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^{13}C NMR on the $S = 1/2$ antiferromagnetically coupled spin chain compound $[PM \cdot Cu(NO_3)_2 \cdot (H_2O)_2]_n$ (PM = pyrimidine)

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Abstract

We present ^{13}C NMR experiments on the $S = 1/2$ antiferromagnetically coupled spin chain compound $[PM \cdot Cu(NO_3)_2 \cdot (H_2O)_2]_n$ (PM = pyrimidine) at temperatures 5–120 K. In the NMR spectra, we observe three pairs of double lines. From the angular dependence of the NMR shift, we assign the three line pairs to the three inequivalent C sites on the pyrimidine molecule $C_4N_2H_4$, with the splitting of the signal from each site into two lines caused by the hydrogen atom bound to C. We obtain the temperature dependence of the NMR shift, which exhibits a qualitatively different behavior for the three inequivalent C sites.

Keywords: ^{13}C NMR; Quantum spin chain; $S = 1/2$ antiferromagnet; Cu complex; Molecular magnet; Field-induced excitation gap

1. Introduction

Molecular spin chain compounds form an important intermediate step en route from molecular building blocks to full-grown 3D molecular magnets. Quantum spin chains, i.e. systems with spin $S = 1/2$ or 1 in particular, have attracted close attention of physicists in recent years. From a theoretical point of view, they are attractive as for such systems there exists a sophisticated array of theoretical models and approaches, including exact solutions for various models. Well-known examples are the uniform $S = 1/2$ antiferromagnetic Heisenberg chain with a gapless continuum of spin excitations and the integer spin antiferromagnetic chain with the appearance of a Haldane gap [1–3]. The existence of these states has been verified experimentally by spectroscopic techniques for various materials [4–7].

For $S = 1/2$ antiferromagnetic Heisenberg chains on low-symmetry crystallographic lattices, additional terms from the Dzyaloshinskii–Moriya (DM) interaction and the anisotropy of the g tensor may have to be taken into account [8–11]. These terms give rise to an effective staggered field h perpendicular to an externally applied field H. It causes a staggered magnetization with a component $m \perp H$ and an anisotropic field-induced gap in the spin excitation spectrum. The gap has nodes in certain field directions, which are determined by the combined effect of staggered g tensor, DM interaction and Heisenberg spin exchange, since $\vec{h} \approx (1/2J)\vec{D} \times \hat{g}_U \vec{H} + \hat{g}_S \vec{H}$. In consequence, the directions of the nodes do not coincide with the main symmetry axes of the underlying crystallographic lattice. By now, it has been found that such a situation is realized in three materials, e.g. in Cu benzoate $Cu(C_6H_5COO)_2 \cdot 3H_2O$ [12,13], intermetallic Yb_4As_3 [14] and in the pyrimidine (PM) complex $[PM \cdot Cu(NO_3)_2 \cdot (H_2O)_2]_n$ [15,16].

As yet, the staggered magnetization m predicted by theory [8–11] for these materials has not directly been verified. m can be obtained by means of nuclear

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magnetic resonance (NMR). Therefore, we started a detailed ^{13}C study on $[\mathrm{PM}\cdot\mathrm{Cu(NO_3)_2}\cdot(\mathrm{H_2O})_2]_n$. In this contribution, we present first results of our NMR investigation of this material.

$[\mathrm{PM}\cdot\mathrm{Cu(NO_3)_2}\cdot(\mathrm{H_2O})_2]_n$ was recently synthesized by Ishida et al. [17,18] and crystallizes in a monoclinic structure, space group $C2/c$, with lattice parameters $a = 12.404$ Å, $b = 11.511$ Å, $c = 7.518$ Å and $\beta = 115°$ at room temperature. All Cu ions are crystallographically equivalent. They are sited inside distorted octahedra with N–O–N–O equatorial planes and O in the axial positions, as indicated in Fig. 1(a). The main axis of the octahedra are tilted by $\pm 30.8°$ out of the ac-plane. As this axis coincides with the g tensor's principal axes, neighboring Cu atoms are only crystallographically but not magnetically equivalent. The Cu–N–O units (and thus the Cu ions) form uniformly spaced chains parallel to the short ac-diagonal. In addition, in Fig. 1(a), we include the main directions of spin space anisotropy, i.e. the direction of the maximum (minimum) staggered susceptibility and field-induced spin excitation gap, which are denoted $c''(a'')$ (for comparison, see Refs. [15,16]).

The intrachain magnetic exchange pathway is provided by the N–C–N moieties of the pyrimidine ring $\mathrm{C_4N_2H_4}$, which connect two neighboring Cu ions as detailed in Fig. 1(b). The C atom on the magnetic exchange pathway, labelled 1, as well as the one on the opposite side of the pyrimidine ring 2 are symmetrically sited with respect to the two Cu ions, while the atoms 3a and 3b are not. As is evident from the plot, the carbon sites 3a and 3b are crystallographically equivalent, while 1, 2 and 3 are inequivalent. To each of the C atoms, one hydrogen atom is bound, which may have either spin up or down. In consequence, in a NMR study, we expect to observe six distinct lines, i.e. three sets of double pairs of lines from the three inequivalent sites and the line splitting caused by the hydrogen spin direction.

