the measurements from 100 mK to 2 K, while an Allan-Bradley resistor was used for the measurements from 2 to 6 K. The thermometers were calibrated against commercial Lake Shore thermometers. The experimental accuracy of the measurements was about 6%. For NBYC, the specific heat of the thermometer, heater, and varnish (GE 7031) can be safely neglected in the aforementioned temperature range. The susceptibility and magnetization of a 141 mg powder sample were measured in a commercial SQUID magnetometer. The sample was glued to a piece of weighing paper using GE 7031 varnish and was placed in a gelcap which was held by a straw. A magnetic field 100 mT was applied during the susceptibility run, and the background contribution of the varnish, gelcap and straw is negligible below 20 K. The ESR experiment was performed with a powder sample and transmission spectrometers using backward wave oscillators[9] and Impatt and Gunn oscillators as microwave sources.[10]

Since NBYC represents a magnetic insulator, only the magnetic and lattice contributions to the total specific heat are considered in the present discussion. The lattice contribution was subtracted by finding the temperature region where the data may be fit by the equation $C(T)=aT^{-2}+bT^{c}$, where aT^{-2} describes the high-temperature behavior of the magnetic specific heat, while bT^{c} represents the low-temperature lattice contribution of structurally anisotropic systems as proposed by Bloembergen and Miedema.[11] For 3.2 K$\leqslant$T$\leqslant$6 K, a least-squares fit yielded $a=1.93$ J K/mol, $b=5.82\times10^{-2}$ J K^{-c-1}/mol, and $c=2.52$. As a result, the magnetic specific heat C_M is characterized by a round peak with a maximum value of 3.5 J/(K mol) at $T_{\max}=1.05$ K (Fig. 2). The magnetic entropy was calculated numerically in the measured temperature region and standard approximations were used to cover the whole temperature interval. The calculation yielded 8.76 J/(K mol) which is close to the theoretical value $R\ln(2S+1)=9.13$ J/(K mol) for a $S=1$ system. The broad maximum, together with the absence of a λ anomaly down to 100 mK, indicates a high degree of short range order in this system. The C_M was compared with the numerical predictions of Blöte[12] where only D and J were involved. The best agreement between the numerical predictions and the experimental data was obtained when $D/k_B=1.45$ K and $D/J=1$ (Fig. 2). The resultant D/J ratio suggests that NBYC should be located near the boundary between the large-D and gapless XY phases.[13] However, the sign of the obtained exchange coupling constant is in contradiction with what can be expected from the crystal structure. In addition, subsequent ESR studies did not reveal the presence of an energy gap with a correspondingly low value. In the ESR spectra, one can distinguish two different kinds of resonances (see inset of Fig. 3), which correspond to the branches A and B in the ESR frequency-field dependence (Fig. 3). From the temperature dependence of the resonances, one can conclude that the main contribution is from ground state excitations. Therefore, we considered the observed resonances as transitions at the Γ point. In the first approximation, the ESR data were analyzed using a single-ion Hamiltonian:

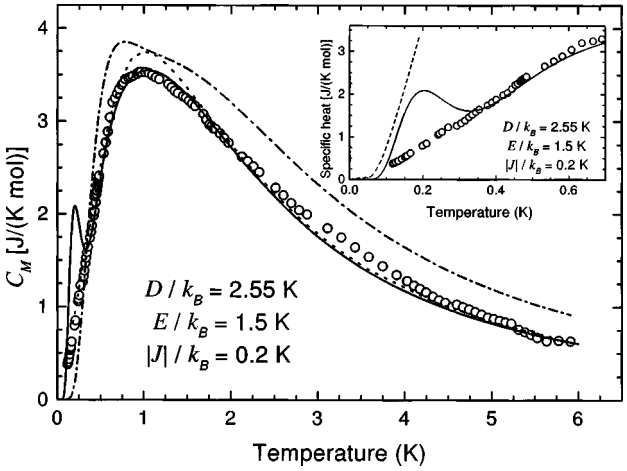

FIG. 2. Temperature dependence of magnetic specific heat of NBYC (circles). The dashed line denotes the numerical prediction of Blöte (Ref. 12) using $D/k_B=1.45$ K, and $D/J=1$, while the solid line represents the prediction of the model (Ref. 5) using the values of the parameters given in the inset. The dotted dashed line denotes the Schottky contribution with $D/k_B=3.5$ K, $E/k_B=1.9$ K. Inset: Low temperature specific heat data of NBYC (circles) compared with the theoretical prediction of model (Ref. 5) (solid line) and dilute exciton approximation (dashed line). See text for more detailed discussion.

