Experimental report

13/02/2019

Proposal: **5-54-254** **Council:** 4/2017

Title: Magnetic structure and possible Schwinger scattering in Cu3Nb2O8

Research area: Physics

This proposal is a new proposal

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Samples: Cu3Nb2O8

Instrument	Requested days	Allocated days	From	To
D3	5	5	25/05/2018	30/05/2018

Abstract:

Cu3Nb2O8 is both magnetically and structurally chiral (space group P-1). This proposal aims to use D3 to study the coupling between magnetic and structural chirality in this material using anomalous Schwinger scattering to investigate the structure, and neutron polarimetry to investigate the magnetic structure. The primary goal of the proposal is to confirm the magnetic structure in a single crystal. The second goal is to observe anomalous Schwinger scattering to determine structural chirality. The proposal requests 5 days on D3 to perform this experiment.

Spin Density Waves and Cycloidal Order in the Multiferroic $Cu_3Nb_2O_8$ Determined with Polarised Neutrons

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1 Introduction

In multiferroics, there exists a coupling between magnetic and electrical order. It is for this reason that they are receiving much attention. This coupling can be important as it can allow tuning of the electric polarisation by the application of a magnetic field and vice versa. Multiferroics could also have uses in sensing applications as they are sensitive to both magnetic and acoustic (through piezoelectricity) signatures.

$Cu_3Nb_2O_8$ (room temperature symmetry $P\bar{1}$) experiences two phase transitions at low temperatures: it magnetically orders at $T_N \approx 26.5K$ with incommensurate propagation vector $\vec{k} = (0.4876, 0.2813, 0.2029)$ (referred to here as the middle temperature - MT - phase) and develops an electric polarisation along $[1, 3, 2]$ below $T_2 \approx 24K$ (low temperature - LT - phase) [1]. Johnson *et al.* reported that the LT phase has a chiral structure that is allowed, as this transition corresponds to the breaking of an inversion centre ($P\bar{1} \rightarrow P1$). However, as the polarisation is definitely not confined to the rotation plane, the mechanism responsible for inducing this is unclear, being incompatible with classic models (e.g. KNB model [2, 3]). Johnson *et al.* proposed a phenomenological model coupling the polarisation through a chiral term to a macroscopic axial vector allowed in certain crystals classes by symmetry. In $P\bar{1}$, there is no specified direction of this axial vector and so the polarisation may be along an arbitrary direction. In this study, we report the magnetic structure found with spherical neutron polarimetry in both ordered phases.

2 Polarised Neutrons

2.1 Blume-Maleev Equations

Scattering from an initial to a final spin state can be expressed as a transformation in spin half space by a matrix[1] $S = N + \vec{M}_\perp \cdot \vec{\sigma}$: $\left|\chi^f\right\rangle = S\left|\chi^i\right\rangle$. The components correspond [4] to (respectively) nuclear scattering and magnetic scattering. We can discount scattering from nuclear spins as these are taken to be disordered[2].

In the Born approximation, the differential cross section can be calculated as:

$$\frac{d\sigma}{d\Omega} = \left\langle\chi^f\middle|\chi^f\right\rangle = \left\langle S^\dagger S\right\rangle = Tr(\rho S^\dagger S) \tag{1}$$

where the expectation is performed with respect to the *inital* spin state. As S is not unitary, the norm of a state is *not* conserved in this process. The final polarisation is given by an average of $\vec{\sigma}$ over the *final* spin state:

$$P_i^{final} = \frac{\left\langle\chi^f\middle|\sigma_i\middle|\chi^f\right\rangle}{\left\langle\chi^f\middle|\chi^f\right\rangle} = \frac{Tr(\rho S^\dagger \sigma_i S)}{\frac{d\sigma}{d\Omega}} \tag{2}$$

