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Incommensurately Modulated Cadmium Apatites

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Two cadmium apatites, $Cd_5(PO_4)_3Br$ and $Cd_5(VO_4)_3I$, earlier reported to be halogenide deficient, were prime suspects of being modulated. In this study, incommensurate ordering was found in satellites occurring in planes perpendicular to c^*. The structure of $Cd_5(PO_4)_3Br$ was refined from single-crystal X-ray diffraction data in the four-dimensional super space group $R{:}P\bar{3}{:}(00\gamma)$: $a = 16.932(2)$ Å, $c = 6.451(1)$ Å, $Z = 6$, $R = 0.043$. The modulation of the structure is due to a misfit between the large halogenide ions and the surrounding rigid Ca–PO_4 substructure. From the refined model of the $Cd_5(PO_4)_3Br$ structure a "chain-packing" model was confirmed with a Br–Br distance of 3.466 Å.

Key Words: **cadmiumapatite; incommensurate modulation; bromine; iodine.**

INTRODUCTION

Fluoroapatite, $Ca_5(PO_4)_3F$ (1), the archetype of the apatites ($M_5(XO_4)_3Y$), crystallizes in the space group $P6_3/m$, the highest symmetry reported for the apatites. However, there are many apatitic super structures reported. Super structures discussed in this paper are due to the nature of the anion positioned on the hexad: Hydroxyapatite, the main inorganic constituent of bone and teeth, $Ca_5(PO_4)_3OH$, and chloroapatite, $Ca_5(PO_4)_3Cl$, are monoclinic ($P2_1/b$) due to ordering of the hydroxide and chloride ions, respectively resulting in a doubled unit cell (2, 3), and the unit cell of $Cd_5(PO_4)_3OH$ is tripled (4) for the same reason. Another example is iodo-oxyapatite, $Ca_{15}(PO_4)_9IO$, where an ordering of the anions along the hexad results in a unit cell tripled along c (5). In all of these examples the super structures are commensurate and the compounds are thus stoichiometric.

There is a class of apatites that have been prime suspects of being noncommensurately modulated along the hexad: apatites containing large anions Y. Two examples from this class are $Cd_5(VO_4)_3I$ and $Cd_5(PO_4)_3Br$, which are reported to be halogenide deficient (6, 7) due to steric hindrance of the halogenide ions. A hypothetical "chain-packing" model was proposed but not confirmed. The super space approach used here gives us the tools for describing and refining the true incommensurate structures. The one-dimensionally modulated apatites are excellent examples of the simplest type of incommensurately modulated structures, and they demonstrate the ability of the apatite structure to compensate for substoichiometries of the halogenide ion.

In single-crystal X-ray diffraction experiments using an area detector, satellite reflections in planes perpendicular to c^* were observed. The satellites of $Cd_5(PO_4)_3Br$ were well ordered and their intensities were quantifiable whereas the satellites of $Cd_5(VO_4)_3I$ were smeared out due to extensive disorder. The superstructure of $Cd_5(PO_4)_3Br$ was solved and the chain-packing model of the bromide ion was confirmed with a Br–Br distance of 3.466 Å, substantially larger than $c/2$ (3.226 Å).

EXPERIMENTAL

Synthesis

Crystals of $Cd_5(PO_4)_3Br$ were grown in excess $CdBr_2$-melt with $Cd_3(PO_4)_2$ at 1023 K during four days and crystals of $Cd_5(VO_4)_3I$ were grown from CdO and V_2O_5 in excess CdI_2 melt at 1013 K during 2 days. Both syntheses were performed in Pt-crucibles that were sealed in evacuated quarts tubes (8). Excess halogenide was dissolved in water and the monophasic residue consisted of hexagonal-prismatic crystals approximately 0.3 × 0.05 mm lateral dimensions.

Refinement from Single-Crystal Diffraction Data

Single crystals were examined by X-ray diffraction techniques on a STOE Image Plate Detection System (IPDS) equipped with a Siemens sealed tube (Mo$K\alpha$ radiation) and an Oxford Cryo Systems 600 cooling stage. Details are given in Table 1. JANA98 was used for the refinement (9).

