Supporting Information for:

Electronic Structure of $PbCr_{(1-x)}S_{(x)}O_4$ Solid Solution: an Inside Look at Van Gogh Yellow Degradation

Ana B. Muñoz-García,* Arianna Massaro, and Michele Pavone.

Department of Chemical Sciences, University of Naples Federico II, Via Cintia 21, 80126 Naples, Italy.

S.1. Structural models for VGY

$PbCr_{(1-x)}S_{(x)}O_4$ is a solid solution with ABO_4 general formula: A-sites are occupied by Pb and B-sites by Cr and S in different ratio. $PbCrO_4$ (x=0) presents two phases, monoclinic (M) and orthorhombic (O): M is the most abundant and belongs to *P21/n* space group; O has been detected in small percentages and belongs to the *Pnma* one.[S1] Also PbSO4 (x=1) belongs to the orthorhombic *Pnma* space group. In all these cases, the unit cell contains four formula units ($A_4B_4O_{16}$) for a total of 24 atoms (Figure S.1.0). In M, every PbCrO4, atom (Pb, Cr, OI, OII, OIII and OIV) occupies 4e Wyckoff sites.[S2] In O crystals, Pb, Cr/S, OI and OII occupy 4c Wyckoff positions and OIII atoms are in 8d ones.[S3,S4]

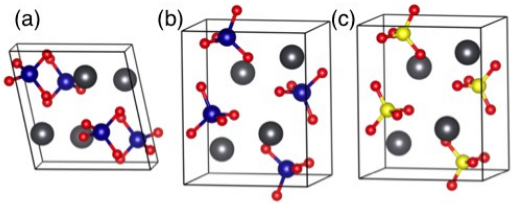

Figure S.1.0. Structural models for lead chromate (a) monoclinic and (b) orthorhombic unit cells and for (c) orthorhombic lead sulfate. Spheres represent atoms, color legend: Pb grey, Cr blue, S yellow, and O red.

Besides pure lead chromate and sulphate (see main text for structural details), we have explored the $PbCr_{(1-x)}S_xO_4$ solid solution with x=0.125, 0.25, 0.50, 0.75 and 0.875. In the following, we describe the corresponding structural models.

- **$PbCr_{0.875}S_{0.125}O_4$**: The 24-atom ABO_4 unit cell is insufficient to describe the 7:1 Cr:S ratio Thereby, a supercell approach is needed in order to get the stoichiometric formula: we substituted 1 Cr atom with 1 S atom in monoclinic 48–atom 2x1x1 $PbCrO_4$ and orthorhombic 1x2x1 $PbCrO_4$ supercells. Figure S.1.1 shows the relaxed structure of the two models.

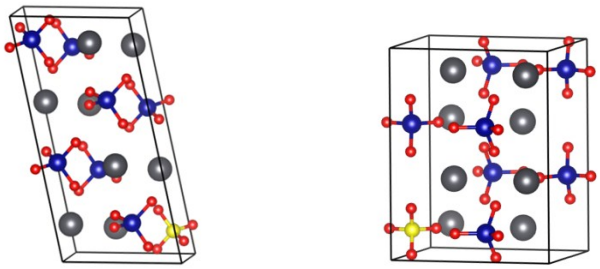

Figure S.1.1 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.875}S_{0.125}O_4$

– **$PbCr_{0.75}S_{0.25}O_4$:** it presents a 3:1 Cr:S ratio, which can be modeled by substitution of 1 Cr atom by 1 S atom in the 24-atom ABO_4 cell (Figure S.1.2)

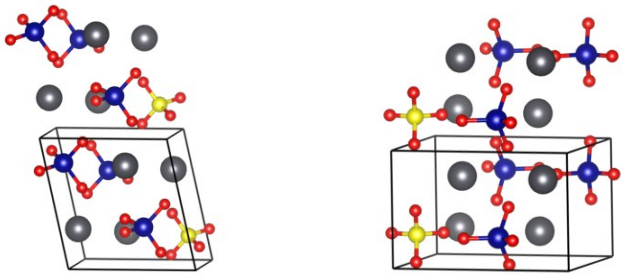

Figure S.1.2 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.75}S_{0.25}O_4$

