

**Supplement to**

**Cr<sub>2</sub>(NCN)<sub>3</sub>, a ferromagnetic carbodiimide with an unusual two-step magnetic transition**

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**Table 1:** Parameters attained from the Rietveld refinement of the neutron powder diffraction data of  $\text{Cr}_2(\text{NCN})_3$ .

$T$ (K)	220	150	108
Space group		$R\bar{3}c$	
$a$ (Å)	5.47771(7)	5.47792(7)	5.48006(7)
$c$ (Å)	28.0070(3)	28.0039(3)	27.9977(3)
$V$ (Å <sup>3</sup> )	727.773(15)	727.747(15)	728.154(15)
Refined pattern range, $2\theta$ (°)		8.00–151.90	
$R_p$	0.0278	0.0287	0.0311
$R_{\text{Bragg}}$	0.0602	0.0604	0.0590
Magnetic space group			$P\bar{1}$
magnetic moment, $\mu_B$			1.47(12)
$R_{\text{Bragg, magn}}$			0.191

**Table 2:** Equivalent displacement parameters  $U_{\text{eq}}$  (Å<sup>2</sup>) in  $\text{Cr}_2(\text{NCN})_3$  measured at  $T = 220$ , 150 and 108 K.

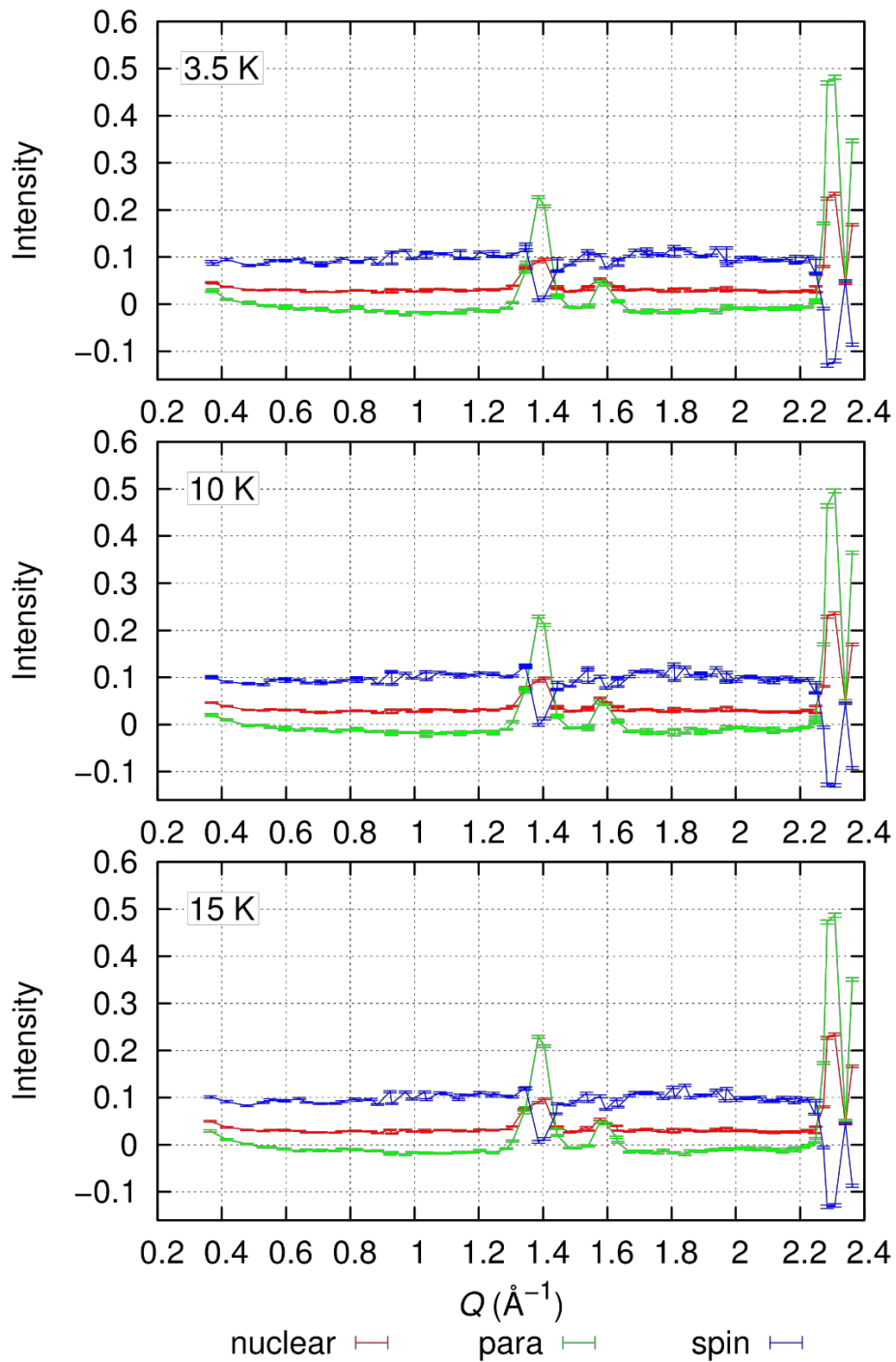
Atom	Wyckoff position	$T$ (K)	$x$	$y$	$z$	$U_{\text{eq}}$ (Å <sup>2</sup> )
		220				
Cr	12c		0	0	0.1662(4)	0.017(2)
C	18e		0.3249(6)	0	¼	0.0165(13)
N	36f		0.6377(4)	0.0017(5)	0.04040(3)	0.0187(7)
		150				
Cr	12c		0	0	0.1663(4)	0.015(2)
C	18e		0.3250(6)	0	¼	0.0143(12)
N	36f		0.6373(3)	0.0021(5)	0.04044(3)	0.0172(7)
		108				
Cr	12c		0	0	0.1658(3)	0.014(2)
C	18e		0.3220(6)	0	¼	0.0110(12)
N	36f		0.6368(3)	0.0013(5)	0.04035(3)	0.0164(7)

