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Supporting information for article:

Lack of 3-fold rotation axis in α-Fe2O3 and α-Cr2O3 crystals

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S1. Trigonal to monoclinic transformation

The transformation of the axes and coordinates between *R*-3*c* and *C*2/*c* was found by using the program WYCKSPLIT (Sosnowska *et al.*, 2012; Przeniosło *et al.*, 2014; WYCKSPLIT, 1991) at the Bilbao Crystallographic Server (BCS) as described in the main paper (eqs. 1-3).

The relation between the trigonal lattice parameters (in hexagonal setting): a^0_h, b^0_h and c^0_h and the lattice parameters (undistorted with superscript 0) in the monoclinic setting: a^0_m, b^0_m, c^0_m and β^0_m are:

$$a_m^0 = \sqrt{\frac{1}{3}\left(a_h^0\right)^2 + \frac{4}{9}\left(c_h^0\right)^2} \qquad (4)$$

$$b_m^0 = a_h^0 \qquad (5)$$

$$c_m^0 = c_h^0 \qquad (6)$$

$$\beta_m^0 = \arccos\left(\frac{-2c_h^0}{\sqrt{3\left(a_h^0\right)^2 + 4\left(c_h^0\right)^2}}\right) \qquad (7)$$

The transformation inverse to eqs. 1-3 (for 'distorted' structures indexed with superscript 1) between the monoclinic axes: $\mathbf{a}^1_m$, $\mathbf{b}^1_m$ and $\mathbf{c}^1_m$ and the axes in pseudohexagonal setting: $\mathbf{a}^1_h$, $\mathbf{b}^1_h$ and $\mathbf{c}^1_h$ is:

$$\vec{a}_h^1 = -\frac{3}{2}\vec{a}_m^1 - \frac{1}{2}\vec{b}_m^1 - \vec{c}_m^1 \qquad (8)$$

$$\vec{b}_h^1 = \frac{3}{2}\vec{a}_m^1 - \frac{1}{2}\vec{b}_m^1 + \vec{c}_m^1 \qquad (9)$$

$$\vec{c}_h^1 = \vec{c}_m^1 \qquad (10)$$

With the eqs. 8-10 one can calculate the lattice parameters of the pseudo-hexagonal distorted structure: a^1_h, b^1_h, c^1_h, α^1_h , β^1_h , γ^1_h from the monoclinic ones: a^1_m, b^1_m, c^1_m and β^1_m:

$$a_h^1 = \sqrt{\frac{9}{4}\left(a_m^1\right)^2 + \frac{1}{4}\left(b_m^1\right)^2 + \left(c_m^1\right)^2 + 3a_m^1 c_m^1 \cos\left(\beta_m^1\right)} \qquad (11)$$

$$b_h^1 = a_h^1 \tag{12}$$

$$c_h^1 = c_m^1 \tag{13}$$

$$\cos\left(\alpha_h^1\right) = \left\{ \frac{\frac{3}{2} a_m^1 c_m^1 \cos\left(\beta_m^1\right) + \left(c_m^1\right)^2}{c_m^1 \sqrt{\frac{9}{4}\left(a_m^1\right)^2 + \frac{1}{4}\left(b_m^1\right)^2 + \left(c_m^1\right)^2 + 3a_m^1 c_m^1 \cos\left(\beta_m^1\right)}} \right\} \tag{14}$$

$$\cos\left(\beta_h^1\right) = \left\{ \frac{-\frac{3}{2} a_m^1 c_m^1 \cos\left(\beta_m^1\right) - \left(c_m^1\right)^2}{c_m^1 \sqrt{\frac{9}{4}\left(a_m^1\right)^2 + \frac{1}{4}\left(b_m^1\right)^2 + \left(c_m^1\right)^2 + 3a_m^1 c_m^1 \cos\left(\beta_m^1\right)}} \right\} \tag{15}$$

$$\cos\left(\gamma_h^1\right) = \left\{ \frac{-\frac{9}{4}\left(a_m^1\right)^2 + \frac{1}{4}\left(b_m^1\right)^2 - \left(c_m^1\right)^2 - 3a_m^1 c_m^1 \cos\left(\beta_m^1\right)}{\frac{9}{4}\left(a_m^1\right)^2 + \frac{1}{4}\left(b_m^1\right)^2 + \left(c_m^1\right)^2 + 3a_m^1 c_m^1 \cos\left(\beta_m^1\right)} \right\} \tag{16}$$

S2. Lattice parameters

Initially a Rietveld refinement of the undistorted trigonal structure was performed for each sample giving the hexagonal lattice parameters a^0_h, and c^0_h. Next the monoclinic undistorted lattice parameters were calculated with eqs. 4-7 giving a^0_m, b^0_m, c^0_m and β^0_m. In the second step the Rietveld refinement of the distorted monoclinic structure was performed with initial parameters a^0_m, b^0_m, c^0_m and β^0_m. The resulting new parameters a^1_m, b^1_m, c^1_m and β^1_m describe the distorted monoclinic structure. In the next step, the pseudo-hexagonal distorted structure parameters: a^1_h, b^1_h, c^1_h, α^1_h , β^1_h , γ^1_h were calculated from the monoclinic ones: a^1_m, b^1_m, c^1_m and β^1_m by using eqs. 11-16. All these parameters are summarized in the following tables.