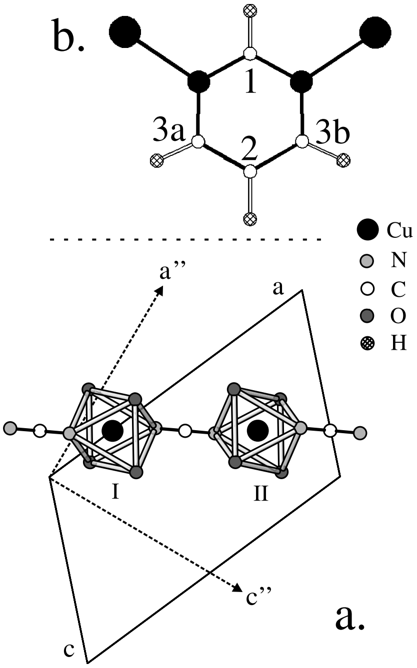

Fig. 1. (a) A single chain of $[\mathrm{PM}\cdot\mathrm{Cu(NO_3)_2}\cdot(\mathrm{H_2O})_2]_n$ in a view onto the ac-plane; for details see text. (b) The pyrimidine complex $\mathrm{C_4N_2H_4}$ interconnects two Cu ions on the chain, as indicated in the figure. The carbon atoms labelled 1, 2 and 3 are crystallographically inequivalent. Atoms 1 and 2 are symmetrically sited with respect to the Cu ions, 3a and 3b are not.

2. Experimental

We have performed NMR experiments using a home-built spectrometer in quadrature detection and a superconducting magnet operating at a constant field of 9.30 T at temperatures between 5 and 120 K. The frequency spectra of ^{13}C were obtained using a progressive saturation sequence with constant delay $\tau = 500$ ms and an echo subsequence at the end, $(\pi/2-\mathrm{del.1})_n - \tau - \pi/2 - \mathrm{del.2} - \pi - \mathrm{del.2} - \mathrm{acq.}$, and using phase cycling to cancel parasitic ^{13}C signal from the Teflon tube around the sample. Typical conditions of excitation were $\pi/2 = 14$ µs and $\pi = 28$ µs for a 90°- and 180°-pulse, respectively. The delay del.1 = 250 µs was set to be much shorter than T_1 and del.2 = 10 µs to be shorter than T_2. Repetition rates were in the range 0.005–0.05 kHz. The spectra were recorded piecewise by 30 kHz sections using Fourier transform NMR at 9.30 T and summation over the frequency range between 99.35 and 99.95 MHz.

The ^{13}C NMR shift was determined with respect to the ^{1}H reference frequency $\nu_\mathrm{R} = 395.945$ MHz of water at room temperature in a field of 9.30 T by $\nu_\mathrm{R}(^{13}\gamma_n/^1\gamma_n)$ (γ is the gyromagnetic ratio) with the tabulated values of $^{13}\gamma_n = 10.705$ MHz/T and $^1\gamma_n = 42.575$ MHz/T. Therefore, in the following figures, the ^{13}C reference frequency is always associated to this ^{1}H reference.

3. Results and discussion

In Fig. 2, we plot a set of representative NMR spectra, taken with the external field applied along the copper chain direction at temperatures between 5 and 120 K. As predicted on the basis of the structural model of the pyrimidine molecule, we observe three pairs of double lines with a temperature-dependent frequency shift.

To establish the correlation between the pairs of NMR lines and the inequivalent C sites, we performed angular-dependent NMR shift measurements at 200 K, which are depicted in Fig. 3. We can model the angular dependence in a computer simulation taking into account the sum of the dipolar contributions of Cu electrons located within a sphere of radius $R = 30$ Å

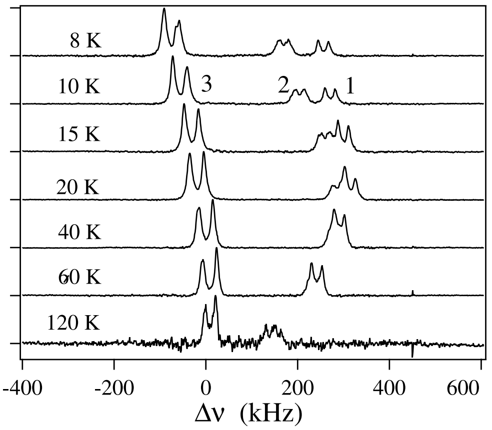

Fig. 2. The temperature dependence of the ^{13}C NMR spectra in [PM·Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$ in an external field of 9.3 T applied along the copper chain direction.

