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Letter

Synthesis and crystal structures of Cs_2MgD_4 and Cs_3MgD_5 B. Bertheville^a, P. Fischer^b, K. Yvon^{a,*}^aLaboratoire de Cristallographie, Université de Genève, 24, Quai E. Ansermet, CH-1211 Genève 4, Switzerland^bLaboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

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Abstract

The title compounds were prepared by sintering stoichiometric mixtures of the binary deuterides in an autoclave under 65 bar pressure at 625 K. Neutron powder diffraction reveals a $\beta\text{-K}_2\text{SO}_4$ type structure for Cs_2MgD_4 (space group $Pnma$, $a=8.5988(4)$, $b=6.6234(3)$, $c=11.5988(5)$ Å) and a Cs_3CoCl_5 type structure for Cs_3MgD_5 (space group $I4/mcm$, $a=8.4022(2)$, $c=12.6951(4)$ Å). In both deuterides magnesium is tetrahedrally coordinated by deuterium. The Mg–D bond distances (1.82–1.88 Å in Cs_2MgD_4 and 1.84 Å in Cs_3MgD_5) are longer by 0.02 Å, on the average, than those in the corresponding rubidium analogues. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Caesium magnesium deuterides; Saline hydrides; Neutron powder diffraction; Crystal structure

1. Introduction

Magnesium is a useful constituent for hydrogen storage materials [1,2]. In combination with alkali metals such as rubidium it forms a series of saline metal hydrides such as RbMgH_3 [3], Rb_2MgH_4 [4], Rb_3MgH_5 [4] and $\text{Rb}_4\text{Mg}_3\text{H}_{10}$ [5]. Caesium analogues such as Cs_2MgH_4 [6] and Cs_3MgH_5 [7] are known, but their detailed crystal structures have not yet been investigated. In this work a neutron powder diffraction analysis of the deuterides Cs_2MgD_4 and Cs_3MgD_5 is presented. It will be shown that the former crystallises with the $\beta\text{-K}_2\text{SO}_4$ type structure as was correctly assumed [6], whereas the latter adopts the Cs_3CoCl_5 type structure rather than the Sr_3SiO_5 type structure proposed previously [7].

2. Experimental

2.1. Synthesis

Stoichiometric mixtures of the binary deuterides CsD and $\alpha\text{-MgD}_2$ were pressed to pellets and sintered in an autoclave at 625 K under a deuterium pressure of 65 bar

for 5 days. The reaction products obtained were of white colour. They were pyrophoric and extremely sensitive to air and moisture. The binary deuterides were prepared by deuteration of metallic caesium (STREM 99.9%) and magnesium powder (CERAC 99.6, –400 mesh).

2.2. X-ray diffraction

The Cs_2MgD_4 and Cs_3MgD_5 samples were characterized by X-ray powder diffraction (Philips PW820 powder diffractometer, Cu $K\alpha$ radiation, sealed sample holder). The patterns suggested that the former contained a majority phase with orthorhombic $\beta\text{-K}_2\text{SO}_4$ type structure, and the latter a phase with body-centred tetragonal Cs_3CoCl_5 type structure. Attempts to obtain single phase samples by modifying the synthesis conditions failed. The Cs_2MgD_4 sample always contained significant amounts of Cs_3MgD_5 and unreacted binary deuterides as secondary phases, whereas the Cs_3MgD_5 sample contained unreacted CsD. Both samples also contained MgO impurities. The refined cell parameters are listed in Table 1 together with those reported for the corresponding hydrides. The refined metal atom positions (not given here) were in agreement with those found in the corresponding Rb analogues [4].

2.3. Neutron diffraction

Data at room temperature were collected on the high-

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Table 1
Cell parameters of ternary caesium magnesium hydrides and deuterides

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Reference
Cs ₂ MgH ₄	8.627(2) ^a	6.654(2)	11.662(3)	669.4	[6]
Cs ₂ MgD ₄	8.5988(4)	6.6234(3)	11.5988(5)	660.59(5)	Present work
Cs ₃ MgH ₅	8.424(2)	–	12.728(3)	903.2	[7]
Cs ₃ MgD ₅	8.4022(2)	–	12.6951(4)	896.25(5)	Present work

^a e.s.d. values in parentheses.