S3. Williamson-Hall analysis

The mean crystallite size and internal strains were estimated by using the Williamson-Hall (Williamson & Hall, 1953) method, in which the observed Bragg peaks integral breadths are fitted as:

$$\beta\cos\theta = K\lambda/D + 2\varepsilon\sin\theta \qquad (17)$$

where β is the integral breadth of peak at position 2θ, K is a constant (K=0.89), λ is the wavelength, D is the average particle size and ε is the internal strain. The data and fitted functions are shown in Fig. S1, while the refined parameters are given in Table 1 (main paper).

Table S1 Values of the parameters of the undistorted α-Fe_2O_3 trigonal structure (with upper index 0) and parameters of the distorted α-Fe_2O_3 monoclinic structure (with upper index 1). The relative changes $\delta a_m = 10^6 \times (a_m^1 - a_m^0)/ a_m^0$ are given for each parameter.

	a_h^0 [Å]	c_h^0[Å]	a_m^0[Å]	b_m^0[Å]	c_m^0[Å]	β_m^0[deg.]				
$Fe_2O_3$0m	5.035569 (64)	13.75111 (22)	9.61736 (18)	5.035569 (64)	13.75111 (22)	162.4045 (33)				
$Fe_2O_3$10m	5.035595 (65)	13.75148 (23)	9.61760 (18)	5.035595 (65)	13.75148 (23)	162.4048 (34)				
$Fe_2O_3$20m	5.035490 (113)	13.75117 (39)	9.61739 (31)	5.035490 (113)	13.75117 (39)	162.4048 (58)				
$Fe_2O_3$30m	5.035697 (112)	13.75167 (40)	9.61774 (31)	5.035697 (112)	13.75167 (40)	162.4047 (59)				
	a_m^1[Å]	b_m^1[Å]	c_m^1[Å]	β_m^1[deg.]	δa_m	δb_m	δc_m	$\delta\beta_m$		
$Fe_2O_3$0m	9.6181698 (10)	5.0352488 (11)	13.750989 (1)	162.40490 (1)	84 (18)	-64 (13)	-9 (16)	3 (20)		
$Fe_2O_3$10m	9.6180410 (44)	5.0353813 (98)	13.751386 (3)	162.40532 (4)	45 (19)	-42 (13)	-7 (16)	3 (21)		
$Fe_2O_3$20m	9.6178865 (26)	5.0352702 (36)	13.751091 (2)	162.40512 (2)	52 (32)	-44 (22)	-6 (28)	2 (36)		
$Fe_2O_3$30m	9.6179209 (23)	5.0352635 (25)	13.750509 (2)	162.40376 (1)	19 (33)	-86 (22)	-84 (29)	-6 (36)		
	a_h^1[Å]	c_h^1[Å]	α_h^1[deg.]	β_h^1[deg.]	γ_h^1[deg.]	δa_h	δc_h	$\delta\alpha_h$	$\delta\beta_h$	$\delta\gamma_h$
$Fe_2O_3$0m	5.035715 (17)	13.750989 (1)	90.01489 (13)	89.98511 (13)	120.00612 (13)	29 (13)	-9 (16)	165 (1)	-165 (2)	51 (1)
$Fe_2O_3$10m	5.035610 (72)	13.751386 (3)	90.00864 (113)	89.99136 (113)	120.00300 (113)	3 (19)	-7 (16)	96 (12)	-96 (12)	25 (9)
$Fe_2O_3$20m	5.035563 (43)	13.751091 (2)	90.00931 (41)	89.99069 (41)	120.00385 (41)	15 (24)	-6 (28)	104(5)	-104(5)	32 (3)
$Fe_2O_3$30m	5.035858 (41)	13.750509 (2)	90.01531 (28)	89.98469 (28)	120.00781 (28)	32 (24)	-84 (29)	170 (3)	-170 (3)	65 (2)

Table S2 Values of the parameters of the undistorted α-Cr_2O_3 trigonal structure (with upper index 0) and parameters of the distorted α-Cr_2O_3 monoclinic structure (with upper index 1). The relative changes, e.g. $\delta a_m = 10^6 \times (a_m^1 - a_m^0)/ a_m^0$ are given for each parameter.

