Experimental Report

16/04/2014

Proposal: **4-01-1312** **Council:** 10/2012

Title: Controversial magnetism in CuNCN, a nitrogen-containing analog of CuO

This proposal is a new proposal

Researh Area: Physics

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Samples: CuNCN

Instrument	Req. Days	All. Days	From	To
D7	5	7	14/05/2013	21/05/2013

Abstract:

Copper oxides exhibit numerous fascinating phenomena and exotic electronic ground states, e.g., high-temperature superconductivity and quantum magnetism. Substitution of O2- with (NCN)2- anion complex is an important step in tailoring physical properties of copper compounds. The neutron scattering studies on recently synthesized CuNCN failed to detect magnetic reflections, while muon spin relaxation reveal freezing of the Cu2+ (S=1/2) magnetic moments. Still, recent study (PRB 85 224431 (2012)) claims that that the system establish long-range magnetic order. Our latest nonpolarized inelastic neutron scattering experiment reveals that the temperature dependence of quasi-elastic excitations at low-Q shows anomalies that coincide with the muon experiment. To establish if these excitations are indeed magnetic and if they originate from ordered phase, we propose polarized inelastic neutron scattering experiment

Polarized inelastic neutron scattering on powder CuNCN

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We performed polarized inelastic neutron scattering experiment on powder CuNCN samples. The results show that there is no detectable elastic magnetic signal at 1.5 K for $0.25 < |Q| < 2.0$ Å^{-1}. Moreover, in this $|Q|$ interval, we also find no trace of any magnetic excitation between 0.2 and 2.5 meV from 1.5 K up to 80 K.

PACS numbers: 75.25.+z, 75.80.+q

INTRODUCTION

The crystal structure of CuNCN is orthorhombic ($Cmcm$, $a = 2.9921(1)$ Å, $b = 6.1782(1)$ Å and $c = 9.4003(2)$ Å) and consists of corrugated layers with a $4+2$ nitrogen environment of Cu^{2+} [1, 2]. It exhibits a nearly temperature independent and surprisingly small bulk magnetic susceptibility [2], with yet elusive anomaly around 80 K. Its origin is controversial and is signed theoretically to long-range magnetic ordering [3] or a resonating-valence-bond spin-liquid phase [4]. Yet, diffraction neutron scattering studies (including polarized) failed to detect magnetic reflections [2, 5]. Local-probe study [6] has revealed that classical magnetic ordering is absent in CuNCN down to the lowest temperatures (60 mK). However, a large enhancement of spin correlations and an unexpected inhomogeneous magnetism have been observed below 80 K, which is still missing unambiguous explanation, as both a fragile gapped spin liquid state and an unconventional spin-glass like state could explain the experiments.

Recent inelastic neutron scattering (INS) experiments [7] revealed two non-dispersive phonon modes at 9.5(3) meV and 4.6(2) meV, which are apparent at 1.5 K as well as 130 K. Still additional lower (E <0.5 meV) or higher (E >20 meV) energy excitations could not be excluded. Moreover, a peculiar temperature evolution of the quasielastic signal, which for $|Q| < 1.5$ Å^{-1} exhibits two anomalies that approximately coincide with magnetic freezing temperatures found by muSR [6], which might be reflect some kind of magnetic correlations.

To clarify the potential magnetic character of the observed quasielastic scattering, we performed polarized INS experiment on D7 at ILL.

EXPERIMENTAL

High purity powder CuNCN samples were synthesized by slow oxidation of the copper(I) precursor $Cu_4(NCN)_2NH_3$ at room temperature [1].

Powder polarized INS measurements were performed in the temperature range between 1.5 K and 80 K for the scattering angle between 0.25 Å^{-1} and 2.7 Å^{-1} in the energy range between -11 meV and 2.7 meV, on D7 time-of-flight spectrometer at Institute Laue-Langevin, Grenoble, France. Complete calibration was performed, including empty can, vanadium and quartz measurements, necessary for subtraction of background and for calibrations of the detectors and analyzers.

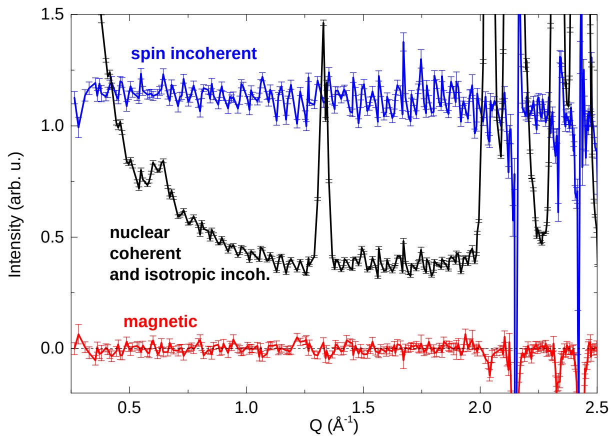

FIG. 1: Elastic scattering signal measured at D7 using polarized neutrons at a temperature of 1.5 K.