Superstructure ordering in the two samples was observed as satellite reflections in planes perpendicular to c^* extracted from single-crystal diffraction data recorded by the

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TABLE 1
Crystal Data, X-Ray Data Collection, and Structure Determination

Crystal data	
Chemical formula	$Cd_5(PO_4)_3Br$
Formula weight	926.9
Crystal system for the incommensurate structure	Rhombohedral
Superspace group	$R{:}P\bar{3}(00\gamma)$ (No. 147.2)
a (Å)	16.932(2)
b (Å)	16.932(2)
c (Å)	6.451(1)
V (Å^3)	1601.7
Z	6
Modulation wave vector	$\mathbf{q} = 0.778c^*$
D_x (Mgm^{-3})	5.763
Radiation type	Mo$K\alpha$
Wavelength (Å)	0.71073
θ range (°)	2.41–24.20
μ (mm^{-1})	14.05
Temperature (K)	150
Crystal form	Hexagonal rod
Crystal size (mm)	$0.28 \times 0.054 \times 0.054$
Crystal colour	Colourless
Data collection	
Diffractometer	Stoe IPDS
Data collection method	Phi rotation scans
Absorption correction	Numerical from crystal shape
$T_{\min}$	0.2567
$T_{\max}$	0.5224
No. of measured reflections	17046
No. of independent reflections	2847
No. of observed reflections	794
No. of independent satellites	2271
No. of observed satellites	260
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.0561
$\theta_{\max}$ (°)	24.20
Range of h, k, l	$-19 < k < 19$
	$-19 < k < 19$
	$-8 < l < 8$
Refinement	
Refinement on	F
R-factors of all observed reflections	
R	0.043
wR	0.077
R-factors of observed main reflections	
R	0.037
wR	0.075
R-factors of observed satellites	
R	0.135
wR	0.180
S	3.67
No. of reflections used in refinement	2847
No. of parameters used	23
Weighting scheme	$w = 1/(\sigma^2(F) + 0.0001F^2)$
$(\Delta/\sigma)_{\max}$	0.0003
$\Delta\rho_{\max}$ (eÅ^{-3})	7.35
$\Delta\rho_{\min}$ (eÅ^{-3})	-16.88

Note. Source of atomic scattering factors was International Tables, Vol. C.

STOE IPDS system. In both samples the satellite reflections were centered around $(1/3\ 1/3\ \gamma)$ (Fig. 1). However, the satellite reflections from the $Cd_5(VO_4)_3I$ crystal were smeared out due to extensive disordering and could not be quantified with standard methods. The only quantitative information that we were able to extract from the $Cd_5(VO_4)_3I$ experiments was the length of the q vector, which was approximately $0.63c^*$.

The satellite reflections in the two examples could not be indexed using rational indices. The superspace approach, developed by Janner, Jansen, and de Wolff (10–13) was therefore suitable in this case. The four-dimensional approach gives a possibility to describe the average structure, with superimposed modulations on the atoms having a period incommensurate with the average unit cell.

Hereafter, the detailed structural discussion concerns the $Cd_5(PO_4)_3Br$ structure. After integration, the data set was corrected for absorption and averaged in the four-dimensional super space group $R{:}P\bar{3}{:}(00\gamma)$. The average structure is $P6_3/m$ but due to the rhombohedral centering the space group must be trigonal; however, the diffraction pattern is hexagonal, which is explained by twinning perpendicular to c^*. The maximal nonisomorphic trigonal space group to $P6_3/m$ is $P\bar{3}$ and consequently the superspace group chosen is $R{:}P\bar{3}{:}(00\gamma)$ with $a = 16.932(2)$ Å, $c = 6.451(1)$ Å. The q vector is thus parallel to c^* and was refined to $0.778c^*$.

The refinement was performed in two distinct steps: (i) The average structure was refined from the basic reflections; (ii) The modulated structure was refined from the whole data set.

The average structure in space group $P6_3/m$ was refined using the coordinates for the average structure (6) as starting positions, the refinement converged rapidly and finished at a final R(obs) of 0.043. However, in order to model the modulation along c, the temperature parameters of Br were highly anisotropic with $U^{33}/U^{11} = 22.2$.

The coordinates were transformed to the tripled cell using the rhombohedral centering and refined. As a first attempt the bromine was positionally and occupationally modulated (since the bromine is positioned on the triad, no modulations in the a–b plane are allowed). No good fit to the experimental data could be obtained using harmonic modulations on the bromine. After a consideration of the F_{obs} map, a nonstandard linear saw-tooth modulation was introduced on the bromine and a better fit was accomplished. The saw-tooth function is determined by three parameters and the function (14)

$$U_z = 2U_z^0(X_4 - X_4^0)/\Delta. \qquad [1]$$

Equation [1] is defined for

$$X_4^0 - \Delta/2 < X_4 < X_4^0 + \Delta/2, \qquad [2]$$

where X_4^0 is the midpoint of the saw-tooth, U_z^0 is the maximum displacement along z, and Δ is the width of the