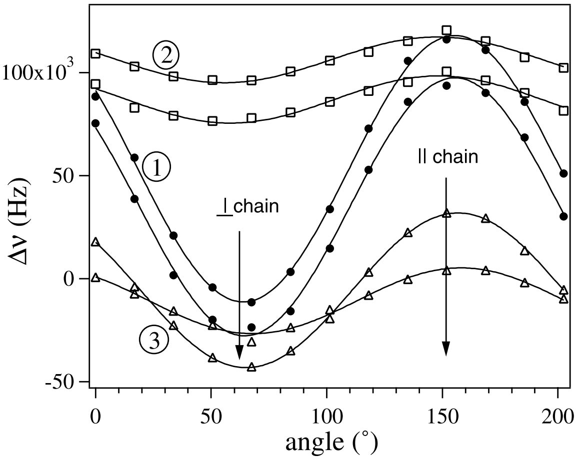

Fig. 3. The angular dependence of the NMR shift of the ^{13}C NMR lines of [PM·Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$ at 200 K. The line pairs labelled 1, 2 and 3 are associated to the corresponding sites on the pyrimidine molecule (Fig. 1(b)). The solid lines represent dipole field calculations as described in the text.

from the carbon atom and of the nearest protons, which are bound to the carbon atoms. In this calculation, the angular dependence of the magnetic moment at the copper site due to the anisotropic g tensor [16] is included. From this analysis, we obtain an angular dependence of the NMR shift, which we indicate by the solid lines in Fig. 3. The matching of lines and experimental data implies a correspondence of the line pairs to the carbon sites 1, 2 and 3 as denoted in Figs. 3 and 4.

From the NMR spectra as depicted in Fig. 2, we obtain the temperature dependence of NMR shift. The result of our analysis is plotted in Fig. 4. Two sets of lines show a very similar temperature dependence. Both have a positive NMR shift and their high T dependencies resemble in their overall features the bulk susceptibility [16]. The third set of lines exhibits a distinctly different behavior. Here, we observe a negative NMR shift. For all lines the low temperature dependence cannot be matched onto the macroscopic susceptibility and is described by a Curie-law with negative coupling constants.

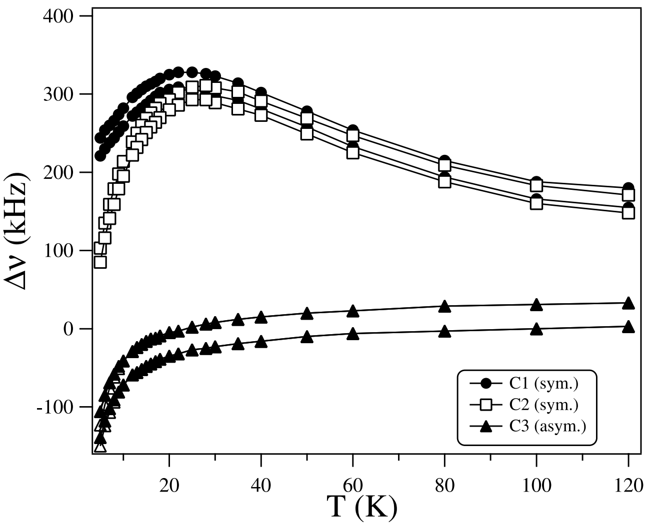

Fig. 4. The temperature dependence of the NMR shift of [PM·Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$. Labels 1, 2 and 3 as in Fig. 3. Solid lines are guides to the eye.

In general, we expect two different contributions to the shift, i.e. a Bonner-Fisher term for an ideal $S = 1/2$ Heisenberg chain and an additional contribution at low temperatures resulting from the staggered field. Then, the maximum in the NMR shift at about ~25 K for the line pairs 1 and 2 indicates that the 1D Bonner-Fisher contributions are dominant. In contrast, the maximum in the susceptibility of the third set of lines is probably hidden via different staggered field contributions; in that sense, the NMR shift directly probes the staggered magnetization. Depending on the distance and angle between the carbon nucleus and copper ions on their own as well as on neighboring chains, the hyperfine coupling can change sign and amplitude independently for both contributions. It leads to the different curves for the NMR shift for inequivalent carbon sites in the low-temperature region.

4. Conclusions

In conclusion, we have performed ^{13}C NMR experiments on [PM·Cu(NO$_3$)$_2$·(H$_2$O)$_2$]$_n$ at temperatures 5–120 K. In our study, we observe three pairs of lines. From the angular dependence of the NMR shift, we associate the different pairs of lines with the inequivalent C sites on the pyrimidine molecule. We obtain the temperature dependence of the NMR shift, which can be described by the sum of a Bonner–Fisher and a Curie term, indicating additional contributions from the staggered field at low temperatures. This reflects different structure factors at the C sites of the pyrimidine molecule with respect to the staggered field. Presently, work is underway to investigate the^{13}C NMR response at low temperatures, in order to study the anisotropic, field-induced spin gap state and the excitations above the gap. In this context, it will be very useful to have the ability to look at different NMR responses in this material because of the structure factor.

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