On the atomic and magnetic ordering of hexagonal NdCuSn

1999 J. Phys.: Condens. Matter 11 4135

(http://iopscience.iop.org/0953-8984/11/21/302)

J. Phys.: Condens. Matter **11** (1999) 4135–4141. Printed in the UK PII: S0953-8984(99)00790-0

On the atomic and magnetic ordering of hexagonal NdCuSn

J V Pacheco†, K Yvon†, E Gratz‡ and P Schobinger-Papamantellos§

† Laboratoire de Cristallographie, Université de Genève, Geneva, Switzerland
‡ Institute for Experimental Physics, TU Vienna, A-1040 Vienna, Austria
§ Institut für Kristallographie, ETH Zurich, Zurich, Switzerland

Received 6 January 1999

Abstract. The magnetic structure of the hexagonal stannide NdCuSn has been studied by neutron powder diffraction at low temperature. Magnetic ordering occurs below ∼10 K and is associated with two magnetic wave vectors, $\boldsymbol{q}_1 = (0, 3/8, 0)$ and $\boldsymbol{q}_2 = (1/2, 0, 0)$ or $(0, 1/2, 0)$. The $\boldsymbol{q}_1$ vector is attributed to a majority fraction (>90%) of the NdCuSn phase having an ordered Cu/Sn sublattice (non-centrosymmetric NdPtSb type structure, space group $P6_3mc$). It can be described as originating from a transverse sine wave modulated arrangement of spins oriented $\parallel c$ with a maximum moment value of 2.2 μ_B/Nd atom, or alternatively by an antiphase domain structure having two amplitudes. The $\boldsymbol{q}_2$ vector is attributed to a minority fraction (<10%) of the NdCuSn phase having a disordered Cu/Sn sublattice (centrosymmetric $CaIn_2$ type structure, space group $P6_3/mmc$). It has a simple antiferromagnetic +− moment arrangement along a or b and the moments are oriented $\parallel c$ with a refined value of about 1.2 μ_B.

1. Introduction

The crystal structure and magnetic properties of the hexagonal stannides LnCuSn (Ln = Nd, Sm, Gd) have recently been studied by x-ray diffraction, magnetization and Mössbauer experiments [1]. Structure refinements on single crystals at room temperature have shown [2] that these compounds crystallize with an ordered Cu/Sn sublattice (corresponding to the non-centrosymmetric NdPtSb type structure, space group $P6_3mc$), although for NdCuSn the data did not exclude the hypothesis that a small fraction (<10%) of the crystal investigated had a disordered Cu/Sn sublattice (corresponding to the centrosymmetric $CaIn_2$ type structure, space group $P6_3/mmc$). Magnetic order occurred at about 10 K. Very recently, the authors of a neutron diffraction study [3] on LnCuSn (Ln = Pr, Nd) have again adopted the disordered model, and proposed for NdCuSn a magnetic structure that consists of a collinear antiferromagnetic arrangement of spins $\parallel c$, and a single wave vector $\boldsymbol{q} = (1/2, 0, 0)$ with a maximum moment value of 1.25 μ_B. In the following report we show that NdCuSn may display two distinct magnetic structures associated with the wave vectors $\boldsymbol{q}_1 = (0, 3/8, 0)$ and $\boldsymbol{q}_2 = (1/2, 0, 0)$ or $(0, 1/2, 0)$ and different maximum moment values $\parallel c$. The relative amount of these structures presumably depends on the degree of ordering of the non-magnetic Cu/Sn sublattice.

2. Experiment

A sample of NdCuSn was prepared by induction melting of the elements in a water cooled copper crucible, and by cooling the ingot down to room temperature within about 10 minutes.

0953-8984/99/214135+07$19.50

These conditions differ significantly from those reported in the previous study [3] which consisted of arc melting and annealing at 600 °C for 100 h. Neutron powder diffraction patterns were recorded at 15 K, 5 K and 1.5 K on the diffractometer D1a at ILL (Grenoble) by using the wavelength $\lambda = 2.99$ Å (2θ range 8–80°; step size 0.05°). The data were corrected for absorption and evaluated by the Fullprof program [4]. The diffraction patterns confirmed the presence of the hexagonal NdCuSn phase, but also showed weak additional peaks which were attributed to the impurity phase $Nd_3Cu_4Sn_4$ (<7%) and a third-order wavelength contamination of the incoming neutrons (<0.1%). These peaks were modelled and included in the refinements.