resolution powder diffractometer HRPT [8] at the Swiss spallation neutron source SINQ at PSI in Villigen ($\lambda = 1.886$ Å, $2\theta_{\max} = 158.95^\circ$, step size = 0.05° in 2θ , $T = 293$ K). The samples Cs₂MgD₄ (1.6 g) and Cs₃MgD₅ (2.1 g) were enclosed in cylindrical vanadium containers of 8 and 9 mm inner diameter, respectively. Rietveld refinements (program FULLPROF [9]) were performed by taking as starting parameters the X-ray metal position values, and by letting the deuterium positions vary about those of the rubidium analogues. For the Cs₂MgD₄ sample five additional phases were included in the refinement (Cs₃MgD₅,

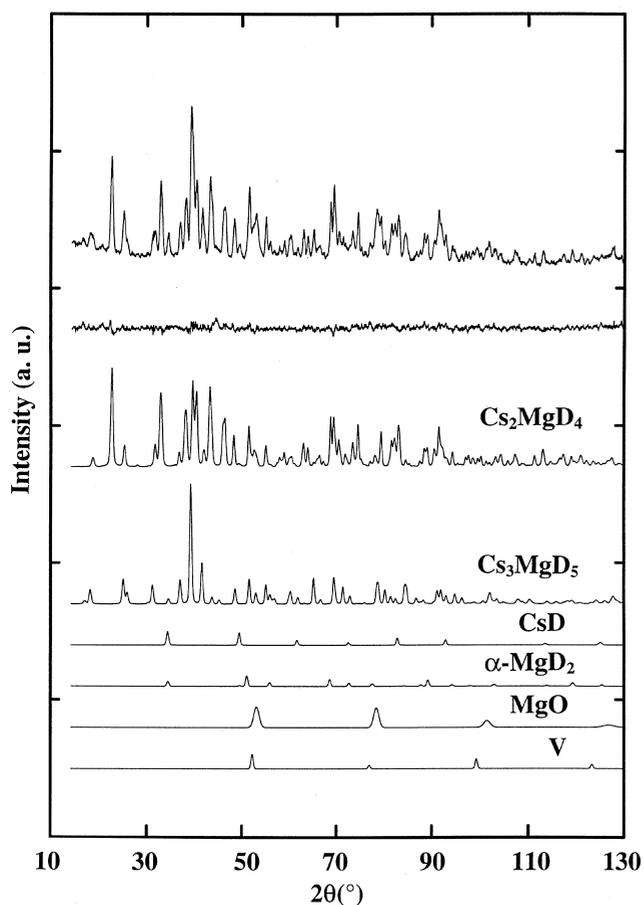


Fig. 1. Observed (top), difference (middle), and calculated (bottom) neutron diffraction patterns of the Cs₂MgD₄ sample ($T = 293$ K, $\lambda = 1.886$ Å).

