Large elastic recovery in zinc dicyanoaurate

Supplementary Information

Chloe S. Coates,[1] Matthew R. Ryder,[2] Joshua A. Hill,[1]
Jin-Chong Tan,[2] and Andrew L. Goodwin[1*]

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[1]Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory,
South Parks Road, Oxford OX1 3QR, U.K.
[2]Department of Engineering Science, University of Oxford,
Parks Road, Oxford OX1 3PJ, U.K.
[*]Electronic address: andrew.goodwin@chem.ox.ac.uk

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S1 Analysis of nanoindentation data

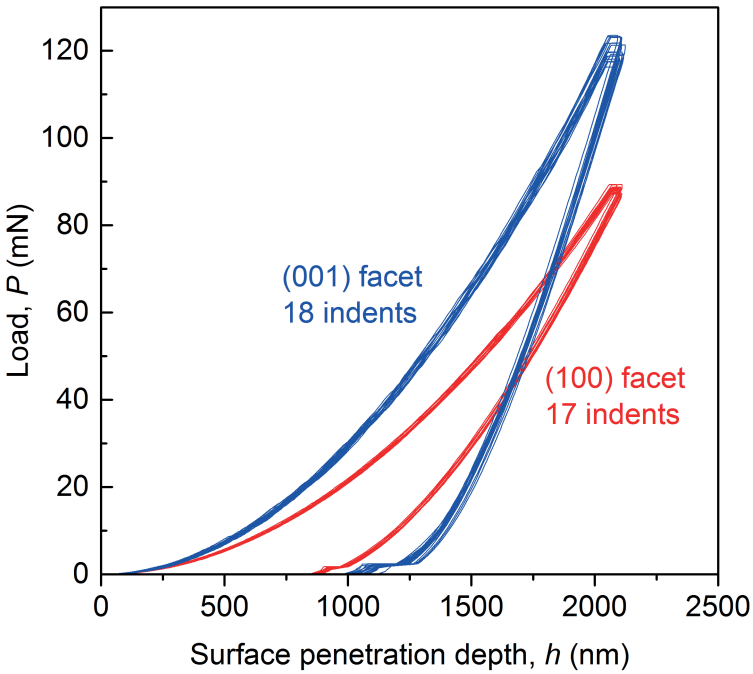

Figure S1: Load-displacement (P–h) data obtained from nanoindentation onto the (001) and (100) facets of $Zn(Au(CN)_2]_2$ single crystals, corresponding to 18 and 17 individual measurements respectively. The maximum surface penetration depth used was 2000 nm.

Poisson's ratio, ν	$E_{100} = E_{010}$ GPa Avg. 17 indents	E_{001} GPa Avg. 18 indents
0 (upper bound)	15.2(3)	22.3(6)
0.2	14.5(3)	21.4(5)
0.44	12.2(2)	18.0(4)
0.5 (lower bound)	11.4(2)	16.7(4)

Table S1: Calculated indentation moduli using a range of values for the Poisson's ratio, from CSM measurements between 200–1900 nm.

Sample preparation

The lattice parameters and symmetry of the selected crystal were confirmed and faces indexed *via* single crystal X-ray diffraction[S1]. All synthesised crystals shared a uniform bicapped hexagonal prism morphology where the faces of the prism (100):(010):(110) were equivalent. A suitable crystal was then mounted in a polyacrylate adhesive and polished using increasingly fine silicon carbide paper with water as the lubricant to ensure a smooth surface for nanoindentation, shown in Fig. S2(a).

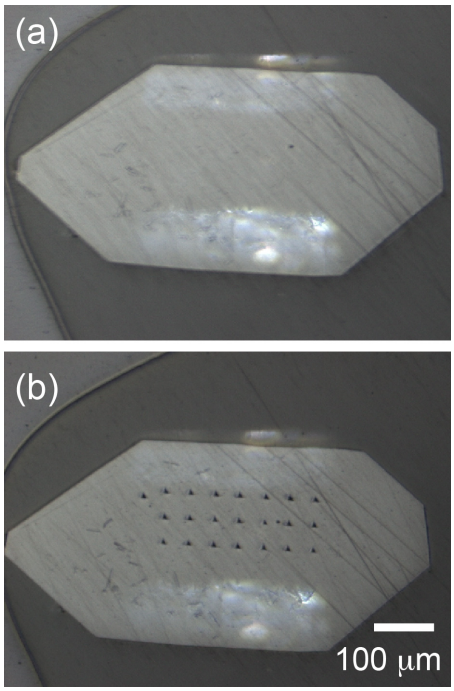

Figure S2: (a) Polished surface of the (100) crystal facet of $Zn(Au(CN)_2]_2$ before testing. (b) Residual indents after indentation experiments to a maximum depth of 2000 nm.