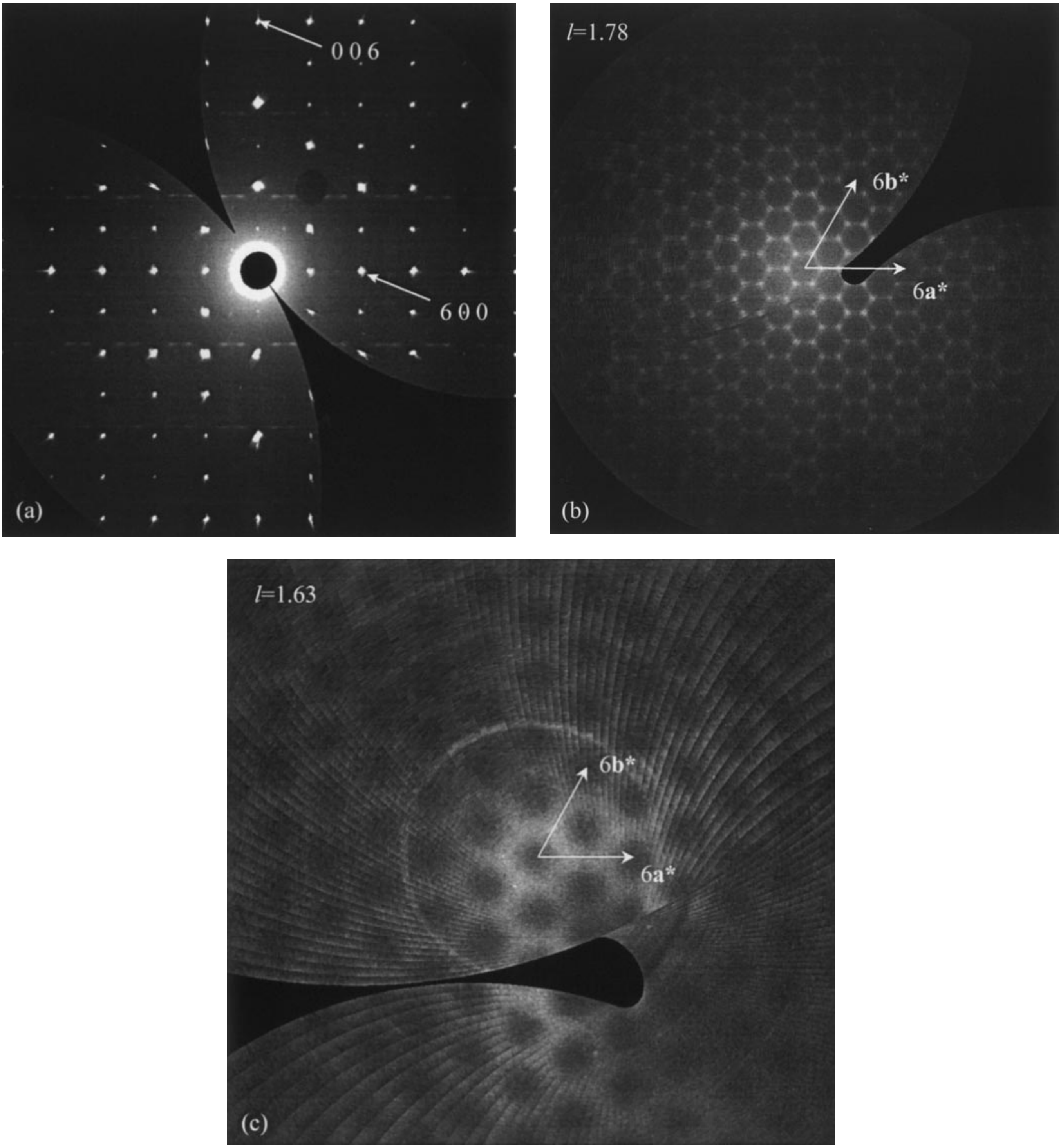

FIG. 1. Extracted reciprocal planes from IPDS raw data of $Cd_5(PO_4)_3Br$ showing the planes (a) ($h\ h\ l$) with planes of extra scattering perpendicular to c^* and (b) the plane ($h\ k$ 1.778) with well ordered satellites at (1/3 1/3 1.778) and (2/3 2/3 1.778). (c) In the corresponding plane ($h\ k$ 1.63) of $Cd_5(VO_4)_3I$ the satellites are more diffuse due to more extensive disordering (or twinning). The indexing is following the *R*-centered average cell.