3. Results

3.1. Nuclear structure

Based on the 15 K data three structure models were tested in the paramagnetic state, the NdPtSb type having an ordered Cu/Sn substructure, the $CaIn_2$ type having a disordered Cu/Sn substructure and a 90%–10% mixture between the ordered and disordered model corresponding the ambiguity limit reported in the previous x-ray single crystal study [2]. For the ordered model the starting parameter values were those of [2]. The refinements included the cell parameters (a,c), two positional parameters (z(Cu), z(Sn), two displacement parameters (B(Nd), B(Cu) = B(Sn)), one preferred orientation parameter and two scale factors (NdCuSn and $Nd_3Cu_4Sn_4$). For the disordered model the same parameters as above were refined except for z(Cu) = z(Sn); for the mixed model only two scale factors were refined (NdCuSn and $Nd_3Cu_4Sn_4$). The diffraction profiles were modelled by pseudo-Voigt functions (No 7 in [4]). As shown by the refinement results summarized in table 1, the agreement factors did not differ much between the various models and thus did not favour one over the other. Significant structural differences, however, occurred in comparison with the single crystal x-ray results, but these were presumably due to the different measuring temperatures. The observed, calculated and difference patterns of the ordered model are represented in figure 1. A structural representation of the ordered and disordered models is given in figure 2.

Table 1. Nuclear structure refinement results of NdCuSn at 15 K.

	Ordered	Disordered	Mixed[a]
Space group	$P6_3mc$	$P6_3/mmc$	$P6_3mc$ and $P6_3/mmc$
a (Å)	4.559 19(6)	4.559 21(6)	fixed[b]
c (Å)	7.5725(2)	7.5725(2)	fixed[b]
z (Cu)	0.7967(9)[c]	0.5320(3)[d]	fixed[b]
z (Sn)	0.2357(9)[c]	0.5320(3)[d]	fixed[b]
B(Nd) (Å^2)	1.23(14)	1.28(10)	fixed[b]
B(Cu) = B(Sn) (Å^2)	2.12(14)	1.75(8)	fixed[b]
GoF	3.7	3.9	3.7
R_n (%)	3.5	4.6	3.4[e]; 3.3[f]
R_{wp} (%)	15.7	16.2	15.6

[a] 90/10 mixture of ordered and disordered model.
[b] Values of ordered and disordered model.
[c] Site 2b.
[d] Site 4f Cu/Sn disorder; z(Cu) = z(Sn).
[e] Ordered phase.
[f] Disordered phase.