**Table 3:** Anisotropic displacement parameters  $U_{\text{ani}}$  ( $\text{\AA}^2$ ) in  $\text{Cr}_2(\text{NCN})_3$  measured at  $T = 4, 108, 150, 220$  and  $300$  K.

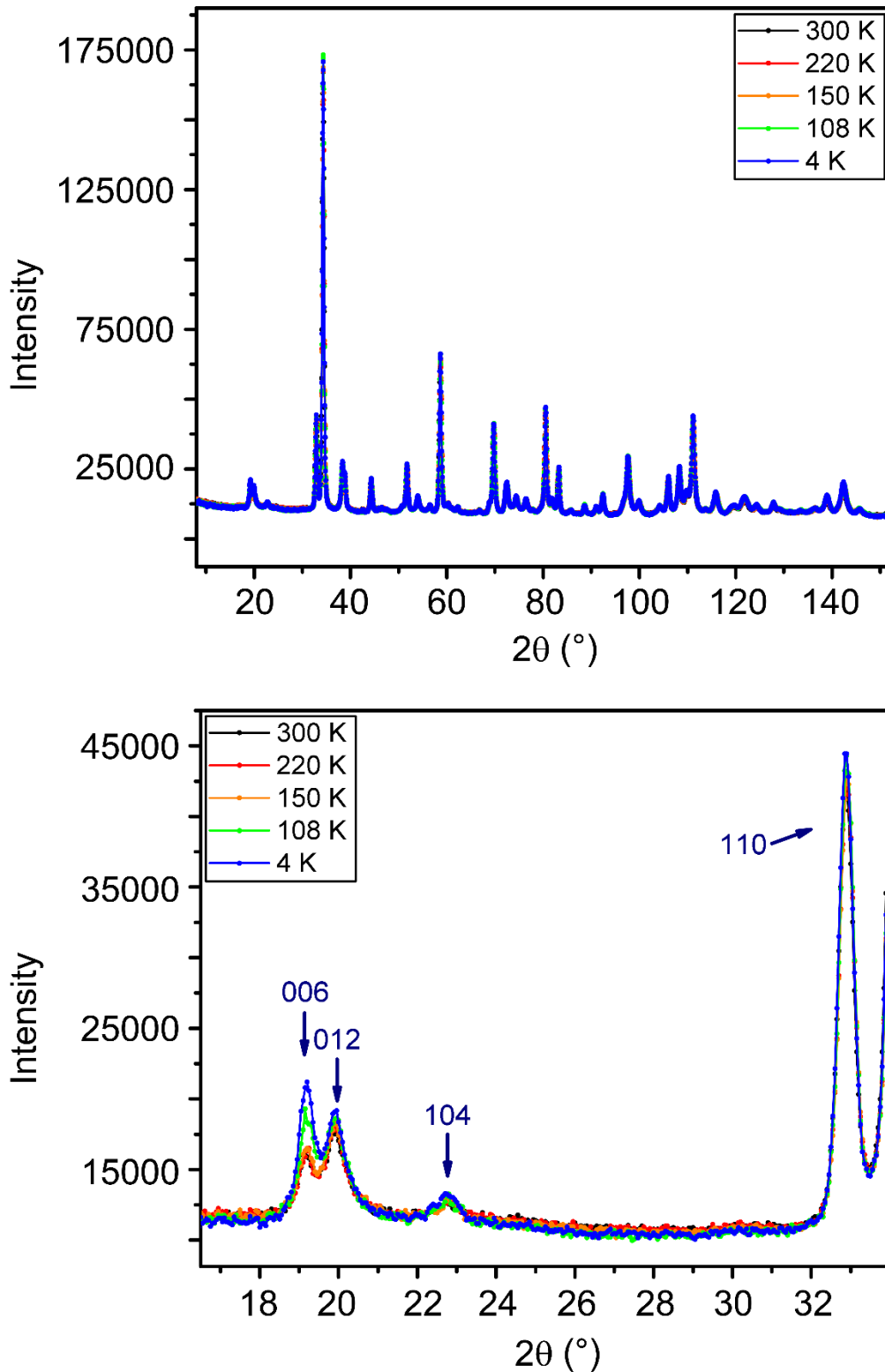
Atom	Wyckoff position	$T$ (K)	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
		300						
Cr	12c		0.024(2)	0.024(2)	0.0097(18)	0.012(2)	0	0
C	18e		0.0185(11)	0.033(2)	0.0047(8)	0.016(2)	-0.0042(7)	-0.0084(7)
N	36f		0.0340(10)	0.0176(6)	0.0100(4)	0.0110(9)	0.0043(7)	0.0035(7)
		220						
Cr	12c		0.021(2)	0.021(2)	0.0093(18)	0.010(2)	0	0
C	18e		0.0156(11)	0.0297(20)	0.0043(8)	0.0148(20)	-0.0045(7)	-0.0089(7)
N	36f		0.0301(10)	0.0170(6)	0.0091(4)	0.0099(9)	0.0040(7)	0.0033(7)
		150						
Cr	12c		0.018(2)	0.018(2)	0.0092(18)	0.009(2)	0	0
C	18e		0.0139(11)	0.0254(19)	0.0035(8)	0.0127(19)	-0.0030(6)	-0.0061(6)
N	36f		0.0293(10)	0.0149(6)	0.0076(4)	0.0091(9)	0.0043(7)	0.0028(7)
		108						
Cr	12c		0.016(2)	0.016(2)	0.0093(19)	0.008(2)	0	0
C	18e		0.0099(10)	0.0186(18)	0.0047(7)	0.0093(18)	-0.0028(6)	-0.0057(6)
N	36f		0.0291(10)	0.0156(6)	0.0045(4)	0.0101(9)	0.0040(7)	0.0026(6)
		4						
Cr	12c		0.0095(18)	0.0095(18)	0.0030(17)	0.0048(18)	0	0
C	18e		0.0096(10)	0.0157(16)	0.0031(7)	0.0078(16)	-0.0023(6)	-0.0046(6)
N	36f		0.0196(9)	0.0157(6)	0.0040(4)	0.0036(9)	0.0045(6)	0.0021(6)