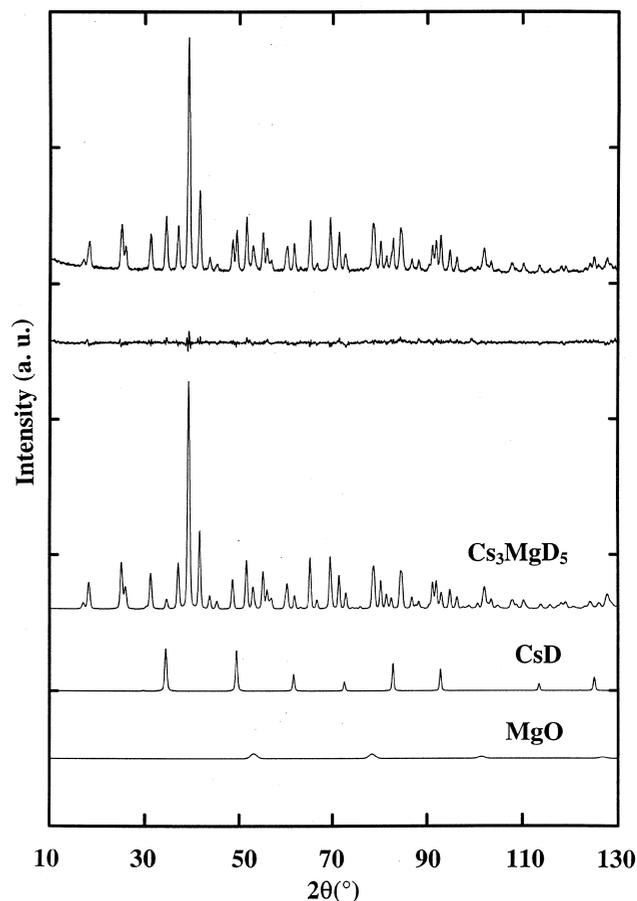


Fig. 2. Observed (top), difference (middle) and calculated (bottom) neutron diffraction patterns of the Cs₃MgD₅ sample ($T = 293$ K, $\lambda = 1.886$ Å).

Table 2
Refinement results^a on neutron diffraction data for Cs₂MgD₄

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} (Å ²)
Cs1	4c	0.1594(6)	1/4	0.4109(6)	2.9(1)
Cs2	4c	0.4856(6)	1/4	0.6973(4)	1.6(1)
Mg	4c	0.2314(6)	1/4	0.0781(6)	1.8(1)
D1	8d	0.3133(5)	0.0209(7)	0.1516(3)	4.7(1)
D2	4c	0.0206(7)	1/4	0.0944(6)	5.6(2)
D3	4c	0.8070(9)	1/4	0.5686(6)	4.3(2)

^a $T = 293$ K, space group *Pnma* (no. 62), $Z = 4$; e.s.d. values in parentheses. $R_{\text{Bragg}} = 7.5\%$, $R_{\text{F}} = 5.3\%$, $R_{\text{p}} = 1.9\%$, $R_{\text{wp}} = 2.5\%$, $S = 2.7$.

Table 3
Refinement results^a on neutron diffraction data for Cs₃MgD₅

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} (Å ²)
Cs1	8 <i>h</i>	0.6828(2)	0.1828(2)	0	2.4(5)
Cs2	4 <i>a</i>	0	0	1/4	3.1(8)
Mg	4 <i>b</i>	0	1/2	1/4	2.2(7)
D1	16 <i>l</i>	0.1240(1)	0.6240(1)	0.1625(1)	5.0(5)
D2	4 <i>c</i>	0	0	0	3.5(7)

^a *T* = 293 K, space group *I4/mcm* (no. 140), *Z* = 4; e.s.d. values in parentheses. *R*_{Bragg} = 6.6%, *R*_F = 5.7%, *R*_p = 2.7%, *R*_{wp} = 3.4%, *S* = 2.4.

Table 4
Selected interatomic distances (Å) and angles (°) in Cs₃MgD₄

Cs1–D2	3.106(8) ^a	D1–Mg	1.877(6)
2D1	3.327(7)	D3	2.972(7)
2D3	3.333(1)	D2	3.013(7)
2D1	3.418(7)	D1	3.035(7)
D3	3.540(9)	Cs2	3.046(6)
2D1	3.619(7)	Cs2	3.179(6)
Mg	3.682(7)	Cs1	3.327(7)
D2	3.859(9)	Cs1	3.418(7)
		D1	3.588(7)
		Cs1	3.619(7)
Cs2–2D1	3.046(6)	D2–Mg1	1.823(8)
D3	3.120(9)	2D1	3.013(7)
D3	3.141(9)	D3	3.105(9)
2D1	3.179(6)	Cs1	3.106(8)
D2	3.397(9)	Cs2	3.397(9)
2D2	3.520(3)	2Cs2	3.520(3)
Mg	3.830(8)	2D1	3.762(7)
		Cs1	3.859(9)
Mg–D3	1.822(9)	D3–Mg1	1.822(9)
D2	1.823(8)	2D1	2.972(7)
2D1	1.877(6)	D2	3.105(9)
D3–Mg–D2	116.9(5)	Cs2	3.120(9)
D3–Mg–D1	106.9(3)	Cs2	3.141(9)
		2Cs1	3.333(1)
		Cs1	3.540(9)

^a e.s.d. values in parentheses.