– **$PbCr_{0.50}S_{0.50}O_4$:** we have modeled the 1:1 Cr:S ratio by substituting 2 out of 4 Cr atoms in the 24-atom ABO_4 unit cell by S. Depending on the relative position of the two substituents in the unit cell, three different configurations arise (Figs S.1.3-5):

• **Configuration A**, with the largest distance between the 2 S atoms:

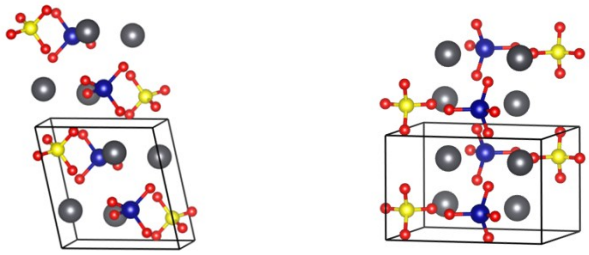

Figure S.1.3 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.50}S_{0.50}O_4$ (configuration A)

• **Configuration B**, with the smallest S – S distance:

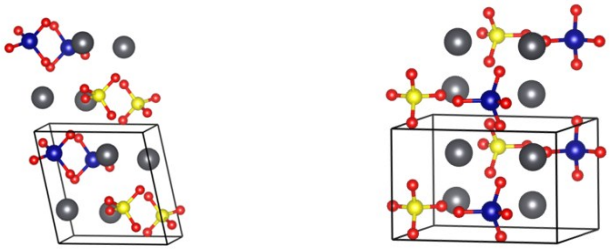

Figure S.1.4 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.50}S_{0.50}O_4$ (configuration B)

• **Configuration C**, with an intermediate S – S distance:

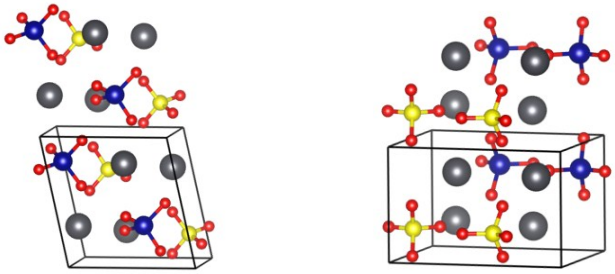

Figure S.1.5 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.50}S_{0.50}O_4$ (configuration C)

– **$PbCr_{0.25}S_{0.75}O_4$:** This lattice presents a 1:3 Cr:S ratio, which can be, in principle modeled with the 24-atom ABO_4 unit. Since this particular solid solution with 1:3 Cr:S ratio is not found experimentally (see main text for details), we have focused on it for analysing the thermodynamic stability of the solid solution and we have considered 48-atom supercells in order to evaluate multiple spatial configurations within the Cr/S sublattice. We substituted 6 Cr atoms with 6 S atoms in 2x1x1 monoclinic and 1x2x1 orthorhombic supercells. Figure S.1.6 shows random configuration among the 7 possible configurations for each space group.

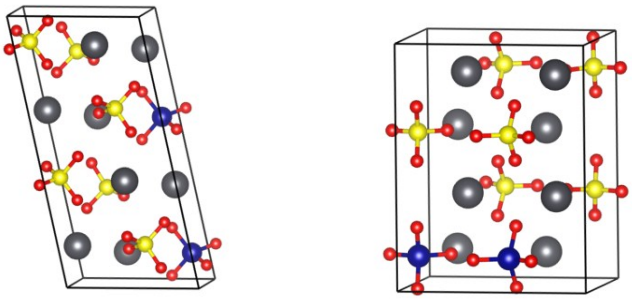

Figure S.1.6 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.25}S_{0.75}O_4$

– **$PbCr_{0.125}S_{0.875}O_4$:** as for $PbCr_{0.875}S_{0.125}O_4$, we have modeled the 1:7 Cr:S ratio by substitution of 7 Cr atoms with 7 S atoms in 48-atoms supercells (Fig. S.1.7)