**Table 4:** Bond lengths (Å) and angles (°) for Cr<sub>2</sub>(NCN)<sub>3</sub>.

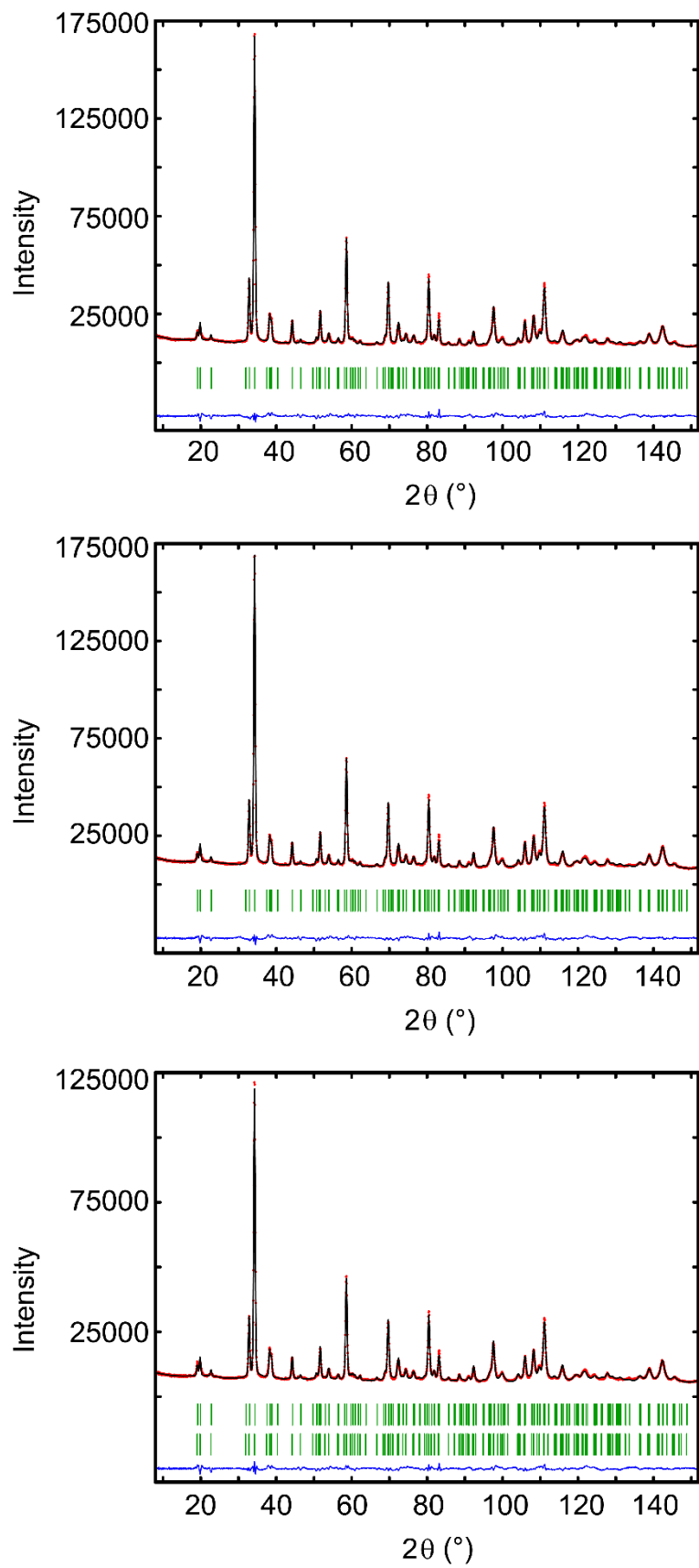
<i>T</i> (K)	300	220	150	108	4
Cr...N	2.092(7) × 3 2.080(6) × 3	2.085(7) × 3 2.083(6) × 3	2.081(6) × 3 2.085(6) × 3	2.091(5) × 3 2.074(5) × 3	2.086(5) × 3 2.077(5) × 3
Cr...C	2.953(9) × 3 2.961(9) × 3	2.945(9) × 3 2.968(9) × 3	2.943(9) × 3 2.969(9) × 3	2.945(7) × 3 2.964(7) × 3	2.946(7) × 3 2.964(7) × 3
N–C	1.2108(9) × 2	1.2110(9) × 2	1.2101(9) × 2	1.2120(9) × 2	1.2124(9) × 2
Cr...Cr (intralayer)	3.1644(2)	3.1626(1)	3.1628(1)	3.1643(2)	3.1653(2)
Cr...Cr (interlayer)	4.710(16)	4.694(16)	4.688(16)	4.715(12)	4.708(12)
N...Cr...N	92.6(3) × 3 92.4(3) × 3 81.3(3) × 3 94.2(3) × 3 172.3(3) × 3	92.7(3) × 3 92.6(3) × 3 81.3(3) × 3 93.9(3) × 3 172.2(3) × 3	92.7(3) × 3 92.8(3) × 3 81.2(3) × 3 93.8(3) × 3 172.0(3) × 3	92.5(2) × 3 92.7(2) × 3 81.1(2) × 3 94.2(3) × 3 171.9(3) × 3	92.5(2) × 3 92.8(2) × 3 81.0(2) × 3 94.2(3) × 3 171.8(3) × 3
N–C–N	176.11(13)	175.98(13)	175.62(13)	177.46(13)	176.50(13)
