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N. Martin[a,b], L.-P. Regnault[a,*], S. Klimko[c], J.E. Lorenzo[d], R. Gähler[e]

[a] *CEA-Grenoble, INAC-SPSMS-MDN, 38054 Grenoble Cedex 9, France*
[b] *Université Joseph Fourier-Grenoble, BP 87, 38402 Saint Martin d'Hères, France*
[c] *Laboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, 91191 Gif-sur-Yvette, France*
[d] *Institut Néel, CNRS/UJF, 38042 Grenoble Cedex 9, France*
[e] *Institut Laue Langevin, BP 156, 38042 Grenoble, France*

Abstract

By using the *Neutron Larmor Diffraction* method and a setup based on the improved *Neutron Resonant Spin Echo* option ZETA recently installed on the three-axis spectrometer IN22 (CRG beam line at the ILL), we have determined the precise relative evolution of the inter- and intra-chain lattice constants of the paradigmatic spin-Peierls compound $CuGeO_3$ as a function of temperature. Our results are consistent with previous results obtained by conventionnal high-resolution diffraction. This method also allows to retrieve independently the sample mosaicities, as well as the widths of various lattice-spacings distributions, thus offering an evaluation of the intrinsic sample quality. In spite of the good definition of the spin-Peierls transition at $T_{SP} = 14.1(1)$K in our sample, we observe a large distribution of lattice constants ($\Delta d/d \simeq 3\times10^{-3}$), while the mosaicity of the sample appears to be quite reasonnable ($\lesssim 20'$).

Keywords: Neutron Larmor diffraction, High-resolution neutron diffraction, Spin-Peierls transition

1. Introduction

Neutron Larmor Diffraction (NLD) is a very powerful technique which was introducted more than one decade ago by M.Th. Rekveldt et al. [1]. As in classical F. Mezei's *Neutron Spin Echo* (NSE) [2], the key is to make use of the spin degree of freedom and the Larmor precession to label the neutron velocity (Larmor encoding). The aim is to relax the usually tight compromise between intensity and accuracy, and to achieve high-resolution diffraction measurement while working with quite modest collimation. As we will see in the next section, the NLD technique (in our case a by-product of the *Neutron Resonance Spin Echo* (NRSE) technique [3]), allows the precise determination of lattice parameters and their distributions, from measurements of the neutron polarization as a function of the total neutron Larmor phase. In this paper, we will report on the Larmor diffraction option recently installed on the thermal three-axis spectrometer IN22 (CRG beam line at the ILL), which is based on an improved version of the ZETA NRSE option [4]. As first application, the NLD technique has been used for the accurate determination of the relative dependences of lattice parameters b and c versus temperature in the inorganic spin-Peierls (SP) compound $CuGeO_3$, in which strong spin-lattice interactions are at the origin of a lattice instability below a characteristic temperature $T_{SP} \approx 14.1$ K, the so-called spin-Peierls transition temperature [5]. Such an instability should significantly affect the lattice constants.

*Corresponding author
Email address: regnault@ill.fr (L.-P. Regnault)

2. The basics of Neutron Larmor Diffraction

The configuration that we will first consider is sketched in Fig.1a). Basically, the sample is surrounded by two homogeneous magnetic field regions of thickness L. A polarized neutron beam with polarization direction perpendicular to $\vec{\mathcal{B}}$ is produced by reflexion of the primary beam on an Heusler crystal. Before being elastically scattered by the sample, neutrons travel through the first magnetic field region and, by virtue of the Larmor precession, they accumulate a phase $\varphi_i = \gamma_n|\vec{\mathcal{B}}|L/v^i_\perp$, where $\gamma_n = 2.916$ kHz.G^{-1} is the neutron gyromagnetic ratio and $v^i_\perp$ is the component of the neutron velocity perpendicular to the field boundary. In the same way, an additionnal precession angle φ_f is undergone after scattering so that the total phase, measured by means of a polarization analyzer, can be written as:

$$\varphi_{tot} = \varphi_i + \varphi_f = \omega_L L\left(\frac{1}{v^i_\perp} + \frac{1}{v^f_\perp}\right), \tag{1}$$

where $\omega_L = \gamma_n|\vec{\mathcal{B}}|$ is the *Larmor pulsation*. Bragg's law stipulates that all neutrons must have the same velocity component perpendicular to the lattice planes generating diffraction (*i.e.* $v^i_\perp = v^f_\perp = \frac{\pi m_n}{\hbar d}$). If the field boundaries are parallel to the lattice planes, it is easy to show from Eq.1 that the total phase is proportionnal to the lattice spacing d [1]:

$$\varphi_{tot} = \frac{2m_n\omega_L L}{\pi\hbar}d \tag{2}$$

As a consquence, any change in d will lead to a corresponding modification of the total Larmor phase:

$$\Delta\varphi_{tot} = \frac{\Delta d}{d}\cdot\varphi_{tot} \tag{3}$$

φ_{tot} is independent of the incoming beam monochromaticity and unavoidable slight misalignment of the setup at first order, but a special care has to be taken when working with large phase values. The data of Section 3 have been corrected from the effects of higher-order terms.

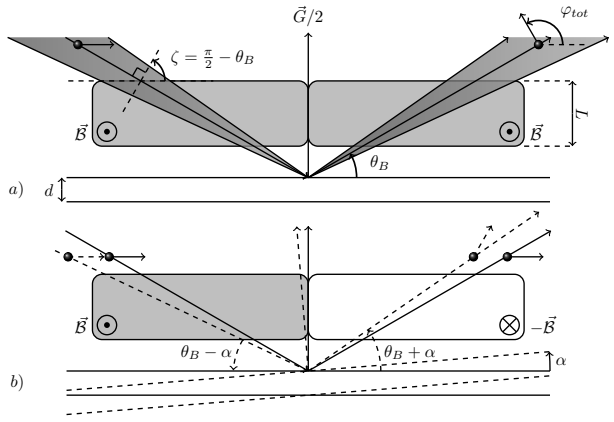

Figure 1: Sketch of a typical *Neutron Larmor Diffraction* setup. a) *"Symmetric configuration"*: Total Larmor phase is proportionnal to lattice spacing d. Each neutron, whatever its velocity or divergence with respect to the main beam axis, participates in the same way to φ_{tot}. If there is a distribution of lattice plane distances, final polarization which is the statistical average of the individual spin phases over the beam, will be reduced as a function of φ_{tot}. b) *"Anti-symmetric configuration"*: In this case, the final polarization is sensitive to lattice planes misalignement at first order. Measurement of P as a function of φ_{tot} yields the mosaicity of the sample along selected direction.

It is worth noting that, in practice, we use a configuration with four pairs of thin radio-frequency (RF) resonance π-flipper coils, separated by zero field regions of length L, to simulate the extended field region (the so-called *Bootstrap* technique [3],[6]). In addition of offering a spectacular increase by a factor of 4 in field-integral $\omega_L L$ (which can be as high as 1.5×10^7 rad.m.s^{-1} with the present ZETA set-up), these devices can be easily rotated by an angle $\zeta = \pm 70°$ with respect to the mean beam axis, thus allowing to fulfill the prerequisites for NLD. Furthermore, in this case ω_L is the pulsation of RF fields and is controlled with high accuracy. Equation (3) has two major consequences which are exploited in order to conduct high resolution diffraction experiments:

i) The Larmor phase φ_{tot} can reach $\approx 10^4$ radians. Given the accuracy on the measurement of precession-region lengths, we can discriminate relative phase changes of the order of 2×10^{-6} and thus evaluate the d-spacing evolution with very high precision,

ii) If we consider the case of an unperfect crystal showing lattice-parameter fluctuations, the polarization at the analyzer (which is defined as the average of the spin projection of the whole neutron beam) is reduced as each d-spacing produces a different phase. This reduction of polarization can be measured as a function of the total phase φ_{tot}, yielding the width δ of the d-distribution. Assuming that this distribution is a sum of gaussian functions, we can write [7]:

$$\begin{aligned} P &= P_0 \langle \cos\varphi(\Delta d/d) \rangle \\ &= P_0 \int \sum_j f_j(\Delta d/d) \cos\varphi(\Delta d/d) d(\Delta d/d) \\ &= P_0 \sum_j w_j \exp\left(-\frac{\varphi_{tot}^2 \delta_j^2}{16 \ln 2}\right), \end{aligned} \tag{4}$$

where P_0 is the spectrometer intrinsic polarization (≈ 0.90, value essentially controled by the Heusler-based polarizer and analyser), w_j are the stastiscial weight corresponding to distributions of width δ_i. This capability is very important as it allows to evaluate a possible phase mixing over the sample volume.

On the other hand, a real single crystal usually shows a finite mosaicity. If we work within the *"anti-symmetric"* configuration (Fig.1b)) for which the field directions are opposite before and after the sample, flight-path lengths are slightly different on each side for neutrons diffracted by misaligned blocks, thus inducing depolarization when considering the whole beam. If we calculate and expand to first order the residual phase induced by a misalignement α of lattice planes, we find [7]:

$$\begin{aligned} \varphi(\alpha) &= \frac{\omega_L L}{v} \cdot \left(\frac{\cos\zeta}{\cos(\zeta + \alpha)} - \frac{\cos\zeta}{\cos(\zeta - \alpha)} \right) \\ &\sim \frac{2\omega_L L}{v} \tan\zeta \cdot \alpha \end{aligned} \tag{5}$$

In the following we will call $f(\alpha)$ the distribution of lattice-planes orientations. We see that within this configuration the phase is sensitive to α at first order. From the latter relation, taking into account the resolution function $\mathcal{R}(\vec{Q})$ of the host spectrometer, we can express the final polarization at the analyzer as:

$$\begin{aligned} P &= P_0 \langle \cos\varphi(\alpha) \rangle \\ &= P_0 \int \mathcal{R}(\vec{Q}(0) - \vec{Q}(\alpha)) f(\alpha) \cos(\varphi(\alpha))\, d\alpha \end{aligned} \tag{6}$$

Thus, measuring P as a function of the total Larmor phase φ_{tot} yields the width of the distribution $f(\alpha)$ through:

$$P = P_0 \exp\left(-\frac{\varphi_{tot}^2 \tan^2\zeta}{16 \ln 2 (1/\delta\omega^2 + 1/\eta^2)}\right), \tag{7}$$

where $\zeta = \pi/2 - \theta_B$ is the flipper-coils tilt angle, θ_B the Bragg angle, $\delta\omega$ the width (FWHM) of the rocking curve across the Bragg peak and η the mosaicity of the sample.

3. Experimental

To perform our experiment, we have used our *Neutron Resonant Spin Echo* (NRSE) option ZETA installed on its host thermal triple-axis spectrometer IN22. Thanks to the optimized

double μ-metal shielding, a high field homogeneity, a powerful cooling system of the static and RF coils, and the possibility to rotate them by angles as large as 70°, high resolution NLD experiments can be easily conducted, although ZETA was originally designed to perform structural and magnetic excitation-lifetimes measurements. A picture of the coil setup is shown in Fig.2.