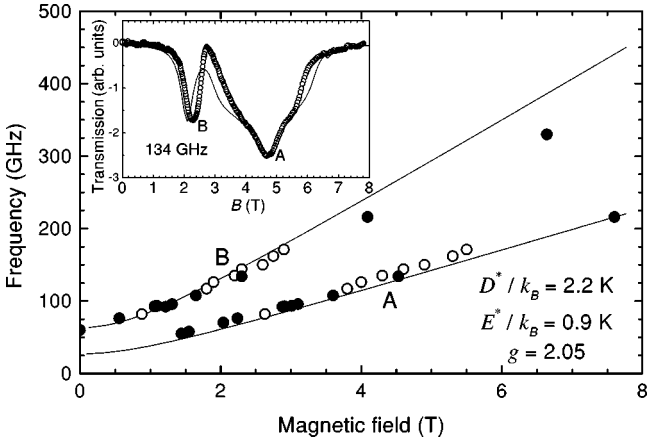

FIG. 3. Frequency-field dependence of the magnetic resonances in powdered NBYC. Circles are indicating the field of maximum absorption (solid and open symbols correspond to measurements at 1.5 and 4.2 K, respectively). Solid lines represent the prediction obtained in the single-ion approximation. Inset: The 134 GHz transmission spectrum at 1.5 K. Experimental data are denoted by open circles, while the solid line corresponds to a calculation as described in the text.

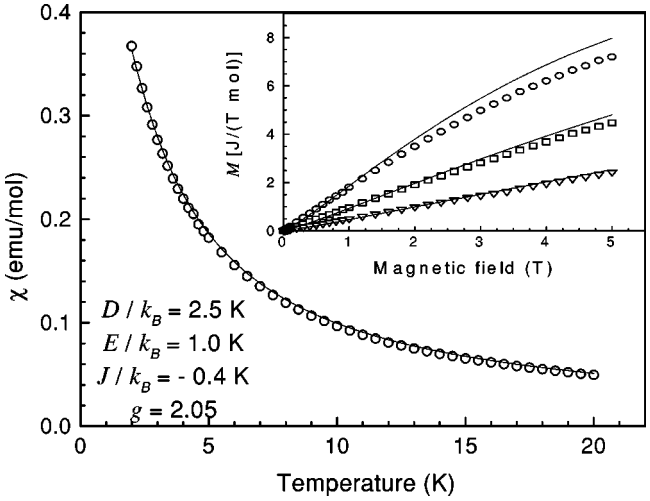

FIG. 4. Susceptibility data of powdered NBYC. The solid line represents the theoretical prediction of model. (Ref. 5) Inset: Field dependence of the magnetization of powdered NBYC studied at 5 K (circles), 10 K (squares), 20 K (triangles). The corresponding theoretical predictions obtained in single-ion approximation are denoted by solid lines.

$$\mathcal{H}=D^*\sum_i\left[(S_i^z)^2-\tfrac{1}{3}S(S+1)\right]$$

$$+E^*\sum_i\left[(S_i^x)^2-(S_i^y)^2\right]+g\mu_B\vec{S}\cdot\vec{B}, \qquad (1)$$