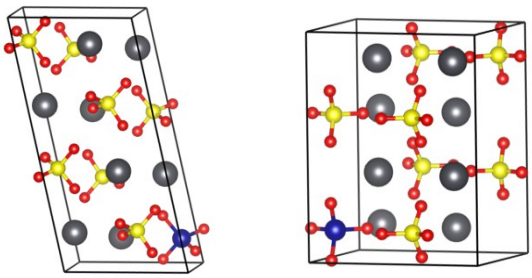

Figure S.1.8 Structural models of monoclinic (left) and orthorhombic (right) $PbCr_{0.125}S_{0.875}O_4$

S.2. Equilibrium Structures: PBE *vs* PBE-D3 lattice constants and Monoclinic *vs* Orthorhombic cell volumes

Table S.2.1 gathers the equilibrium lattice constants obtained with PBE and PBE-D3(BJ) methods, in comparison with experimental values.

Table S.2.1 Comparison between experimental lattice parameters and PBE/PBE – D3 (BJ) equilibrium structures. For $PbCrO_4$ (monoclinic): β=102.40° (experimental), β=102.54° (theoretical). *Data without experimental counterpart

Level of theory		Lattice parameters (Å)					
		Monoclinic $P2_1/n$			*Orthorhombic Pnma*		
		a	***b***	***c***	***a***	***b***	***c***
$PbCrO_4$	***Experimental* [Ref. 1]**	*7.128*	*7.437*	*6.801*	*8.667*	*5.548*	*7.118*
	PBE	7.274	7.605	6.912	8.712	5.617	7.165
	PBE-D3(BJ)	7.131	7.513	6.809	8.647	5.575	7.111
$PbSO_4$	***Experimental* [Ref. 2]**	-	-	-	*8.482*	*5.398*	*6.959*
	PBE	(7.070	7.285	6.755)*	8.528	5.530	7.057
	PBE-D3(BJ)	(7.054	7.269	6.740)*	8.489	5.419	7.047

Ref 1. Monico L., Janssens K., Hendriks E., Brunetti B.G., Miliani C., *J. Raman. Spectrosc.,* **45**, 1034-45, (2014)
Ref 2. Miyake M., Minato I., Morikawa H., Iwai S., *Am. Mineral.,* **63**, 506-510, (1978)

Table S.2.2 lists the equilibrium volumes of monoclinic and orthorhombic at PBE-D3(BJ) level of theory.

Table S.2.2 Calculated equilibrium volumes of monoclinic and orthorhombic VGY solid solution at PBE-D3 level of theory. In parenthesis, forms that are not detected experimentally.

Structure	Equilibrium Volume (Å^3)	
	Monoclinic $P2_1/n$	*Orthorhombic Pnma*
$PbCrO_4$	356.12	342.85
$PbCr_{0.875}S_{0.125}O_4$	354.69	(353.98)
$PbCr_{0.75}S_{0.25}O_4$	352.62	(351.92)
$PbCr_{0.50}S_{0.50}O_4$	347.90	(344.95)
$PbCr_{0.125}S_{0.875}O_4$	(352.53)	333.96
$PbSO_4$	(337.51)	324.17

S.3. Exploring segregation in VGY

We have hypothesized a possible tendency towards phase separation between lead chromate and lead sulphate already in the bulk state as a first cause of the degradation.

Sulphur segregation has been simulated by optimization of the three different configurations of $PbCr_{0.50}S_{0.50}O_4$ solid solution described in S.1. Among these structures, it is possible to distinguish between a more segregated (smallest distance between sulphur atoms, B), a more homogeneous structure (largest S–S distance, structure A) and a intermediate situation (configuration C). Fig. S.3 shows the energy differences with respect to the most stable configuration after relaxation.

