Supporting Information

Deformation twinning of ferrocene crystals assisted by the rotational mobility of cyclopentadienyl rings

Y. Miyamoto and S. Takamizawa*

Graduate School of Nanobioscience; Yokohama City University; 22-2 Seto: Kanazawa-ku, Yokohama 236-0027: Japan

*E-mail: staka@yokohama-cu.ac.jp

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Single-crystal X-ray diffraction experiment

Table S1. Crystallographic data.

Compound	ferrocene	nickelocene	ruthenocene
Condition	single crystal	single crystal	single crystal
T /K	298	297	292
Empirical formula	$C_{10}H_{10}Fe$	$C_{10}H_{10}Ni$	$C_{10}H_{10}Ru$
Crystal size /mm^3	0.39x0.34x0.29	0.50x0.40x0.31	0.40x0.32x0.31
M	186.03	188.89	231.25
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2(1)/n	P2(1)/n	Pnma
a /Å	5.9252(13)	5.9142(9)	7.1076(12)
b /Å	7.6035(16)	7.8676(11)	8.9737(16)
c /Å	9.0354(19)	9.1622(13)	12.782(2)
α /°	90	90	90
β /°	93.165(5)	91.895(3)	90
γ /°	90	90	90
V /Å^3	406.44(15)	426.09(11)	815.2(2)
Z	2	2	4
Dcalcd/Mg m^{-3}	1.520	1.472	1.884
μ(Mo Kα)/mm^{-1}	1.777	2.202	1.845
Reflections collected	2895	3029	5710
Independent reflections (R_{int})	1003(0.0208)	1053(0.0176)	1075(0.0247)
Goodness of fit	1.030	1.101	1.165
$R_1(I > 2\sigma)$ (all data)	0.0285(0.0411)	0.0254(0.0299)	0.0190(0.0206)
${}_wR_2(I > 2\sigma)$ (all data)	0.0689(0.0754)	0.0659(0.0692)	0.0452(0.0465)
Least diff. peak (hole) /eÅ^{-3}	0.184(-0.384)	0.197(-0.492)	0.265(-0.568)

Table S2. Crystallographic data of mechanically twinned crystals

Compound	ferrocene	ferrocene	nickelocene	nickelocene
Condition	twin_mother	twin_daughter	twin_mother	twin_daughter
T /K	298	298	298	298
Empirical formula	$C_{10}H_{10}Fe$	$C_{10}H_{10}Fe$	$C_{10}H_{10}Ni$	$C_{10}H_{10}Ni$
Crystal size /mm^3	0.43x0.34x0.30	0.43x0.34x0.22	0.32x0.30x0.20	0.30x0.22x0.12
M	186.03	186.03	188.89	188.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)/n
a /Å	5.934(2)	5.928(2)	5.913(5)	5.8966(19)
b /Å	7.607(3)	7.607(3)	7.866(7)	7.859(2)
c /Å	9.038(3)	9.043(4)	9.157(7)	9.135(3)
α /°	90	90	90	90
β /°	93.232(7)	93.154(8)	91.835(16)	91.841(6)
γ /°	90	90	90	90
V /Å^3	407.3(2)	407.2(3)	425.7(6)	423.1(2)
Z	2	2	2	2
Dcalcd/Mg m^{-3}	1.517	1.517	1.474	1.483
μ(Mo Kα)/mm^{-1}	1.773	1.774	2.204	2.218
Reflections collected	2680	2630	2719	2691
Independent reflections (R_{int})	977 (0.0377)	958 (0.0406)	1047 (0.1972)	996 (0.0398)
Goodness of fit	1.119	1.132	1.009	1.031
R_1(I > 2σ) (all data)	0.0557 (0.0671)	0.0668 (0.0810)	0.1168 (0.1494)	0.0491 (0.0621)
$_wR_2$(I > 2σ) (all data)	0.1795 (0.1858)	0.2245 (0.2340)	0.3008 (0.3235)	0.1175 (0.1323)
Least diff. peak (hole) /eÅ^{-3}	0.852 (-0.497)	1.073 (-0.507)	2.513 (-0.940)	0.795 (-0.348)

Table S3. Crystallographic data of mixed crystal of ferrocene/ruthenocene.