RESULTS

To get an estimate about the sensitivity of the instrument in comparison to previously reported results [5] and to check for any elastic magnetic scattering, we first performed XYZ polarization measurements at 1.5 K between 0.25 Å^{-1} and 2.7 Å^{-1}. This experiment allows to separate nuclear coherent, isotope incoherent and (nuclear-) spin incoherent from (electronic-) magnetic scattering [8]. As anticipated, our results are in agreement with previous results [5], showing no sign of any magnetic signal with much higher precision (Fig. 1), i.e., our signal to noise ratio is at least 2 times better.

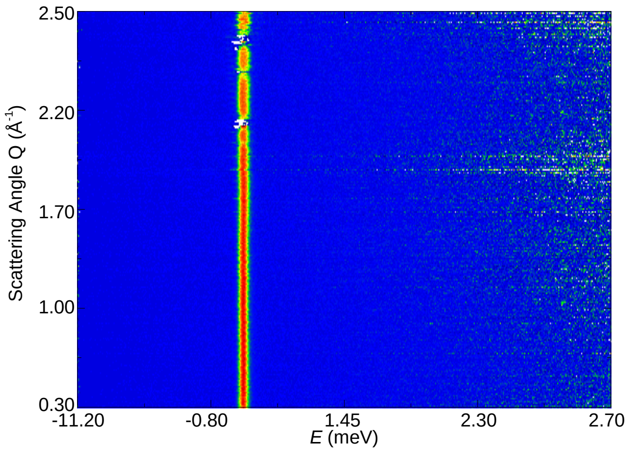

FIG. 2: Energy map at 1.5 K measured in a spin-flip channel.

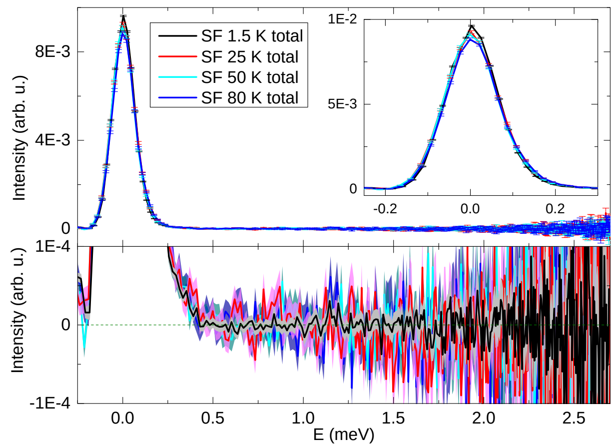

FIG. 3: Temperature dependence of SF-scattering energy cuts for $|Q|$ interval between $0.25\,\text{Å}^{-1}$ and $2.7\,\text{Å}^{-1}$ with subtracted empty can background and calibrated by vanadium and quartz references.

Next, we changed setup to inelastic mode in the energy range of -11 meV to 2.7 meV. The polarized INS experiment was performed in non-spin-flip (NSF) and spin-flip (SF) configurations [8]. This allows to separate the magnetic inelastic signal from nuclear (phonon-induced) one, as SF signal includes only magnetic and (nuclear-)spin incoherent contributions, whereas NSF signal includes also nuclear coherent and isotope incoherent contributions. Our results implies that in the region between $0.3\,\text{Å}^{-1}$ and $2.5\,\text{Å}^{-1}$ there is no no sign of magnetic excitations between 0.25 meV and 2.7 meV (Fig. 2) at 1.5 K. To double check this, we plot energy energy cuts measured between 1.5 K and 80 K (Fig. 3), integrating over the entire Q range, which should emphasize the weakest INS signal. These reveal a tiny increase of intensity at 1.15 meV and $T = 1.5$ K. In addition, NSF results (not shown) show that in this range also phonon excitations are absent at least up to 80 K.

CONCLUSIONS

We found no detectable elastic magnetic signal at 1.5 K in the range of $0.25 < |Q| < 2.0\,\text{Å}^{-1}$. Moreover, in this $|Q|$ interval, we also find no trace of any magnetic excitation between 0.2 and 2.5 meV from 1.5 K up to 80 K. Still a subtle increase at 1.15 meV at 1.5 K might indicate a potential magnetic excitations, which however are highly questionable. Due to experimental limitations, we cannot detect energy excitations with $E > 2.5$ meV. Considering also the previous INS study [7], the magnetic excitations, if present, exists only for $E > 20$ meV.

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