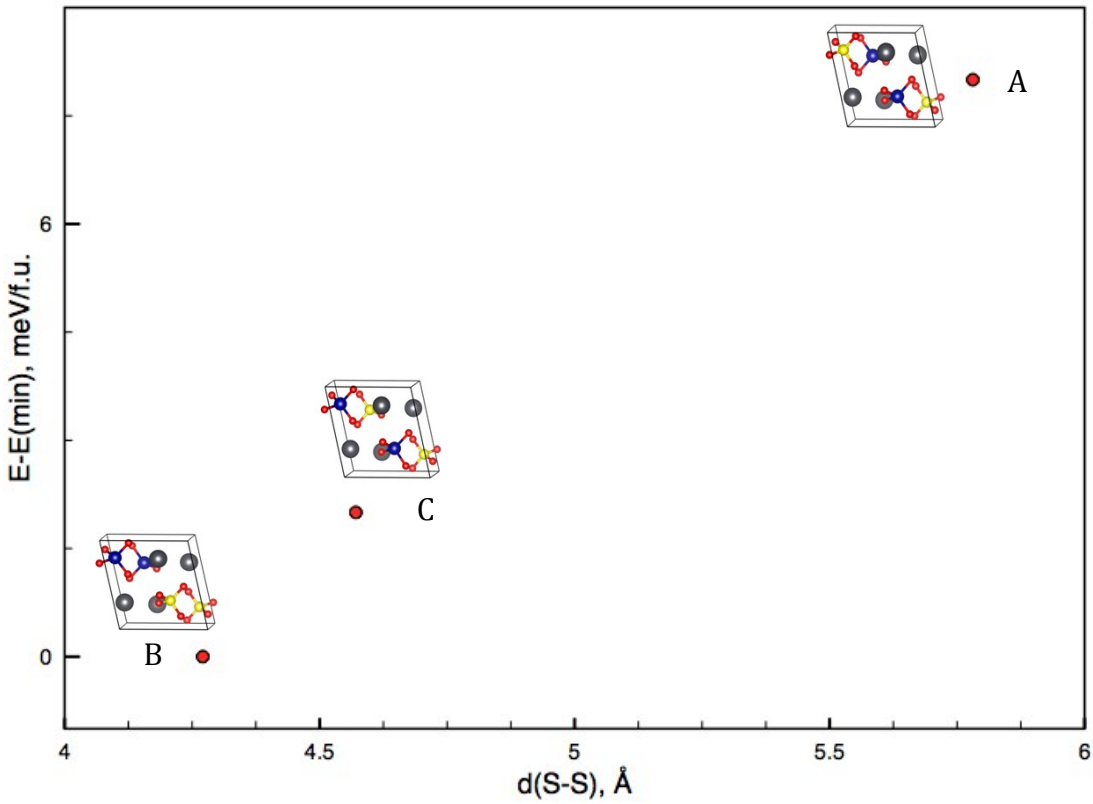

Figure S.3 Difference in energy ($E - E_{(min)}$) of each $PbCr_{0.50}S_{0.50}O_4$ configuration (see S.1. for details) compared with the minimum-energy configuration as a function of S – S distance.

From our calculations, we can state that the "segregated" configuration B is the most stable, while the "homogeneous" solution A is the less stable. One reason behind this tendency of atoms at the B site of the ABO_4 structure to aggregate can be found in the significant difference between Cr-O and S-O distances (~ 1.66 and 1.49 Å, respectively, in both the parent solids and in VGY with $x = 0.5$), that brings an important size mismatch among the BO_4 moieties. The overall stress on the bulk structure is minimized when the dissimilar moieties are close in the cell.

S.4. Bader (AIM) Charge analysis of $PbCrO_4$

Table S.4 gathers the calculated Bader charges of Pb, Cr and O species in monoclinic $PbCrO_4$, which give a qualitative indication of their oxidation state in this solid. From our calculations, Pb presents a oxidation state close to the +2 formal oxidation state for A-site

in ABO_4 compounds. Cr and O oxidation states, however, are very far from the formal +6 and -2 expected, which is a clear indication of the high degree ov covalency of Cr-O bonds. Thus, $PbCrO_4$ can be regarded as $(CrO_4)^{2-}$ highly moieties electrostatically attracted to Pb^{2+} cations. For this reason, it is reasonable to describe Cr, not as Cr(IV) with d^0 configuration, but with some occupation at the *d* orbitals, which hybridize with oxygen *p* orbitals.

Table S.4 Calculated Bader charges of Pb, Cr and O in monoclinic $PbCrO_4$ at PBE and PBE+U levels of theory

Specie	Bader Charges		
	Formal	PBE	PBE+U (U-J_{Cr}=3.2 eV)
Pb	+2	+1.544	+1.542
Cr	+6	+1.820	+1.828
O	-2	-0.816	-0.818

S.5. PBE(+U) bandgaps in VGY

Table S.5 lists the calculated eignevalue gaps of the VGY solid solution at the PBE and PBE+U levels of theory. The PBE+U values have been used to estimate the G_0W_0 –related bandgaps according to eq. 3 of the main text.