Compound	ferrocene/ruthenocene
Condition	single crystal
T /K	298
Empirical formula	$C_{10}H_{10}Fe_{0.89}Ru_{0.11}$
Crystal size /mm^3	0.20x0.06x0.06
M	191.01
Crystal system	Monoclinic
Space group	P2(1)/n
a /Å	5.942(4)
b /Å	7.696(6)
c /Å	9.122(7)
α /°	90
β /°	92.908(18)°
γ /°	90
V /Å^3	416.6(5)
Z	2
Dcalcd/Mgm^{-3}	1.523
μ(Mo Kα)/mm^{-1}	1.742
Reflections collected	2923
Independent reflections (R_{int})	1056 (0.0846)
Goodness of fit	0.836
R_1(I > 2σ) (all data)	0.0533 (0.1498)
$_wR_2$(I > 2σ) (all data)	0.1194 (0.1598)
Leastdiff.peak (hole) /eÅ^{-3}	0.459 (-0.674)

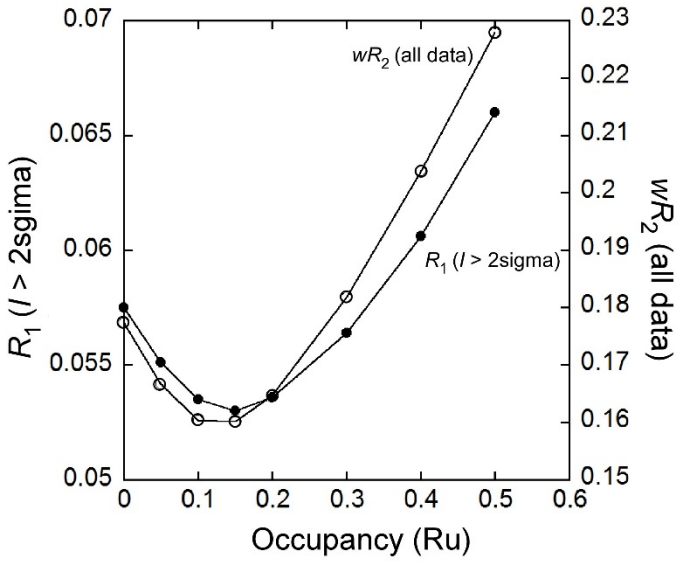


Figure S1. Dependence of R_1 and wR_2 on the occupancy of ruthenium in the ruthenium-doped ferrocne crystal. The crystallographical composition was settled on $(FeCp_2)_{0.89}(RuCp_2)_{0.11}$ according to that determined by the visual spectrum shown in Figure S7.

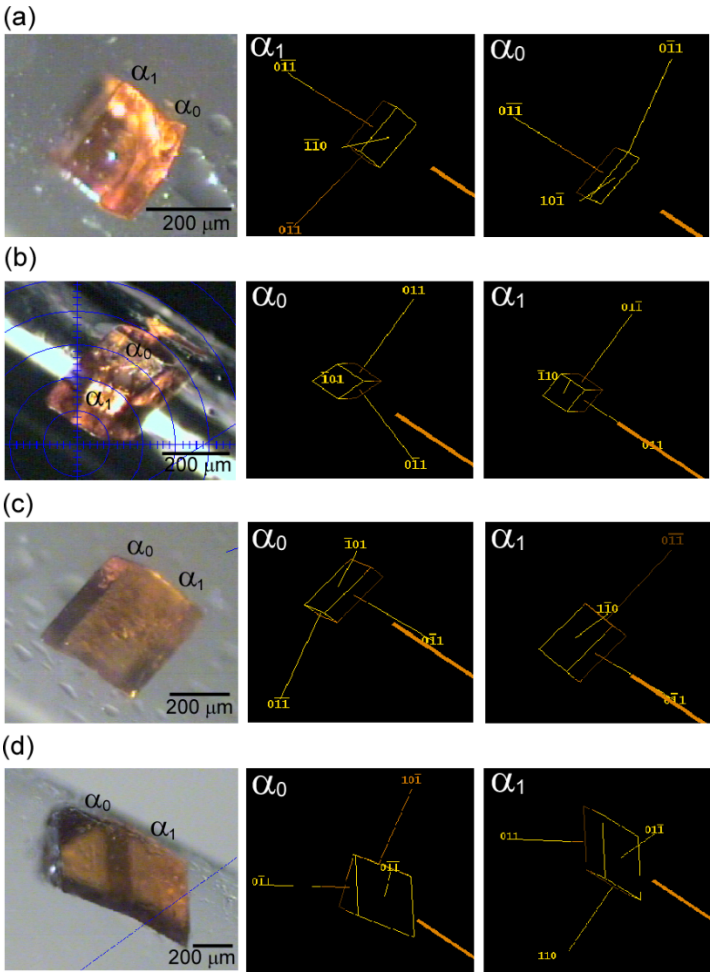


Figure S2. Crystal surface indexes of ferrocene. Twinning interfaces are $(011)\alpha_0//(0)\alpha$ (a), $(011)\alpha_0//(01)\alpha_1$ (b), $(01)\alpha_0//(01)\alpha_1$ (c), $(01)\alpha_0//(011)\alpha_1$ (d). Table 2 was collected from the crystal shown in (d).