	a_h^0[Å]	c_h^0[Å]	a_m^0[Å]	b_m^0[Å]	c_m^0[Å]	β_m^0				
$Cr_2O_3$0m	4.959356 (14)	13.596155 (49)	9.505597 (39)	4.959356 (14)	13.596155 (49)	162.46904 (74)				
$Cr_2O_3$10m	4.959351 (16)	13.596342 (56)	9.505715 (45)	4.959351 (16)	13.596342 (56)	162.46929 (86)				
$Cr_2O_3$20m	4.959745 (30)	13.596136 (102)	9.505653 (81)	4.959745 (30)	13.596136 (102)	162.46773 (155)				
$Cr_2O_3$30m	4.959867 (68)	13.595963 (236)	9.505564 (188)	4.959867 (68)	13.595963 (236)	162.46712(360)				
	a_m^1[Å]	b_m^1[Å]	c_m^1[Å]	β_m^1[deg.]	δa_m	δb_m	δc_m	$\delta\beta_m$		
$Cr_2O_3$0m	9.5058546 (6)	4.9598613 (4)	13.596130 (1)	162.471660 (1)	27 (4)	102(3)	-2(4)	16 (5)		
$Cr_2O_3$10m	9.5059280 (8)	4.9598050 (5)	13.596238 (1)	162.471880 (2)	22 (5)	92(3)	-8(4)	16(5)		
$Cr_2O_3$20m	9.5057583 (16)	4.9601164 (8)	13.596092 (1)	162.470670 (3)	11 (8)	75(6)	-3 (8)	18 (10)		
$Cr_2O_3$30m	9.5059443 (32)	4.9601049 (18)	13.596295 (3)	162.471510 (6)	40 (20)	48 (14)	24 (17)	27 (22)		
	a_h^1[Å]	c_h^1[Å]	α_h^1[deg.]	β_h^1[deg.]	γ_h^1[deg.]	δa_h	δc_h	$\delta\alpha_h$	$\delta\beta_h$	$\delta\gamma_h$
$Cr_2O_3$0m	4.959046 (11)	13.596130 (1)	90.00681 (7)	89.99319 (7)	119.98912 (7)	-63 (4)	-2 (4)	76(1)	-76(1)	-91(1)
$Cr_2O_3$10m	4.959015 (13)	13.596238 (1)	90.00697 (9)	89.99303 (9)	119.98946 (9)	-68 (4)	-8 (4)	77 (1)	-77 (1)	-88(1)
$Cr_2O_3$20m	4.959275 (25)	13.596092 (1)	90.00480 (18)	89.99520 (18)	119.98878 (18)	-95 (8)	-3 (7)	53 (2)	-53 (2)	-94(2)
$Cr_2O_3$30m	4.959173 (52)	13.596295 (3)	90.00626 (37)	89.99374 (37)	119.98756 (37)	-140 (17)	24 (17)	70(4)	-70(4)	-104(3)

Table S3 Splitting of the Wyckoff positions between the *R*-3*c* (trigonal – hexagonal setting) and *C*2/*c* (monoclinic) space groups for Fe/Cr (12c) and O (18e) as determined with Wycksplit). The values of z(Fe/Cr) and x(O) were taken as: z(Fe)=0.1447 x(O)=0.3062 for α-Fe_2O_3 (Hill *et al.*, 2008) and z(Cr)=0.1518 and x(O)=0.3058 for α-Cr_2O_3 (Hill *et al.*, 2010).

		R-3c			C2/c
Fe/Cr	12c	(0,0,z)	→	8f	(0,0,z)
O	18e	(x,0,1/4)	→	8f	(-3/2x, -1/2x, -x+1/4)
O	18e	(-x, -x, 1/4)	→	4e	(0, x, 1/4)

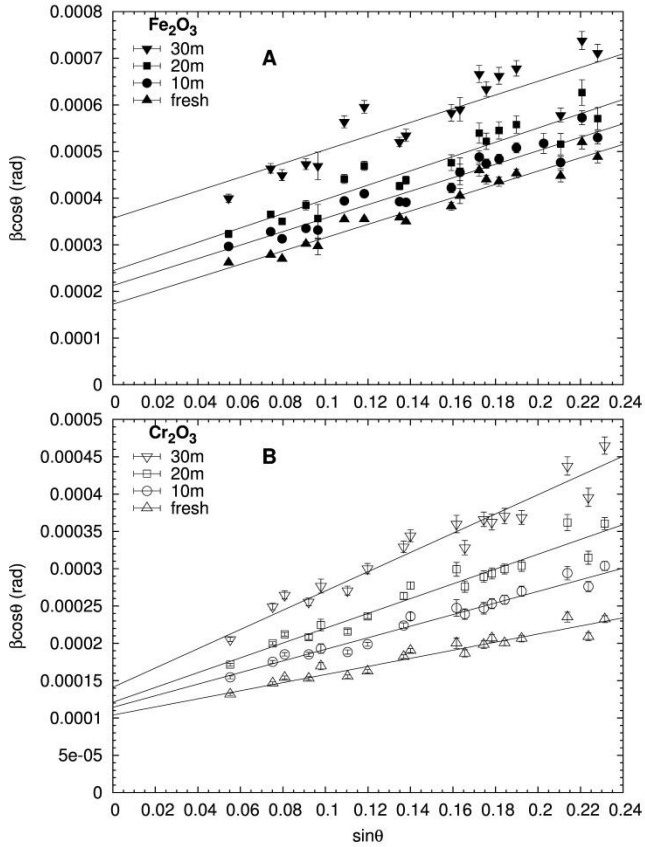

Figure S1 Williamson-Hall plot showing the β×cosθ dependence on sinθ, where β is the integral breadth and 2θ the scattering angle, for α-Fe_2O_3 (A) and α-Cr_2O_3 (B) after different milling times.