S2 Elasticity from tensorial analysis

Result	a	Error vs. Expt.	c	Error vs. Expt.
Experimental (CIF)	8.4160		20.8316	
B3LYP	8.78828	3.235%	20.41062	−2.021%
PBE	8.48797	0.855%	20.72554	−0.509%

Table S2: Geometry of $Zn[Au(CN)_2]_2$.

The elastic stiffness coefficients, C_{ij} (GPa) obtained from *ab initio* calculations are given below, as calculated using the PBE functional and B3LYP functional respectively.

$$C_{ij} = \begin{pmatrix} 44.832 & 36.778 & 64.149 & 0 & 0 & 0 \\ 36.778 & 44.831 & 64.149 & 0 & 0 & 0 \\ 64.149 & 64.149 & 112.45 & 0 & 0 & 0 \\ 0 & 0 & 0 & 11.029 & 0 & 0 \\ 0 & 0 & 0 & 0 & 11.029 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.026 \end{pmatrix} \tag{S1}$$

$$C_{ij} = \begin{pmatrix} 46.145 & 37.672 & 61.981 & 0 & 0 & 0 \\ 37.672 & 46.145 & 61.981 & 0 & 0 & 0 \\ 61.981 & 61.981 & 101.899 & 0 & 0 & 0 \\ 0 & 0 & 0 & 10.931 & 0 & 0 \\ 0 & 0 & 0 & 0 & 10.931 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.236 \end{pmatrix} \tag{S2}$$

Elastic property	PBE	B3LYP	Expt. (298 K)
K_a (TPa^{-1})	51.02	46.55	55(16)
K_c TPa^{-1})	−49.32	−46.81	−48(14)
B (GPa)	18.97	21.62	16.7(16)
E_{100} (GPa)	8.23	8.44	16.8(3)
E_{001} (GPa)	11.60	10.23	22.1(4)
E_{max} (GPa)	25.33	24.77	
E_{min} (GPa)	8.23	8.45	
G_{max} (GPa)	11.03	10.93	
G_{min} (GPa)	2.91	2.77	
ν_{max}	1.10	1.07	
ν_{min}	0.02	0.00	

Table S3: Elastic properties of $Zn[Au(CN)_2]_2$ as calculated using elastic compliances (given below) from DFT in ElAM[S2]. Note: The calculations have not been corrected for dispersion interactions, as the semi-empirical correction resulted in over binding of the structure in both cell parameters and as a result deviated from experiment by > 15%.

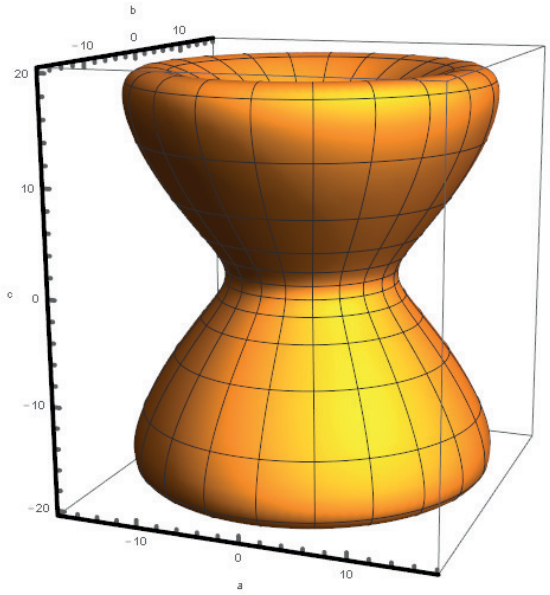

Figure S3: 3-D Young's modulus representation surface $E(\theta, \psi)$ of $Zn[Au(CN)_2]_2$ in GPa.