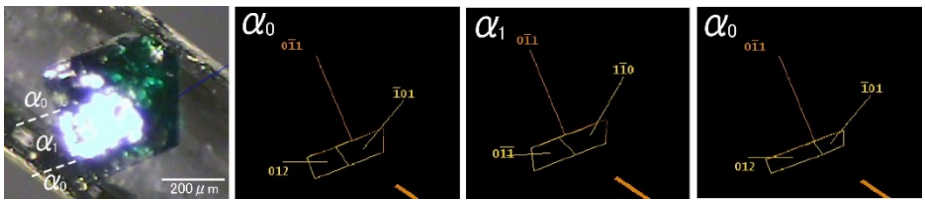


Figure S3. Crystal surface indexes of nickelocene. Table 2 was collected from this crystal.

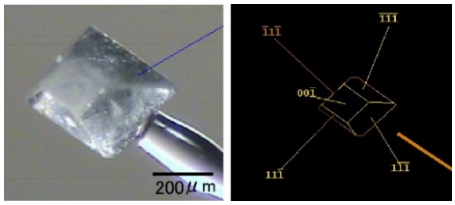


Figure S4. Crystal surface indexes of ruthenocene.

Uniaxial Compression test

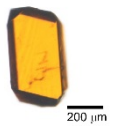
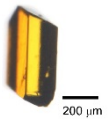
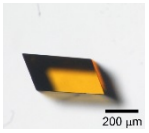
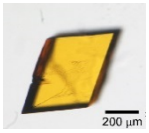
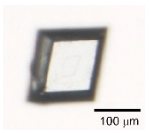
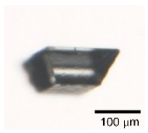
	Com-pound	Compression surface	Area/μm^2	Thickness /μm	Compression speed/μm min^{-1}	Top view	Side view
1	$FeCp_2$	(01)	142955	169	84.5		
2	$FeCp_2$	(011)or(01)	92912	445	44.5		
3	$RuCp_2$	(001)	10096	75	37.4		

Table S4. Conditions of uniaxial compression tests.

