Magnetic properties of the Zn-doped Haldane-gap material NENB

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Abstract. Experimental studies of the spin-1 Haldane-chain material [Ni(C₂H₄N₂)₂NO₂](BF₄) (NENB) doped with diamagnetic Zn(II) ions in a range up to nominally 5% by means of the magnetic-susceptibility and the electron-spin resonance (ESR) techniques are reported. The presence of fractional \( S = 1/2 \) chain-end states, revealed by ESR and susceptibility measurements is found to be responsible for spin-glass freezing effects. It is suggested that a higher doping with Zn ions suppresses the spin-glass behaviour by creating shorter and isolated chain fragments.

1. Introduction

Antiferromagnetic (AFM) quantum spin-1 chains have been the subject of intense theoretical and experimental studies, especially due to the Haldane conjecture [1]. In accordance with the valence-bond-solid (VBS) model proposed by Affleck et al. [2], each \( S = 1 \) spin can be regarded as a symmetric combination of two \( S = 1/2 \) moments forming a spin-singlet ground state. The first excited state is a magnetic spin triplet separated from the ground state by an energy gap. The value of the energy gap for an \( S = 1 \) isotropic Heisenberg AFM chain has been theoretically estimated to be \( \Delta = 0.41J \) (where \( J \) is the spin-spin exchange coupling) [3] and its presence was experimentally revealed in a number of materials (see for instance Ref. [4]). Many studies have also been devoted to the investigation of spin-1/2 states in Haldane materials [5] as a consequence of the VBS model in real systems. The interaction among chain-end moments then can lead to spin-glass behavior [6] or even to AFM order of chain-end moments [7].

In this paper, we study magnetic properties of the new Haldane compound NENB doped with diamagnetic Zn(II) ions. The presence of the Haldane state in NENB is confirmed experimentally and the analysis of the frequency-field dependence of magnetic excitations yields \( g_l = 2.14 \), \( D/k_B = 7.5 K \), and \( |E/k_B| = 0.7 K \) for the \( g \) factor and the crystal-field anisotropy constants, respectively. The influence of doping by Zn(II) ions on low-temperature magnetic properties of NENB is discussed.
Figure 1. Field dependence of the magnetic ESR excitations of NENB observed at 1.5 K (modes A, B, E, F and J) and 4.3 K (modes C and D) with the magnetic field aligned along the $b$ axis. Solid lines represent the fit obtained by use of the effective spin Hamiltonian (Eq. 1) to the experimental data. The dashed line is a guide to the eyes.

2. Experimental details

Single crystals of NENB were grown by the reaction of $[\text{Ni(C}_2\text{H}_8\text{N}_2\text{)}_3](\text{BF}_4)_2$ with Ni(BF$_4$)$_2$·6H$_2$O and NaNO$_2$ in aqueous solution. Careful, slow evaporation in a partially covered container yielded ruby-red crystals. Each Ni$^{2+}$ ion is pseudo-octahedrally coordinated. The four nitrogen atoms of the two ethylenediamine ligands (ethylenediamine = C$_2$N$_2$H$_8$) make a slightly distorted square planar symmetry with bridging NO$_2^-$ ions creating the octahedral axis approximately parallel to the chain direction. The individual chains are well isolated by the inorganic counterions BF$_4^-$ [8, 9]. Zn-doped crystals were grown by replacing some of the Ni(BF$_4$)$_2$·6H$_2$O with Zn(BF$_4$)$_2$·xH$_2$O in varying proportions and harvesting the crystals at low conversion (typically 10-20% yield).

The static susceptibility was measured using a commercial SQUID magnetometer equipped with a 7-Tesla magnet in the temperature range from 1.8 to 300 K. The sample was attached with a small amount of Apiezon N grease to the inside of a straw held by a sample-holder rod. ESR experiments were performed in the Voigt geometry with the external field up to 16 T applied along the $b$ axis using a tunable-frequency ESR setup [10] at the National High Magnetic Field Laboratory, Tallahassee (USA) and at the Dresden High Magnetic Field Laboratory, Dresden (Germany).