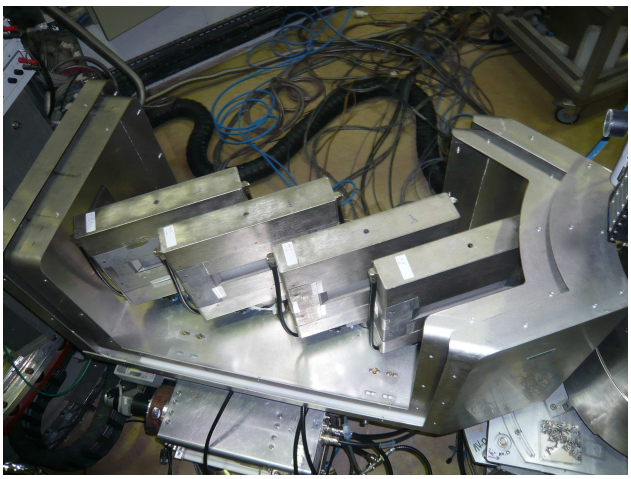

Figure 2: View of the first "arm" of ZETA in the absence of the double μ-metal shielding. The two pairs of RF flipper coils are tilted w.r.t. the beam axis by an angle of 70°, showing the high flexibility of the setup.

Turning to $CuGeO_3$, this compound crystallizes within the orthorhombic space group P_{bmm} with cell parameters a = 4.81 Å, b = 8.47 Å, and c = 2.94 Å. We used a single crystal of volume 0.4 cm^3, synthetized by traveling floating zone method with an image furnace. Our sample displays a sharp spin-Peierls transition at T_{SP} = 14.1(1) K. On the phenomenological point of view, the 3D lattice of atoms, subjected via the spin-lattice couplings to the strong low-energy quantum fluctuations of the spin-1/2 linear chain sub-system, can undergo a dimerization associated with tiny out-of-phase displacements of Cu^{2+} ions (∼ 0.006 Å) along the (0,0,1) chain direction. This structural distortion is induced by an alternating rotation of GeO_4 tetrahedras around the c-axis [8]. This has a strong effect on the super-exchange mediated by Cu-O-Cu bondings and, obviously, on the evolution of the inter-chain constant b [9]. Deeper informations about the physics of $CuGeO_3$ can be found in [5].

Long ago, the inter-chain (b) and intra-chain (c) lattice constants have been measured by means of conventional diffraction as a function of temperature [8]. For this determination, the authors have used a triple-axis spectrometer with two different (wavelength and horizontal-collimation) configurations, λ = 3.31 Å (2.36 Å) and 10'-10'-10'-10' (10'-20'-10'-10'), for the (0,6,0)((0,0,2)) reflexion, respectively[1]. We have repeated this kind of measurement by using NLD on the (0,4,0) and (0,0,1) Bragg peaks, employing a wavelength of λ = 2.36 Å and natural collimations 30'-40'-40'-110'. The tilt angles of the π-flipper coils were $\zeta_{(0,4,0)} = \pm 55.7°$ and $\zeta_{(0,0,1)} = \pm 66.2°$. Our results agree very well with those of K. Hirota et al. within the error bars (see Fig.3). NLD error bars, which are mainly of statistical origin, are smaller than the size of points. The major improvement is the rather precise definition of the sharp spontaneous thermal contraction occuring along the **b**-axis at T_{SP}. Below 14.2 K, the relative evolution of parameter b can be fitted to a single power-law of the form $(1 - T/T_{SP})^{\beta}$ with $\beta \approx 0.5$, in agreement with previous determinations [9]. The intra-chain parameter c seems to be less affected by the spin-Peierls transtion, though one can clearly observe a break in the curve slope. An intriguing new feature is seen in the decrease of c below T ∼ 5 K but we cannot conclude on the reality of this sudden change as we couldn't reach smaller temperature to confirm this observation. Above T_{SP}, the data are best reproduced from the functional $aT^2 + bT^4$, at least up to temperatures of the order of 65 K. If the quartic term is rather general[2], the quadratic term is a pure signature of the quasi-1D antiferromagnetic correlations, which leave an imprint on the structural properties at temperatures larger than T_{SP}, through the spin-lattice couplings.