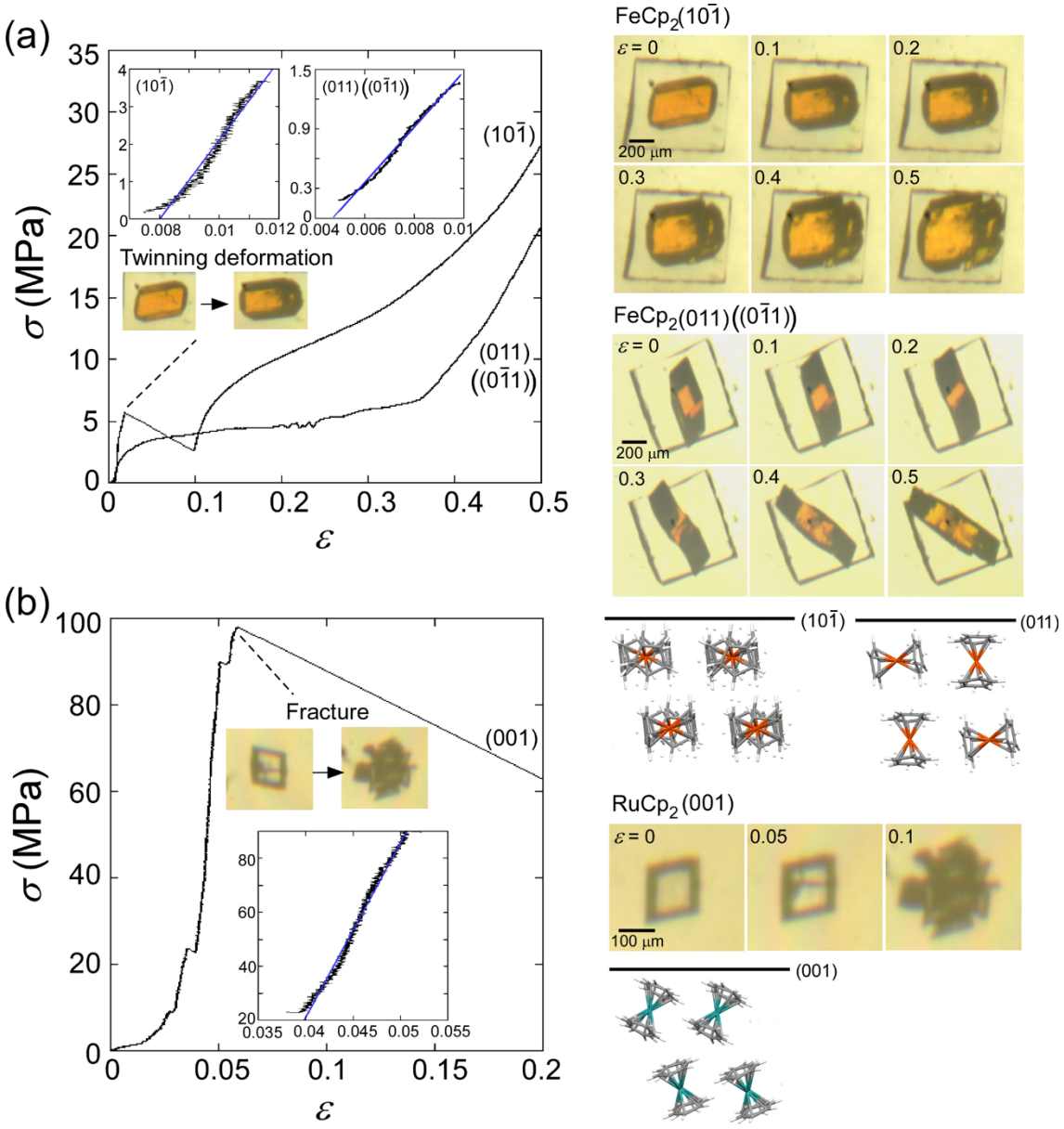


Figure S5. (**Figure 3** in the paper) Stress-strain curves at 20 °C. (a) Normal direction of $FeCp_2$ (10) and that of $FeCp_2$ (011) ((01)). (b) Normal direction of $RuCp_2$ (001). Test conditions are listed in Table S3. Young's modulus values were 1.1 GPa ($FeCp_2$ (10)), 0.3 GPa ($FeCp_2$ (011)), and 6.4 GPa ($RuCp_2$ (001)), which were estimated from the inset graphs by the least-square method (blue line). Beside the S-S curves, we show photographs of each strain and crystal structure projected perpendicularly in the compression directions.

Visible and ultraviolet spectrum

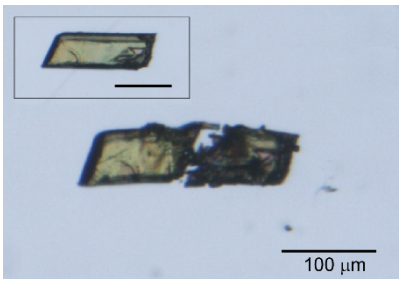


Figure S6. Photograph of mixed crystal of ferrocene/ruthenocene ($(FeCp_2)_{0.89}(RuCp_2)_{0.11}$).

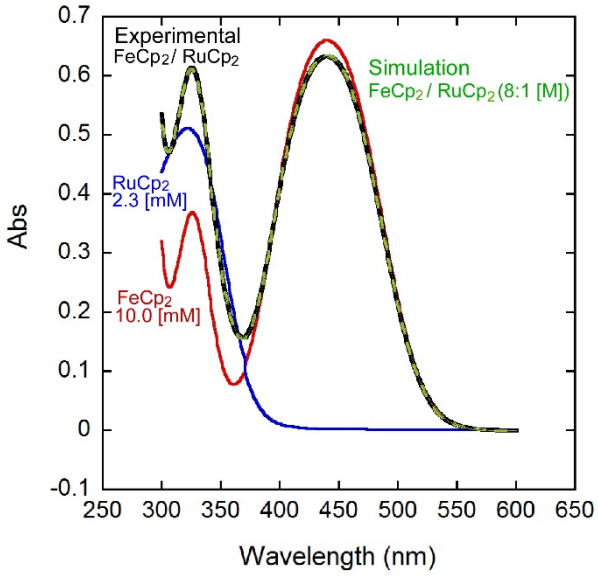


Figure S7. UV-VIS spectra for 10.0-mM toluene solution of ferrocene (red), 2.3-mM toluene solution of ruthenocene (blue), and toluene solution of mixed crystals (black). The simulation absorption spectrum (green) in which the molar ratio of ferrocene and ruthenocene is 8.0: 1 (9.6 mM: 1.2 mM) corresponds with the spectrum of the toluene solution containing the dissolved mixed crystals. Thus, the composition of the mixed crystals was calculated to be $(FeCp_2)_{0.89}(RuCp_2)_{0.11}$.