Using the density matrix formalism, we have expressed averages as a trace where $\rho = |\chi\rangle\langle\chi|$ is the density matrix for a state $|\chi\rangle$. We can also write an expresion for ρ in terms of the incident polarisation: $\rho = \frac{1}{2}(\mathbb{I} + \vec{P} \cdot \vec{\sigma})$. By computing these traces, we can calculate the cross-section and final polarisation[3]:

$$\begin{aligned}\frac{d\sigma}{d\Omega} = |N|^2 + |\vec{M}_\perp|^2 + N(P_i M^*_{\perp i}) + ...\\ + N^*(P_i M_{\perp i}) - i\epsilon_{ijk} P_i (M_{\perp j} M^*_{\perp k})\end{aligned} \tag{3}$$

$$P_i^{final} = P_{ij} P_j + P'_i \tag{4}$$

where we have split the final polarisation into two parts; P_{ij} are the components of the polarisation tensor and $\vec{P}'$ is the polarisation created by the scattering:

$$\begin{aligned}P_{ij} = \frac{1}{\frac{d\sigma}{d\Omega}}\Big((|N|^2 - |\vec{M}_\perp|^2)\delta_{ij} + i(N^* M_{\perp k} - ...\\ - N M^*_{\perp k})\epsilon_{ijk} + M_{\perp i} M^*_{\perp j} + M_{\perp j} M^*_{\perp i}\Big)\end{aligned} \tag{5}$$

$$P'_i = \frac{1}{\frac{d\sigma}{d\Omega}}\Big(N M^*_{\perp i} + N^* M_{\perp i} + i\epsilon_{ijk}(M_{\perp j} M^*_{\perp k})\Big) \tag{6}$$

If we define the 'standard' co-ordinates ($x \parallel$ to the scattering vector, z vertical and y completing a right-handed coordinate system), the x component of $\vec{M}_\perp$ is always zero and we can, therefore, write an explicit form for $\frac{d\sigma}{d\Omega}$, P_{ij} and $\vec{P}'_i$ in these co-ordinates [5]. Here $\frac{d\sigma}{d\Omega} P_{yz} = 2\mathcal{R}e\{M_{\perp y} M^*_{\perp z}\}$ and P_{zy} are the only non-zero, non-diagonal terms in P_{ij} and these can probe magnetic chirality.

In an experimental situation, the magnitude and direction of the scattered polarisation from an incident polarisation parallel to each of the standard co-ordinates is measured. This allows us to measure the polarisation matrix which gives the jth component of scattered polarisation from an incident polarisation which is in the ith direction [5]. Polarimetry can not be used to fully determine the magnetic structure; the propagation vector must be known and only the relative magnitude and direction of the magnetic structure can be found (unless there is a shared nuclear and magnetic peak) [5].

[1]Where $\{\sigma_i\}$ are the Pauli matrices

[2]If the spins are disordered and we take an average, then any terms linear in the nuclear spins must average to zero. Furthermore, any higher order terms must come from this disorder and, therefore, will not contribute to coherent scattering [4]

[3]Using Einstein summation convention

2.2 CRYOPAD

Developed at the ILL [6], CRYOPAD (Cryogenic Polarization Analysis Device) is a method of performing spherical neutron polarimetry. It consists of a cryostat surrounded by two cylindrical Meissner shields with superconducting coils in-between. The Meissner shields ensure the sample space is field free. The coils along with an incoming and outgoing nutator, allow the polarised neutron beam to be orientated in any direction and measured in any direction using a He^3 detector [5]. This allows any components of the polarisation matrix to be measured as the ratio of $(n^+ - n^-)$ to $(n^+ + n^-)$ where n^+, n^- are the numbers of spin up and spin down neutrons detected along the desired measurement axis respectively.

3 Results and Discussion

Using the CRYOPAD method on D3 (ILL, Genoble), the polarisation matrix elements of $Cu_3Nb_2O_8$ were studied using spherically neutron polarimetry. The full matrix was determined for multiple magnetic Bragg peaks at $\approx 3.5K$ and just below T_N at $\approx 26.4K$. These data-sets were refined in Mag2Pol [7] to determine the magnetic structures in the two ordered phases.