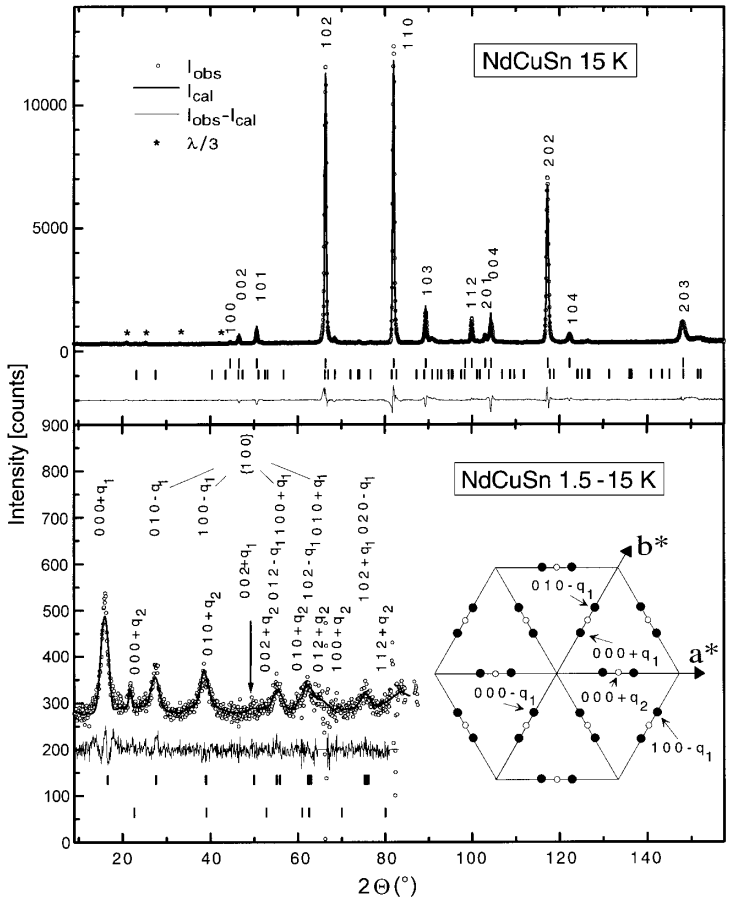

Figure 1. Observed, calculated and difference neutron diffraction patterns of hexagonal NdCuSn (ordered structure model); top: 15 K (bars of second row indicate impurity phase $Nd_3Cu_4Sn_4$; stars indicate 3d order ($\lambda/3$) contamination); bottom: 1.5 − 15 K difference diagrams; inset: magnetic satellites in basal plane of reciprocal space, for one wave vector (star) $\pm\boldsymbol{q}_1 = (0, 3/8, 0)$ and $\boldsymbol{q}_2 = (1/2, 0, 0)$.

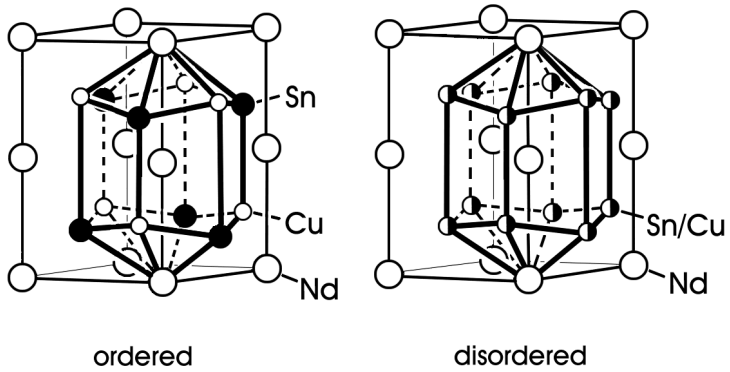

Figure 2. Ordered (left) and disordered (right) nuclear structure of NdCuSn, viewed approximately perpendicular to the hexagonal axis.

3.2. Magnetic ordering

Upon cooling, magnetic ordering became apparent at about 10 K and was essentially completed at 1.5 K. The magnetic satellites in the diffraction patterns were rather weak and showed significant line broadening. Interestingly, the broadening was not uniform as some satellites were sharper than others. As the temperature was lowered, the intensity of the satellites increased, but their positions did not change significantly. The indexing was performed on a difference pattern between the 1.5 K and 15 K data (figure 1), thus minimizing a possible influence of the impurity phase $Nd_3Cu_4Sn_4$. Two magnetic wave vectors were found, $\boldsymbol{q}_1 = (0, 3/8, 0)$ and $\boldsymbol{q}_2 = (1/2, 0, 0)$ or $(0, 1/2, 0)$ (see inset of figure 1). Their lengths and directions were practically independent of temperature. A profile refinement based on the ordered model and the $1.5 - 15$ K difference pattern suggested that $\boldsymbol{q}_1$ was associated with a sine wave amplitude modulated magnetic structure with a $8 \times \boldsymbol{b}$ bigger cell in which the Nd spins were polarized along $\boldsymbol{c}$ and had a maximum amplitude of $\mu_{0Nd} = 2.08(2)\ \mu_B$. The relative diffuseness of the reflections suggested rather short magnetic ordering distances. The vector $\boldsymbol{q}_2$ was associated with an uniaxial antiferromagnetic structure with a $2 \times \boldsymbol{a}$ or $2 \times \boldsymbol{b}$ bigger cell in which the Nd spins were polarized along $\boldsymbol{c}$ and had a refined moment value of $\mu_{Nd} = 0.37(2)\ \mu_B$. The relative sharpness of the reflections suggested that the magnetic ordering extended over longer distances. During the refinement the scale factor was fixed at the value of the nuclear refinement (ordered model), and the different widths of the diffraction peaks were modelled by two sets of pseudo-Voigt function parameters, corresponding to an average magnetic domain size of 84 Å for the $\boldsymbol{q}_1$ phase and 312 Å for the $\boldsymbol{q}_2$ phase. The observed, calculated and difference patterns are shown in the bottom part of figure 1, and a list of observed and calculated magnetic intensities is given in table 2. The agreement factors for the magnetic refinement are $R_{m_1} = 11\%$, $R_{m_2} = 35\%$, $R_{wp} = 39.9$, GoF $= 1.5$. The relatively poor values for R_{m_2} and R_{wp} are mainly a consequence of the low counting statistics, and can be considered as satisfactory for these types of analysis.