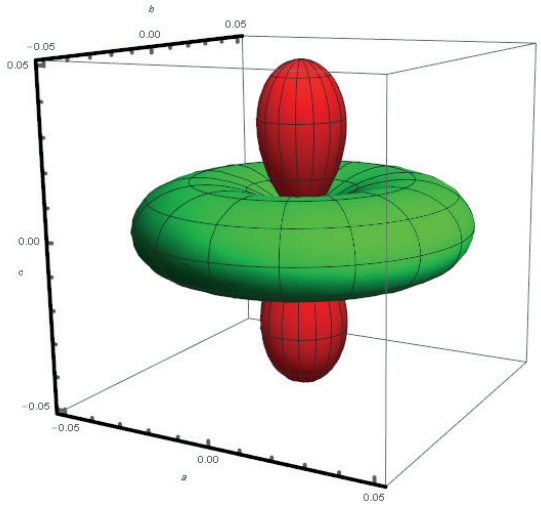

Figure S4: 3-D linear compressibility representation surface $\beta(\theta, \psi)$ of $Zn[Au(CN)_2]_2$. Green and red represent the positive and negative values in TPa^{-1}.

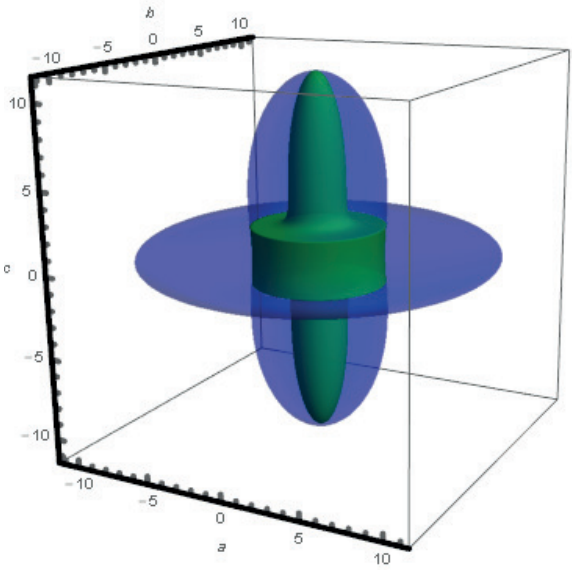

Figure S5: 3-D shear modulus representation surface $G(\theta, \psi, \chi)$ of $Zn[Au(CN)_2]_2$. Blue and green represent the maximum and minimum moduli in GPa.

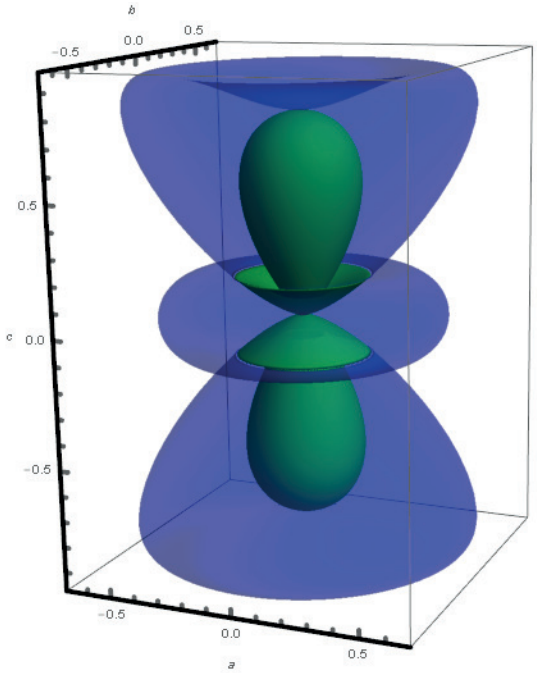

Figure S6: 3-D Poisson's ratio representation surface $\nu(\theta, \psi, \chi)$ of $Zn[Au(CN)_2]_2$. Blue and green represent the maximum and minimum values.

S3 References

[S1] CrysAlisPRO, Oxford Diffraction/Agilent Technologies UK Ltd., Yarnton, England (2014)

[S2] A. Marmier, Z. A. D. Lethbridge, R. I. Walton, C. W. Smith, S. C. Parker and K. E. Evans, *Comput. Phys. Commun.*, **181**, 2102 (2010)