saw-tooth along t (cf. site occupancy parameter). A second bromine at approximately $z = 3/4$ had to be introduced with a modulation in antiphase to the first bromine at $z = 1/4$ due to antiphase boundaries along the c axis. After evaluating the results from the refinement, it was concluded that no atoms other than the bromine were modulated nor were there any significant deviations from the underlying $P6_3/m$ symmetry. Thus, the extra atoms (O32 and Cd12)

TABLE 2
Positional and Equivalent Displacement Parameters for $Cd_5(PO_4)_3Br$

Atom	Occupancy factor	x	y	z	U_{eq}
O1	1	0.2879(2)	0.2175(2)	1/4	0.0095(4)
O2	1	0.3496(2)	0.1088(2)	1/4	0.0095
O31	1	0.2053(2)	0.0639(1)	0.0609(4)	0.0095
O32	1	−0.2053	−0.0639	0.5609	0.0095
P	1	0.26197(7)	0.11732(7)	1/4	0.0041(3)
Cd11	1	1/3	1/3	0.00591(7)	0.0090(2)
Cd12	1	−1/3	−1/3	0.50591	0.0090
Cd2	1	0.07684(2)	0.17757(2)	1/4	0.0067(2)
Br1*	0.704(2)	0	0	0.279(1)	0.0017(6)
Br2*	0.296	0	0	0.779	0.0017

Note. (*) denotes modulated atoms.

generated by the lowering of the space group symmetry from $P6_3/m$ to $P\bar{3}$ were restricted to the positions generated by the 6_3 axis of the average structure. For the same reason the special positions (x y 1/4) of the O1, O2, P, and Cd2 atoms were kept at $z = 1/4$. The displacement factors of the oxygens were restricted to be equal, this restriction was also imposed upon the cadmium atoms at (1/3 1/3 z) and (2/3 2/3 z). The final refinement using the restrictions mentioned above converged at $R(\text{obs}) = 0.0374$ for the main reflections and $R(\text{obs}) = 0.1350$ for the satellites. Experimental details are given in Table 1 and the refined atomic positional and thermal parameters are given in Table 2.

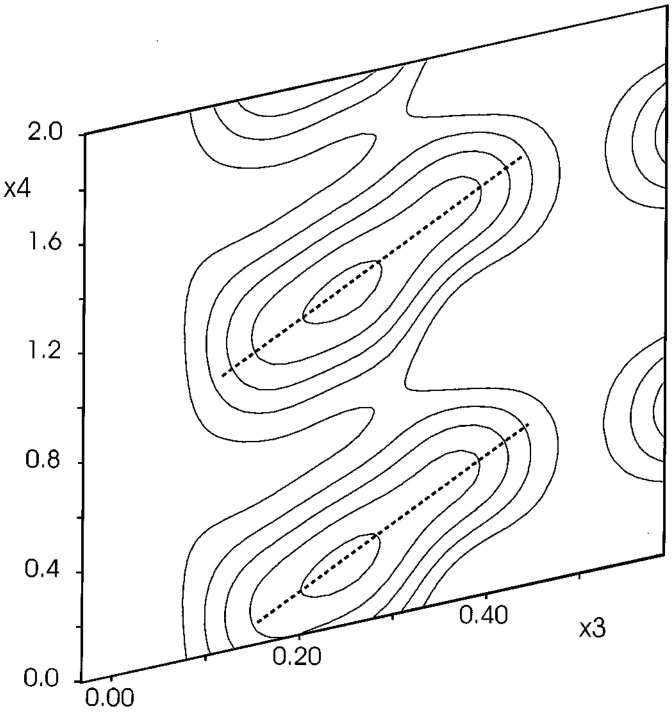

FIG. 2. The electron density calculated from $F(\text{obs})$ in four-dimensional space with $x1 = 0$ and $x2 = 0$, positive contours every 10 electrons. The dotted line indicates the refined saw-tooth behavior of the bromine. Note the "forbidden" regions around $z = 0$.