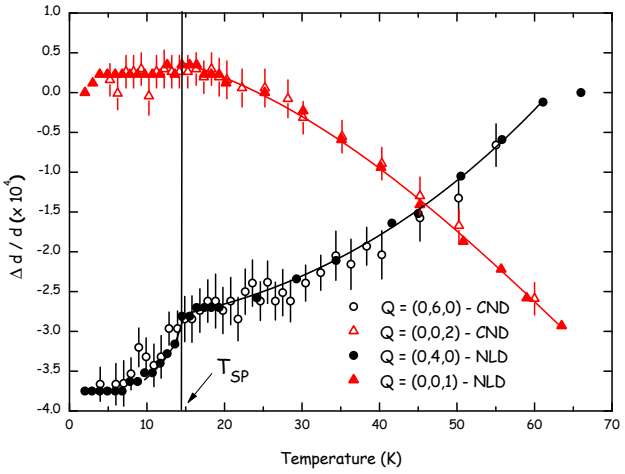

Figure 3: Lattice spacing evolutions as a function of temperature. Black closed triangles correspond to the inter-chain parameter b, which shows a well-defined contraction at T_{SP}. Red closed circles represent the evolution of the intra-chain constant c, which is less affected by the spin-Peierls transition. For sake of comparison, we have also reproduced the results of K. Hirota *et al.*, extracted from [8] (open symbols).

As a complementary measurement, we wanted to check whether the quality of this peculiar sample could be affected by successive heating/cooling cycles. Thus, we used ZETA in the "symmetric" and "antisymmetric" mode to determine lattice spacings spread along both **b**- and **c**-axis as well as its intrinsic mosaicity. In the first case, we have used Eq.4 to fit the data of Fig.4, with j = 2 and the following parameters:

[1] Collimations are given here in the usual order *i.e.* before monochromator - sample - analyzer - detector.

[2] In a Debye model, assuming that Grüneisen parameters are constant, thermal expansivity coefficient of a given material is expected to follow the same law as specific heat (*i.e.* $\propto T^3$) for T not much higher than θ_D. This implies a T^4 dependence for the relative evolution of lattice constants ([10]).

Axis	$\delta_1(10^{-3})$	w_1	$\delta_2(10^{-4})$	w_2
b	2.9(1)	0.73(2)	3.0(3)	0.26(1)
c	2.1(1)	0.79(3)	2.9(5)	0.22(3)

It is surprising to note that the relative-distribution widths, δ_1, are much larger than the thermal expansivity of the material, $\Delta d/d$. This result can be understood if $d(T) \approx d(0)(1 + F(T))$ over the whole parameter range, where F(T) is a function only depending on T, but obviously material-dependent. Apparently, the rather poor definition of parameters b and c do not affect much the occurence in our sample of a well-defined spin-Peierls transition. Another matter of thinking is the fact that the data are better reproduced if we invoke the presence of two d-distributions. The one with the highest stastistical weight is of the order of 10^{-3}, while the other present widths one order of magnitude smaller. It is not clear so far if both distributions are really present within the sample or if this result is only a measurement artifact. However, such a two-scale distribution has also been reported in other materials [7]. In any case, the largest value gives the right estimate of the disorder within the sample.

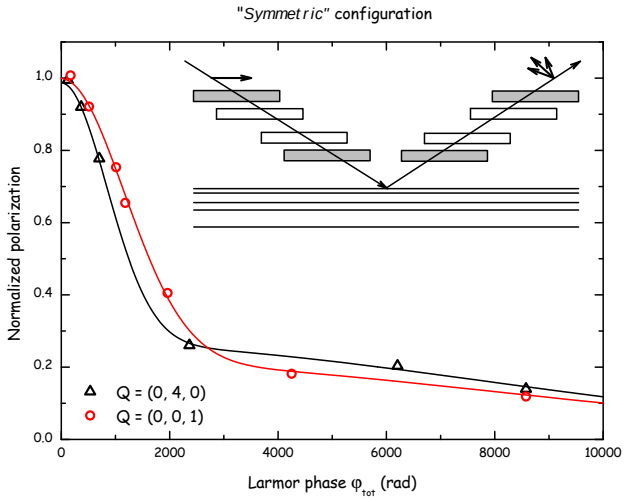

Figure 4: Polarization as function of the total Larmor phase measured at $\vec{Q} = (0, 4, 0)$ and $\vec{Q} = (0, 0, 1)$ in the *"symmetric"* configuration. The data have been recorded at T = 66K and corrected from higher-order effects of the beam divergence, as φ_{tot} reach $\sim 10^4$ radian and we worked with natural collimations (see section 3).