The above results contrast with those of the previous study [3] in which a fully disordered structure model was assumed and the presence of only one wave vector $\boldsymbol{q} = (1/2, 0, 0)$ and a collinear antiferromagnetic ordering with a moment value of 1.25 μ_B was reported. These different findings, combined with the structural ambiguity pointed out during the previous single crystal x-ray study [2] and the different preparation conditions of the samples, suggest that the wave vector $\boldsymbol{q}_1$ should be attributed to an ordered majority fraction (90%) and $\boldsymbol{q}_2$ to a disordered minority fraction (10%) of the NdCuSn structure. As expected, a final structure refinement based on such a 'mixed' magnetic model yielded practically the same agreement factors but lead to larger moment values. The maximum Nd moment associated with $\boldsymbol{q}_1$ increased to 2.19(2) μ_B, while that associated with $\boldsymbol{q}_2$ increased to 1.19(7) μ_B, thus coming close to the previously reported value of 1.25 μ_B [3]. Note that the ambiguity concerning the proposed magnetic order of NdCuSn originates in part from the limited knowledge of nuclear order in that compound, as was pointed out in the previous single crystal x-ray study [2]. It is due to the limitations of current methodology and the particular structure of NdCuSn and would persist even if single crystals suitable for neutron diffraction were available. On the other hand, the model has the advantage of being consistent with both the present data and those reported in [3].

3.2.1. The amplitude modulated magnetic structure $\boldsymbol{q}_1 = (0, 3/8, 0)$. In real space the magnetic moment value of the j_{th} atom at position $\boldsymbol{R}_{nj} = \boldsymbol{r}_j + \boldsymbol{R}_n$ with $\boldsymbol{R}_n = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$, in the nth cell (n is integer and $j = 1$) of a periodic arrangement is given by [5]:

$$\boldsymbol{\mu}_{nj} = \sum_{\{q\}} \boldsymbol{S}_{qj} \exp\{-2\pi \mathrm{i} \boldsymbol{q} \cdot \boldsymbol{R}_n\} = \sum_{\{q\}} \boldsymbol{T}_{\boldsymbol{q}} \exp\{-2\pi \mathrm{i} \boldsymbol{q} \cdot \boldsymbol{R}_{nj}\} \tag{1}$$

Table 2. Observed and calculated magnetic intensities of phase $\boldsymbol{q}_1$ and phase $\boldsymbol{q}_2$ in NdCuSn ($T = 1.5$ K, $\lambda = 2.99$ Å).

Wave vector $\boldsymbol{q}_1 = (0, 0.375, 0)$					
h	k	$l \pm \boldsymbol{q}_1$	2θ	I_{calc}	I_{obs}
0	0	0±	16.325	430.0	468.4
0	1	0−	27.376	153.3	177.7
1	−1	0+	38.695	78.0	73.6
1	0	0−			
0	0	2±	49.629	15.4	6.4
0	1	−2−	54.827	13.9	13.3
0	1	2−			
1	−1	0−	55.566	39.5	34.6
1	0	0+			
1	−1	−2+	62.061	16.3	13.6
1	−1	2+			
1	0	−2−			
1	0	2−			
0	1	0+	62.746	30.2	20.7
1	−1	2−	75.315	15.8	16.2
1	−1	−2−			
1	0	−2+			
1	0	2+			
0	2	0−	75.942	23.2	21.6
Wave vector $\boldsymbol{q}_2 = (1/2, 0, 0)$ or $(0, 1/2, 0)$					
h	k	$l \pm \boldsymbol{q}_2$	2θ	I_{calc}	I_{obs}
0	0	0−	21.825	31.5	44.6
0	−1	0−	38.282	10.5	9.1
0	0	−2−	51.948	2.9	3.3
0	1	0−	60.115	9.0	11.3
0	−1	2−	61.770	4.3	4.1
1	0	0−	69.212	3.5	5.4
0	1	2−	79.263	8.0	0.0