Table 5
Selected interatomic distances (Å) and angles (°) in Cs₃MgD₅

Cs1–2D2	3.076(2) ^a	D1–Mg	1.845(1)
2D1	3.086(2)	D1	2.948(1)
4D1	3.339(2)	2D1	3.046(2)
2Mg	3.846(1)	Cs1	3.086(2)
		2Cs1	3.339(2)
		2Cs2	3.507(1)
Cs2–2D2	3.174(1)	D2–4Cs1	3.076(2)
8D1	3.507(1)	2Cs2	3.174(1)
4Mg	4.201(1)	8D1	3.914(1)
Mg–4D1	1.845(1)		
4Cs1	3.846(1)		
D1–Mg1–D1	106.01(7)		
D1–Mg1–D1	111.23(5)		

^a e.s.d. values in parentheses.

CsD, α-MgD₂ [10], MgO and V) and for the Cs₃MgD₅ sample two (CsD and MgO). For the former 47 parameters were allowed to vary: one zero correction, six background, six scale factors, 12 profile parameters (four for the Cs₂MgD₄ phase and eight for the five secondary phases), three lattice parameters, 13 positional parameters, and six isotropic temperature factors. For the latter 28 parameters were allowed to vary: one for the zero correction, six for the background, 15 for the Cs₃MgD₅ phase (one scale factor, two cell, eight atomic, and four peakshape parameters) and six for the secondary phases (four for CsD and two for MgO). The observed, calculated and difference neutron powder patterns are shown in Figs. 1 and 2. The refinement results are summarised in Tables 2 and 3, and selected interatomic distances are listed in Tables 4 and 5. The coordination polyhedra around the various atom sites are represented in Figs. 3 and 4.

3. Results and discussion

Cs₂MgD₄ and Cs₃MgD₅ are salt-like compounds. They are isostructural with their rubidium analogues [4] and the corresponding deuterides based on zinc [11,12]. Both compounds contain tetrahedral MgD₄²⁻ anions, and Cs₃MgD₅ also contains an additional deuteride species D⁻ bonded to Cs only. Due to matrix effects the Mg–D bond distances in Cs₂MgD₄ (1.82–1.88 Å) and Cs₃MgD₅ (1.84 Å) are longer by 0.02 Å, on the average, than the corresponding distances in the rubidium analogues Rb₂MgD₄ (1.79–1.87 Å [4]) and Rb₃MgD₅ (1.82 Å [4]). As expected, they are shorter than those for octahedral coordinated Mg in binary α-MgD₂ (1.94 Å [10]). The D–Mg–D bond angles (Cs₂MgD₄: 107–117°; Cs₃MgD₅: 106–111°) deviate only little from the tetrahedral angle. Caesium has nine-fold (Cs2) and 11-fold (Cs1) deuterium coordinations in Cs₂MgD₄ (Fig. 3), and eight-fold (Cs1) and ten-fold (Cs2) deuterium coordinations in Cs₃MgD₅ (Fig. 4). The Cs–D bond distances (Cs₂MgD₄: 3.11–3.86 Å (Cs1), 3.05–3.52 Å (Cs2); Cs₃MgD₅: 3.08–3.34 Å (Cs1), 3.17–3.51 Å (Cs2)) are longer by 0.2 Å, on the average, than those in the rubidium analogues (Rb₂MgD₄: 2.77–3.97 Å (Rb1), 2.86–3.48 Å (Rb2); Rb₃MgD₅: 2.87–3.22 Å (Rb1), 3.06–3.34 Å (Rb2)). All deuterium sites have six-fold metal coordinations. They are surrounded by five Cs and one Mg atoms except for D2 in Rb₃MgD₅ which is surrounded by six Cs atoms. The calculated hydrogen storage efficiencies are 1.37 wt% (40.01 g H₂ l⁻¹) for Cs₂MgH₄ and 1.18 wt% (37.06 g H₂ l⁻¹) for Cs₃MgH₅. No fluoride analogues are known. The only compound known in the Cs–Mg–F system is Cs₄Mg₃F₁₀ [13].