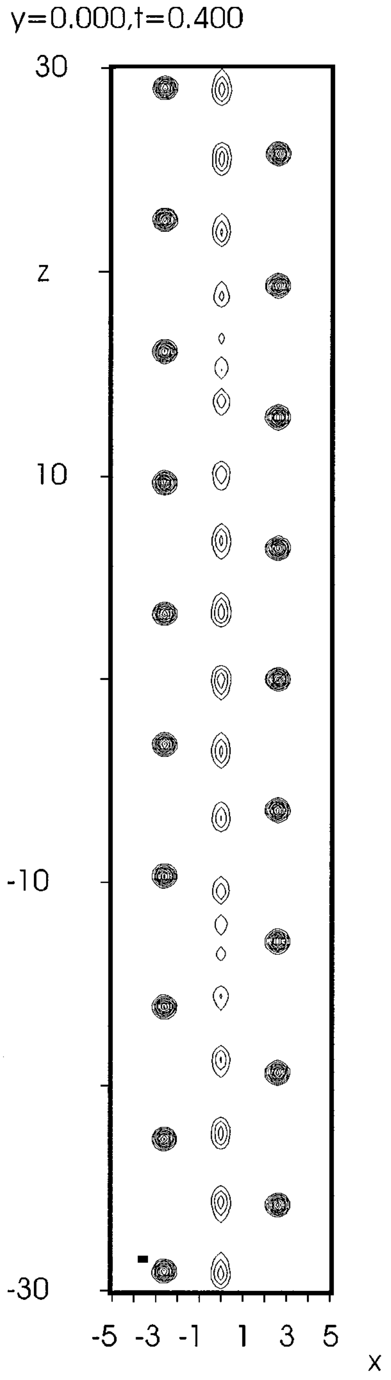

FIG. 3. T map from $F(\text{obs})$ at t = 0.4. The c axis is parallel with z and the a axis is parallel with x in the graph, scaling is in Å units. Positive contours are at every 13 electrons. The saw-tooth behavior of the bromine is seen as a linear displacement from $z = 1/4$ going from unit cell to unit cell.

STRUCTURAL DESCRIPTION

The average $Cd_5(PO_4)_3Br$ structure is isostructural with fluoroapatite (1). However, due to the short *c* axis (6.452(2) Å) compared to the radius of the bromide ion and the relatively weak interaction between the bromine and the surrounding structure, the bromine is modulated giving a Br–Br distance of 3.466 Å. The behavior of the bromine is best described via a saw-tooth function with the refined parameters $X_4^0 = 0.292(3)$, $U_z^0 = 0.1655(8)$, and $\Delta = 0.838(7)$, i.e., it is displaced $\pm$ 1.068(5) Å from the average position centering the Cd2-triangle at $z = 1/4$. The saw-tooth behavior of the bromine is shown in Fig. 2, where the displacement along the *c* axis is plotted against *x*4 in an electron density map cut out of the four-dimensional superspace. The bromine pushes itself through the structure from one extreme position at $z = 0.08$ to the other extreme at $z = 0.42$. The bromine-chain is not continuous, there are "forbidden" sites around $z = 0$ and $z = 1/2$, and the saw tooth is truncated with a width of 0.838(7), comparable to the site-occupancy factor refined to 0.838(11) in the average structure (6). It is thus not possible to describe the behavior of the $Cd_5(PO_4)_3Br$ as a composite structure with a continuous Br chain running along *c*. Within one period of the saw-tooth (approximately 8 bromine atoms long) the Br–Br distance is constant, 3.47 Å, and the minimum Br–Br distance between two periods is 4.28 Å due to the forbidden sites around $z = 0$ (Fig. 3). The phases of the modulation waves in the three unique Br columns within the unit cell are shifted 1/3 relative to each other, and this ordering is responsible for the tripling (*R*-centering) of the unit cell.

DISCUSSION

The $Cd_5(PO_4)_3Br$ is the first example of an incommensurately modulated apatite. The structure is geometrically modulated by an incommensurate Br–Br distance, which is explained by the relatively large Br anions. The modulation is analogous to the "chimney-ladder" structures (15), e.g., $Cr_{11}Ge_{10}$. Prior to this study there was a question mark concerning the Br–Br distance within the structure. The Br–Br distance was refined using the extra information present in the satellites and was found to be 3.466 Å, significantly shorter than the traditional diameter of the bromide ion 3.64 Å (16). The cadmium bromide apatite is sub-stoichiometric with respect to the halogenide ions and charge neutrality may be restored via, e.g., cadmium vacancies (approximately 1%) or a small number of O^{2-} substituting halogenide ions. However, data did not support a detailed analysis of these mechanisms.

The coupling between the Br columns is weak (twinning and disorder seen as diffuse scattering between satellites), but, it is significant and probably accomplished by electrostatic forces c.f. the doubling of the unit cells of hydroxyapatite and chloroapatite.

Concerning the $Cd_5(VO_4)_3I$ structure, the diffraction pattern indicates that the space group and thus nature of the modulation is identical to that of $Cd_5(PO_4)_3Br$. However, disorder smears out the satellites and makes it impossible to refine the structure in four dimensions.

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