where $(\boldsymbol{S}_{qj}, \boldsymbol{S}_{-qj})$ are the observed Fourier coefficients associated with the propagation vector(s) $\pm\boldsymbol{q}_i$. In a sine wave modulated structure as found above the moment value μ_{nj} of the jth atom in the nth cell may be derived from the moment value (Fourier coefficients) in the *zeroth* cell:

$$\boldsymbol{\mu}_{nj} = \sum_{\boldsymbol{q}} S_{qj} \exp\{-2\pi \mathrm{i}\boldsymbol{q} \cdot \boldsymbol{R}_n\} = \boldsymbol{\mu}_{0j} \cos(2\pi \boldsymbol{q} \cdot \boldsymbol{R}_n + \phi_j) = \mu_{0j}\boldsymbol{z} \cos(2\pi \boldsymbol{q} \cdot \boldsymbol{R}_n + \phi_j) \quad (2)$$

where $\boldsymbol{z}$ is a unit vector in the direction of the varying moment component, μ_{0j} the amplitude of the sinusoidal variation and ϕ_j a phase factor of the jth atom relative to the origin of the wave usually taken at atom (1). As the phase of Nd at $(0, 0, 1/2)$ was found to be zero the structure can be fully described for only the Nd atom at $(0, 0, 0)$ and by calculating with expression (2) the moment value for $n = (0, 8, 0)$ cells as shown in figure 3. It is obvious that the moment value depends on an arbitrary choice of the phase ϕ and cannot be defined by diffraction. For entropy reasons the best choice of ϕ is that which leads to the smallest scattering among the moment values [6]. In the present case $\phi = \pi/8$ and therefore $\mu_0 \cos 2\pi(3/8n + 1/16) = \mu_0 \cos \pi(6n + 1)/8$. The moment distribution displayed in figure 3 shows two different Nd moment values of $\pm 1.97\ \mu_B$ for the atoms at $n = 0, 1, 4, 5$, and of