Table S.5 Band gaps of $PbCr_{(1-x)}S_xO_4$ equilibrium structures at PBE and PBE+U levels of theory

Structure		Band gap (eV)			
		Monoclinic $P2_1/n$		*Orthorhombic Pnma*	
		PBE	PBE+U	PBE	PBE+U
$PbCrO_4$		*1.68*	*1.89*	*1.95*	*2.16*
$PbCr_{0.875}S_{0.125}O_4$		1.73	1.94	1.98	2.19
$PbCr_{0.75}S_{0.25}O_4$		1.85	2.05	2.05	2.26
$PbCr_{0.50}S_{0.50}O_4$	**A**	1.92	2.12	2.06	2.27
	B	1.92	2.12	2.19	2.38
	C	1.94	2.13	2.18	2.37
$PbCr_{0.125}S_{0.875}O_4$		2.04	2.24	2.28	2.47
$PbSO_4$		*4.36*	-	*4.03*	-

S.6. PDOS of VGY solid solution

Figs. S.6.1, S.6.2 and S.6.3 display the computed projected density of states of $PbCr_{0.875}S_{0.125}O_4$, $PbCr_{0.75}S_{0.25}O_4$ and $PbCr_{0.5}S_{0.5}O_4$ (configuration B, the most stable – see S.3 for details), respectively. Together with that of $PbCr_{0.875}S_{0.125}O_4$ (see Fig. 8 in the main

text), they show that the electronic strucutre of VGY solid solution for all x retains the band edges features of $PbCrO_4$ (Fig. 6 in the main text), while S sates are very intern and do not participate in the band edges character.

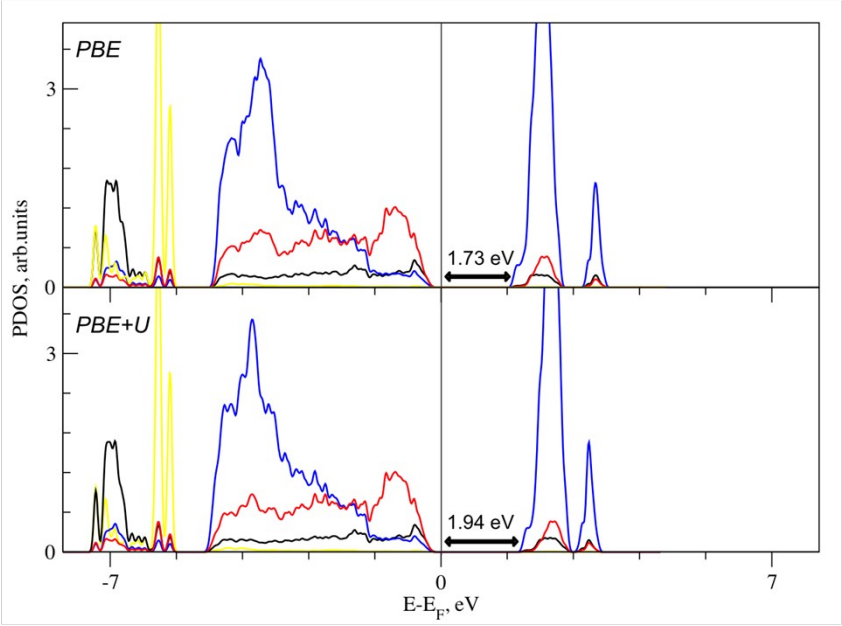

Figure S.6.1 Projected density of states (PDOS) of monoclinic $PbCr_{0.875}S_{0.125}O_4$ equilibrium structure at PBE and PBE+U levels of theory. Color legend: Pb *d* states are in black, Cr *d* states in blue, and O *p* states in red. The Fermi energy (E_F) is set to zero. Eigenvalue gaps are indicated (in eV).