Cr...N–C	124.6(6) × 3 126.2(6) × 3	124.5(6) × 3 126.5(6) × 3	124.7(6) × 3 126.5(6) × 3	124.0(5) × 3 126.9(5) × 3	124.4(5) × 3 126.6(5) × 3



**Fig. S1:** Preliminary spin-polarized neutron powder diffractograms of  $\text{Cr}_2(\text{NCN})_3$  conducted at  $T = 3.5$  (top), 10 (middle), and 15 K (bottom). Only the low-angle region is measured involving the (006), (012), (104) and (110) reflections. Due to the resolution of the instrument only one reflection is observed for the (006) and (012) reflections. The measurements were performed at the cold diffuse neutron spectrometer (DNS) at the research neutron source Heinz Maier-Leibnitz (FRM II), in Garching, Germany.



**Fig. S2:** Neutron powder diffractograms of  $\text{Cr}_2(\text{NCN})_3$  collected at  $T = 4, 108, 150, 220$  and  $300$  K (top), with focus on the (006) and (012) reflections (bottom). Due to shorter measurement time at  $T = 108$  K intensities are corrected for comparison with the other measurements.



**Fig. S3:** Rietveld refinement plot of  $\text{Cr}_2(\text{NCN})_3$  at  $T = 220$  (top), 150 (middle) and 108 K (bottom).