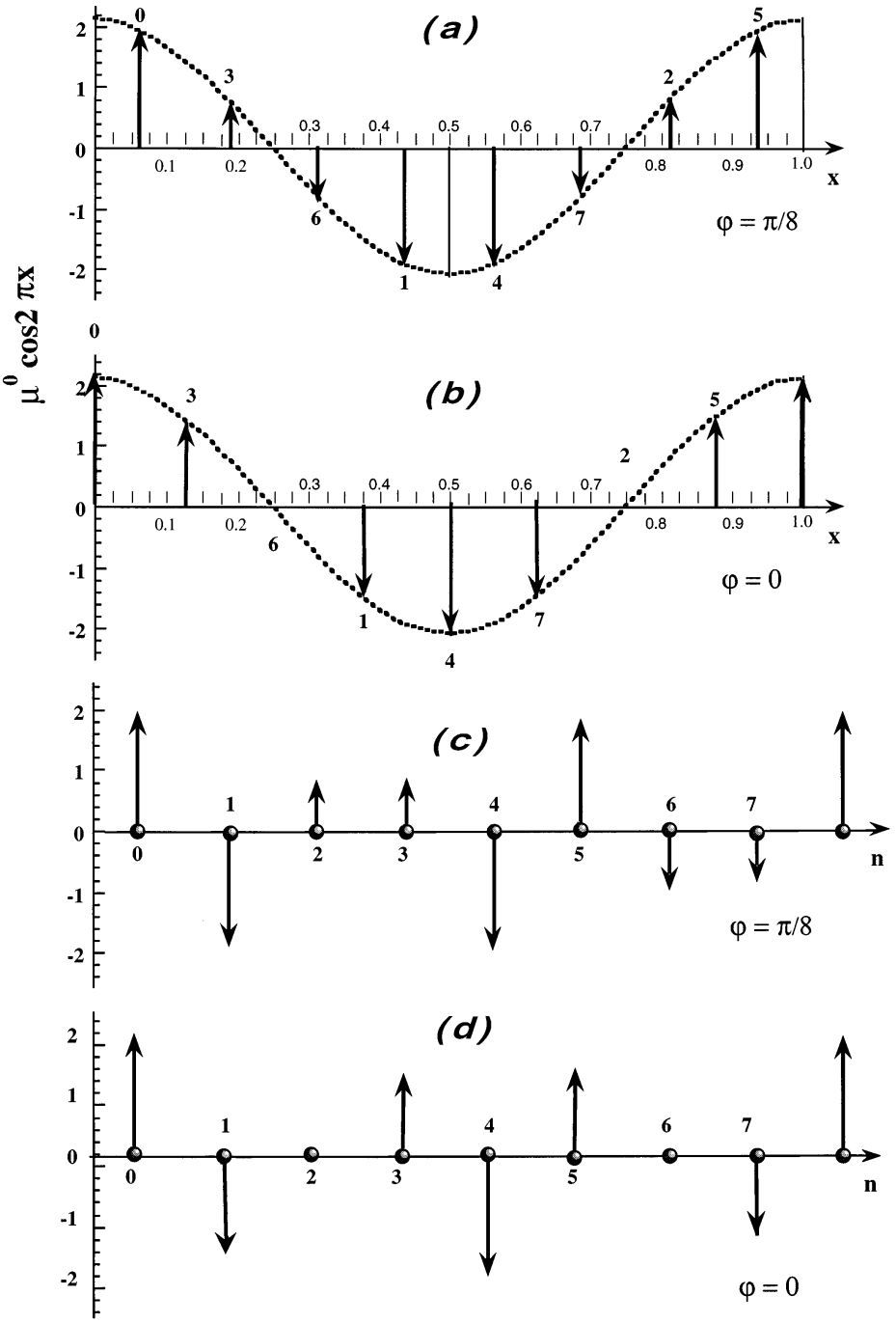

Figure 3. Transverse sine wave modulations ($\mu_0 \cos 2\pi x$, $x = \boldsymbol{q}_1 n + \varphi$) for the wave vector $\boldsymbol{q}_1 = (0, 3/8, 0)$ with a refined amplitude value of 2.13 μ_B for (a) $\varphi = 2\pi/16$ and (b) $\varphi = 0$. Also shown is the moment distribution along $\boldsymbol{b}$ for eight cells for (c) $\phi = \pi/8$ (antiphase domain with two amplitudes) and (d) $\phi = 0$ (antiphase domain with three amplitudes).

$\pm 0.81\ \mu_B$ for the atoms at $n = 2, 3, 6, 7$. It should be noted that this magnetic structure can also be considered as an antiphase domain structure with two amplitudes where the moment values change along b in the following sequence for $n = 8$ atoms: $\mu_1(+-)\mu_2(++)\mu_1(+-)\mu_2(--)$. For $\phi = 0$ one obtains also two moment values $\mu_1 = \pm 1.97\ \mu_B$, $\mu_2 = 0$ in the sequence $\mu_1(+ - 0 + - + 0+)$. Clearly, a single crystal would allow one to characterize the magnetic structure further.

4. Conclusion

The nuclear and magnetic structure of NdCuSn appears to be more complicated than previously thought. In contrast to a previous study which reports on a disordered nuclear structure and a magnetic structure having only one propagation vector, the present study gives evidence for an essentially ordered nuclear structure and two magnetic wave vectors. The most likely reason for this discrepancy is differences in sample preparation which may influence the degree of order of the non-magnetic components. Thus more work is necessary to characterize the structural and magnetic properties of this stannide.

Acknowledgments

The authors thank Mrs T Fernandez-Diaz (ILL) for help with the data acquisition. The work was supported by the Swiss National Science Foundation.

References

[1] Hatzl R, Reissner M, Forsthuber M, Gratz E, Steiner W, Wiesinger G and Yvon K 1996 *Conf. Proc. ICAME-95* vol 50, ed I Ortalli (Bologna: SIF) pp 347–50
[2] Pacheco J V, Yvon K and Gratz E 1998 *Z. Kristallogr.* **213** 510
[3] Baran S, Hofmann M, Leciejewicz J, Slaski M and Szytula A 1998 *J. Phys.: Condens. Matter* **10** 2107
[4] Rodríguez-Carvajal J 1993 *Physica* B **192** 55;
see also `ftp://bali.saclay.cea.fr/pub/divers/fullp/doc`
[5] Rossat-Mignod J 1987 *Neutron Scattering (Methods of Experimental Physics 23, Part C 69)* (New York: Academic)
[6] Elliott R J 1961 *Phys. Rev.* **124** 346