3. Results and discussion

The excitation spectrum of pure NENB in a magnetic field parallel to the $b$ axis (which is the chain axis) is plotted in Fig. 1. In order to assign the observed modes to field-dependent transitions in the energy scheme of the magnetic excitations we analyzed the data using the effective spin Hamiltonian, written as [11]

$$\mathcal{H} = \Delta + D'(S_z^i)^2 + E'[\langle S_x^i \rangle^2 - \langle S_y^i \rangle^2] - \mu_B S g B,$$

where $\Delta$ is the Haldane gap, $D'$ and $E'$ represent reduced parameters of the crystal-field anisotropy (uniaxial- and rhombic-distortion parameters, respectively) of the Ni ions, while
Figure 2. a) Magnetic susceptibility of nominally pure NENB compared to Zn-doped samples measured in a magnetic field of 0.01 T, applied along the b axis. The solid line represents the $S = 1$ Heisenberg AFM chain model with $D/J = 0.2$ (see the text for details). b) The difference between FC and ZFC susceptibility of nominally pure and Zn-doped NENB.

The magnetic susceptibility of nominally pure and Zn-doped NENB measured in a field of $B = 0.01$ T applied parallel to the $b$ axis is shown in Fig. 2a. The pronounced maximum at 55 K has been compared to the model of an $S = 1$ Heisenberg AFM spin-chain including the influence of anisotropy [16] using the parameters obtained from our ESR data analysis. From the theoretically expected value $\Delta/|J| = 0.41$ [3] we have estimated the exchange coupling $J/k_B = -42.5$ K. Although a theoretical prediction is not available for the exact value of $D/|J| = 0.175$, the overall agreement with the experimentally determined susceptibility data for $D/|J| = 0.2$ and $g_\parallel = 2.15$ is very good (see Fig. 2a).

The presence of fractional $S = 1/2$ chain-end spins might be a possible explanation for the observation of a weak Curie-like low-temperature upturn observed in the susceptibility. As shown in Fig. 2b, we have observed also a non-zero difference between the zero-field-cooled (ZFC) and field-cooled (FC) susceptibility. Such behavior can be accounted for by the formation of a spin-glass state, which is a pronounced signature of the $S = 1/2$ chain-end interaction [6]. The difference between the FC and ZFC susceptibility at low temperatures decreases with increasing...
doping of diamagnetic Zn(II) ions. In addition, the maximum at 12 K in nominally pure NENB
shifts to lower temperatures being gradually suppressed in Zn-doped samples. This indicates
that the spin-glass behavior in NENB is suppressed with a higher concentration of doping.

The strong spin-glass effect in nominally pure single crystals of NENB suggests that the
concentration of intrinsic defects in the sample is relatively high. Additional doping of
nonmagnetic Zn ions does not effectively create more free chain-end moments, but only leads to
the shortening of the chain fragments. Since for short fragments the interaction among chain-
end moments within a single fragment is relatively strong, the chain-end moments behave as
$S = 1$ ($S = 0$) molecular entity for odd (even) number of spins at low temperatures [17]. We
speculate that the shortening and isolation of chain fragments then leads to the weakening of
exchange interaction among the chain-end moments of neighboring fragments and thus to the
suppression of the spin-glass effect.

4. Conclusions
Based on the analysis of the ESR and magnetization data, the spin-Hamiltonian parameters of
NENB have been estimated, yielding the exchange coupling $J/k_B = -42.5$ K and crystal-field
anisotropy parameters $D/k_B = 7.5$ K and $|E/k_B| = 0.7$ K. The study of nonmagnetic doping of
NENB with Zn(II) ions suggests that doping leads to the suppression of the spin-glass behaviour
in NENB by creating shorter and isolated chain fragments.

Acknowledgments
This work was partially supported by the DFG. Part of this work was performed at the National
High Magnetic Field Laboratory, Tallahassee, USA, which is supported by NSF Cooperative
Agreement No. DMR-0084173, by the State of Florida, and by the DOE. S.A.Z. acknowledges
the support from the NHMFL through the VSP No. 1382.

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