where D^* and E^* correspond to the effective splitting of the energy levels at the Γ point. The shape of ESR line was calculated by integrating the contributions of all orientations of single crystals in a magnetic field using a procedure applied in the analysis of magnetic resonance in NENC and TMNIN.[14,15] For all contributing excitations, the difference of occupation numbers and the transitions matrix elements were taken into account. In order to obtain reasonable quantitative agreement, it was necessary to include in-plane anisotropy E into the analysis. The best fit of the shape of ESR line yielded $D^*/k_B=2.2$ K, $E^*/k_B=0.9$ K, and $g=2.05$. Since the absorption maximum corresponds to the resonance when the external magnetic field B is parallel to the x axis, the frequency-field dependence in Fig. 3 was analyzed using the single-ion model for $B\|x$. The remarkable feature of the observed frequency-field dependence is a small slope of branch B which corresponds to $\Delta m=2$ transitions. In high fields, the increase of this branch is expected to be $2g\mu_B B$ (see solid line B in Fig. 3). However, the experimentally observed slope deviates somewhat from the theoretical expectation. This behavior might be ascribed to the powder nature of the specimen, but further ESR studies performed with larger single crystals are required to verify this conjecture. Considering the ESR analysis as discussed above, C_M was reanalyzed, using only D and E, to verify the presence of the exchange coupling in the studied system. The fitting of the specific heat data in a single ion approximation yielded $D/k_B=3.5$ K and $E/k_B=1.9$ K. However, as can be seen in Fig. 2, the quantitative agreement between the data and the corresponding Schottky contribution is unsatisfactory, even though the positions of the maxima coincide reasonably. This result supports the assumption of the existence of a weak exchange coupling between paramagnetic Ni^{2+} ions. Consequently, more detailed analysis of C_M was carried out using the theoretical predictions[5] with D, J, and E taken into account. In the high-temperature region, the specific heat data can be satisfactorily described with the values of $D/k_B=2.55$ K, $|J|/k_B=0.2$ K, and $E/k_B=1.5$ K. The reasonable agreement of the D and E values, as obtained from the analysis of the ESR and the reanalysis of the C_M data, supports our assumption about the subcritical exchange coupling and the significant influence of in-plane anisotropy. Even though the model is valid up to $D/|J|=2.5$ when $E=0$,[5] there is an apparent disagreement at low temperatures where there is a kinklike anomaly on the ascending side of the specific heat. In order to clarify whether the resulting D, J, and E parameters are still appropriate for NBYC or whether the predicted anomaly is an artificial artifact of the model, the susceptibility and magnetization of NBYC were experimentally studied. The behavior of the susceptibility data (Fig. 4) in the temperature range from 2 to 20 K is not characterized by a round maximum typical for anisotropic Heisenberg chains. Furthermore, a plateau characteristic for Heisenberg chains with subcritical exchange coupling was not observed down to 2 K. Nevertheless, considering the results of the ESR and specific heat analyses, the susceptibility data were evaluated using the theoretical prediction[5] which incorporates D, J, and E. In the fit, the g factor was fixed to be 2.05 as obtained from ESR analysis. Using this approach, it was found that the susceptibility data can be well described using $D/k_B=2.5$ K, $E/k_B=1$ K, and $J/k_B=-0.4$ K. The field dependence of the magnetization was studied at 5, 10, and 20 K (inset of Fig. 4). Since the corresponding theoretical prediction for the magnetization is not available, the data were analyzed within the single-ion approximation using the D and E values as obtained from susceptibility analysis and g from ESR. The small systematic deviation between the theoretical predictions and experimen-

tal data may be attributed to neglecting the exchange coupling and to the powdered character of the sample. The good agreement of the D, J, and E parameters, obtained from the analysis of the ESR and the thermodynamic data, suggests that, at low temperatures, the region of validity of the theoretical model[5] is shifted significantly to higher $D/|J|$ ratios with increasing E/D ratio. For completeness, we also studied the influence of the in-plane anisotropy on the reliability of the calculation of the low-temperature specific heat in the dilute approximation. For NENC, it is noteworthy that incorporating the E term substantially improved the agreement between the experimental data and the specific heat contribution arising from the noninteracting excitons.[4,6] This fact contrasts with the situation in NBYC where the dilute approximation also fails to describe the low-temperature data (see inset in Fig. 2). Therefore, the validity of dilute approximation is restricted to low values of the in-plane anisotropy even though E was not considered as a perturbation in the calculations.[5]

Our studies of the magnetic and thermodynamic quantities revealed that NBYC can be considered as an $S=1$ Heisenberg chain with subcritical exchange coupling and strong in-plane anisotropy. From the analysis of the experimental data, the critical $D/|J|$ ratio, below which the theoretical treatment[5] remains valid, is shifted to higher values with increasing in-plane anisotropy. The presence of the E term can lead to significant renormalization of the D and $|J|$ parameters, even for relatively high $D/|J|$ ratios. Consequently, the presence of in-plane anisotropy should be considered in attempts to find a system located at the boundary between the Haldane and large-D phases.

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