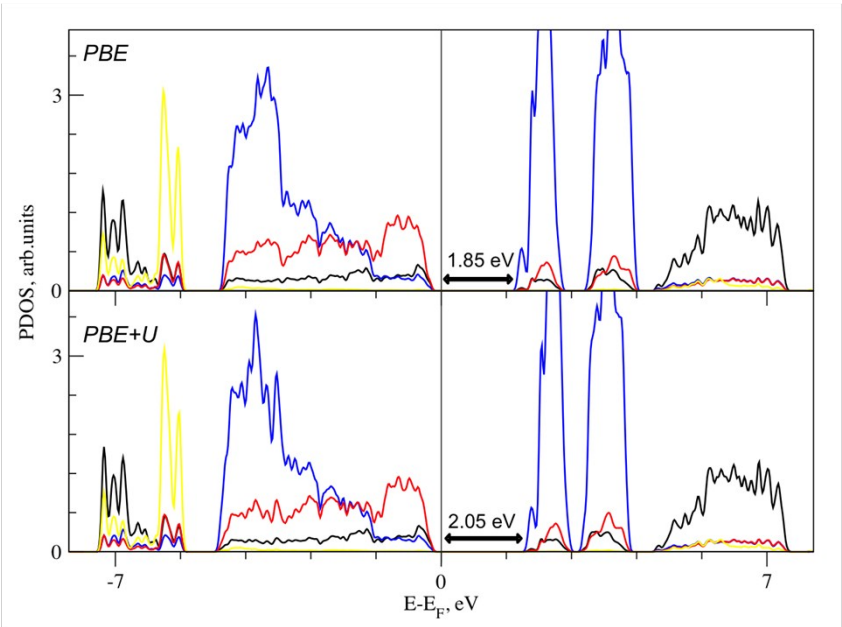

Figure S.6.2 Projected density of states (PDOS) of monoclinic $PbCr_{0.75}S_{0.25}O_4$ equilibrium structure at PBE and PBE+U levels of theory. Color legend: Pb *d* states are in black, Cr *d* states in blue, and O *p* states in red. The Fermi energy (E_F) is set to zero. Eigenvalue gaps are indicated (in eV).

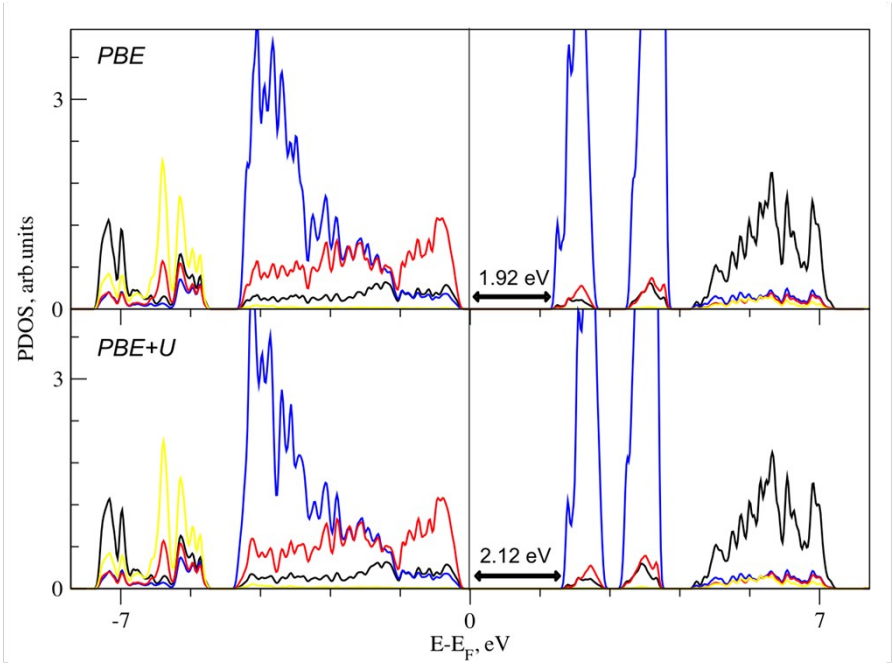

Figure S.6.3 Projected density of states (PDOS) of monoclinic $PbCr_{0.5}S_{0.5}O_4$ equilibrium structure (configuration B) at PBE and PBE+U levels of theory. Color legend: Pb *d* states are in black, Cr *d* states in blue, and O *p* states in red. The Fermi energy (E_F) is set to zero. Eigenvalue gaps are indicated (in eV).

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