The sample mosaicity was measured in the *"anti-symmetric"* mode. A rapid decay of the polarization is observed as a function of φ_{tot}, as documented from Fig.5. A fit of experimental data to Eq.7 gives the following values, where $\delta\omega$ is the width (FWHM) of the corresponding rocking curve:

Axis	$\eta_{FWHM}(')$	$\delta\omega_{FWHM}(')$
b	17.7(9)	35.4(6)
c	15.2(2)	36.9(4)

The values of mosaic spreads which have been extracted for the **b** and **c** directions are found far below the widths of the corresponding rocking scans and reflect better the intrinsic mosaicity of the sample. The precise knowledge of η is crucial when considering, *e.g.*, the design of innovative materials or data correction of NRSE experiments.

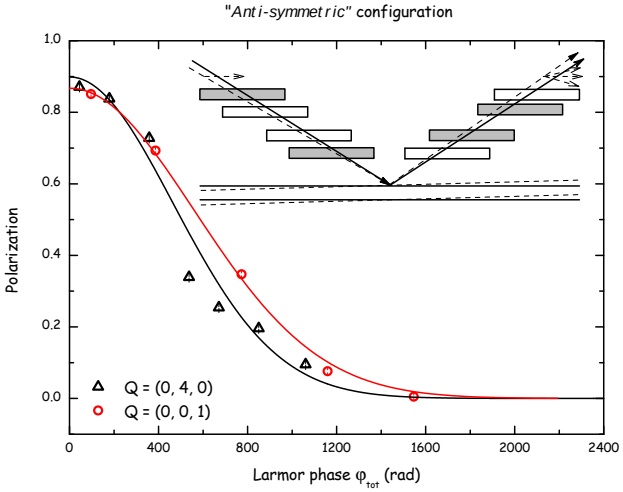

Figure 5: Polarization as a function of φ_{tot} in the *"anti-symmetric"* mode at T = 66 K. The decay is interpreted as the effect of the intrinsic sample mosaicity convoluted with the host spectrometer resolution function (see section 2).

4. Conclusion

By means of Neutron Larmor Diffraction, we have carried out a thorough study of a single-crystalline sample of the spin-Peierls compound $CuGeO_3$. Our results tend to show that this technique is reliable and will most probably become in a close future a method of choice for a better characterization of a large variety of samples, in particular systems showing structural phase transitions. Technical limitations restrict the precision of such measurements to values far below what can be obtained in dilatometry experiments, but the unique feature of Larmor diffraction is to allow an evaluation of the sample quality with the same setup and over its full volume.

Acknowledgements

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References

[1] M.Th. Rekveldt, T. Keller and R. Golub, Europhys. Lett. **54**, 342 (2001).
[2] F. Mezei, Z. Physik **255**, 146 (1972).
[3] R. Golub and R. Gähler, Phys. Lett. A **123**, 43 (1987).
[4] S. Klimko, C. Stadler, P. Böni, R. Currat, F. Demmel, B. Fåk, R. Gähler, F. Mezei and B. Toperverg, Physica B **335**, 188 (2003).
[5] J.-P. Boucher and L.-P. Regnault, J. Phys. I France **6**, 1939 (1996) and references therein.
[6] R. Gähler and R. Golub, J. Phys. France **49**, 1195 (1988).
[7] T. Keller, M.Th. Rekveldt and K. Habicht, Appl. Phys. A **74**, S127 (2002).
[8] K. Hirota et al., Phys. Rev. Lett. **73**, 736 (1994).
[9] Q.J. Harris et al., Phys. Rev. B **50**, 12606 (1994).
[10] N.W. Ashcroft and N.D. Mermin, *Solid state physics*, Saunders College Publishing (1976).