The three Cu^{2+} ions occupy the Wyckoff positions $1a$ and $2i$; the latter are identical in all but the LT phase where the inversion centre is broken (this symmetry was taken into account in the MT phase by constraining the moments of the $Cu(2i)$ to be identical). Constraints regarding the lengths of the moments were also implemented into Mag2Pol (SPN is unable to refine the lengths of the moments unless there is nuclear-magnetic overlap [5]).

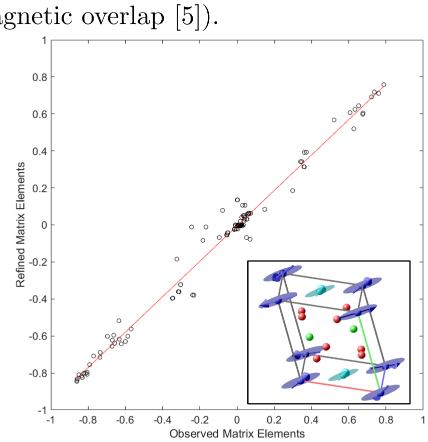

Figure 1: Plot of observed against refined (in Mag2Pol) matrix elements at $\approx 3.5K$ - LT phase. A straight line is included as a guide to the eye. The refined structure corresponds to cycloidal order (INSET) in agreement with Johnson *et al.* Dark and light blue indicate $Cu(1a)$ and $Cu(2i)$ sites respectively. The $Cu(2i)$ site is approximately π out of phase with the $Cu(1a)$ site and slightly out of phase with each other (reflecting the breaking of the inversion centre). The magnetic structure image was generated in Mag2Pol.

In the LT phase a cycloidal structure (figure 1) was refined in agreement with Johnson *et al.* Here the spin rotation is confined to the plane spanned by the real and imaginary parts of $M_\perp(\vec{Q})$. In this study, we find a rotation plane defined by a normal with angular coordinates (θ, ϕ) to be $(80.84°, 59.64°)$ for the $Cu(1a)$ site and $(81.00°, 59.44°)$ for $Cu(2i)$. This shows a discrepancy of $\approx 7°$ to the structure reported from a powder sample by Johnson *et al.* - plane normal of $(75.5°, 54.9°)$ [1]. As this measurement was performed in a powder sample, this may account for this difference. In the structure reported here, the electric polarisation is still out of the rotation plane ($\approx 17°$ to the plane normal).

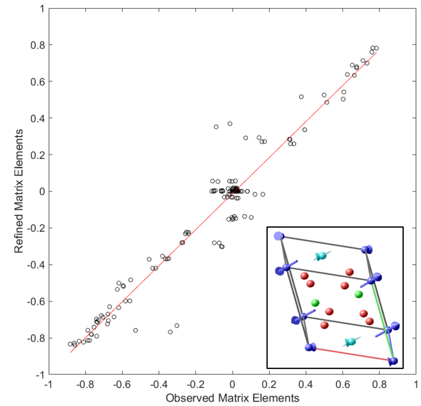

Figure 2: Plot of observed against refined (in Mag2Pol) matrix elements at $\approx 26.4K$ - MT phase. A straight line is included as a guide to the eye. The refined structure corresponds to a spin density wave (INSET). Dark and light blue indicate $Cu(1a)$ and $Cu(2i)$ sites respectively. All Cu sites are now roughly in phase with the two $Cu(2i)$ sites identical. The magnetic structure image was generated in Mag2Pol.

In the MT phase, a spin density wave (SDW) structure is refined (figure 2). This corresponds to either one of the real or imaginary part of $M_\perp(\vec{Q})$ becoming small compared to the other. In the refined structure, $\mathcal{R}e\{M_\perp(\vec{Q}\})$ becomes almost zero resulting in a highly elliptical rotational envelope which manifests as a modulation of the spins - an SDW. Also, all Cu sites are now in phase.

4 Conclusions

In conclusion, spherical neutron polarimetry was used to study the magnetic structure of $Cu_3Nb_2O_8$. The structure was refined to SDW below $T_N \approx 26.5K$, which becomes cycloidal below $\approx 24K$. This was found to be generally in agreement with the powder structure reported by Johnson *et al.*

Acknowledgments

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