As to the potassium analogues only K₂MgH₄ is known to exist [14]. It crystallizes with the K₂NiF₄ structure type

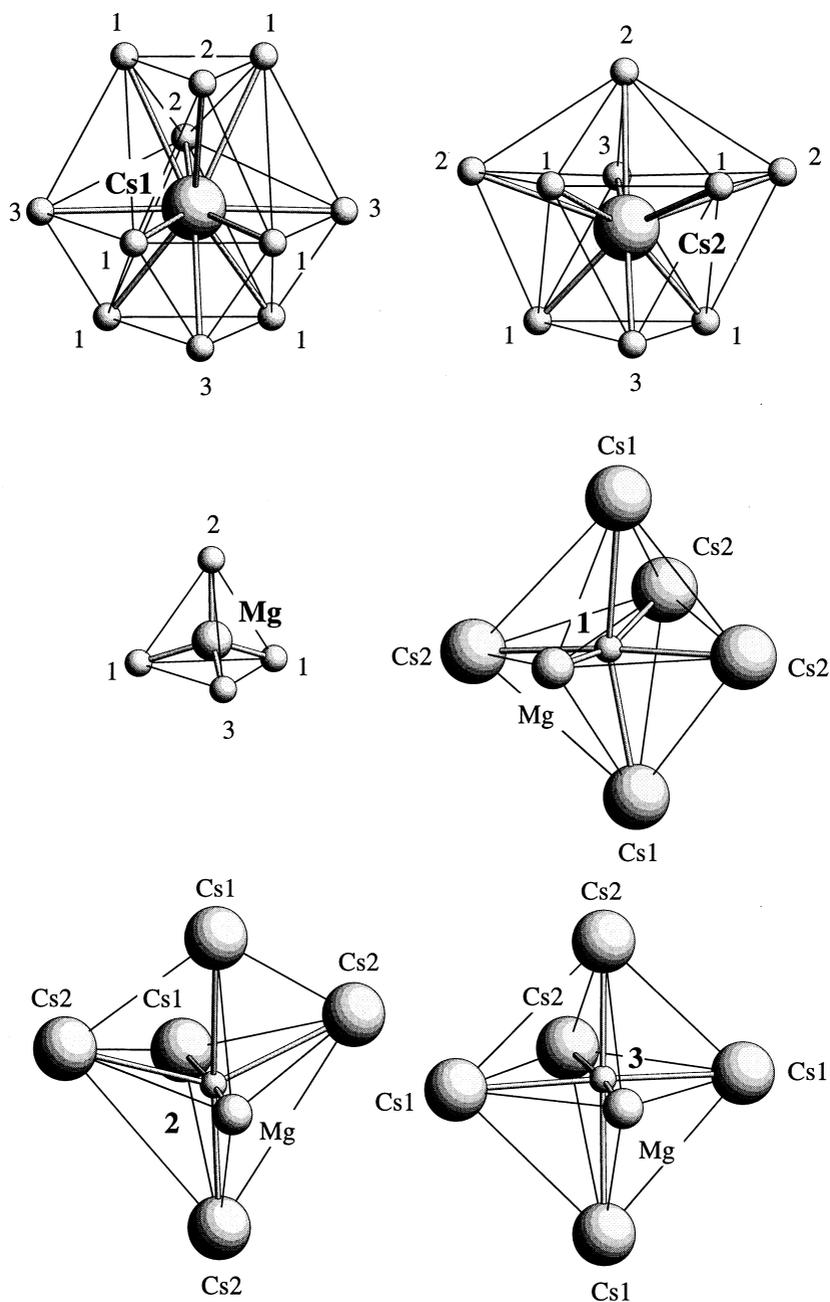


Fig. 3. Metal and deuterium co-ordinations in Cs_2MgD_4 ; D sites numbered; site symmetries m (Cs1, Cs2, Mg, D2, D3) and l (D1).

rather than the $\beta\text{-K}_2\text{SO}_4$ structure type which means that hydrogen in that compound surrounds magnesium in an octahedral rather than a tetrahedral configuration. Attempts to synthesise a hypothetical hydride ' K_3MgH_5 ' containing tetrahedral MgH_4^{2-} anions have so far failed. On the other hand, the corresponding zincates all exist (for M_2ZnD_4 and M_3ZnD_5 , $\text{M}=\text{K}, \text{Rb}, \text{Cs}$; see Refs. [11,12,15,16]). Since zinc has a smaller atomic radius than magnesium in these type of compounds, the size ratio between the tetrahedral hydride anions and the metal cations M may be

a critical parameter for structural stability. Further experiments are necessary to confirm this hypothesis.

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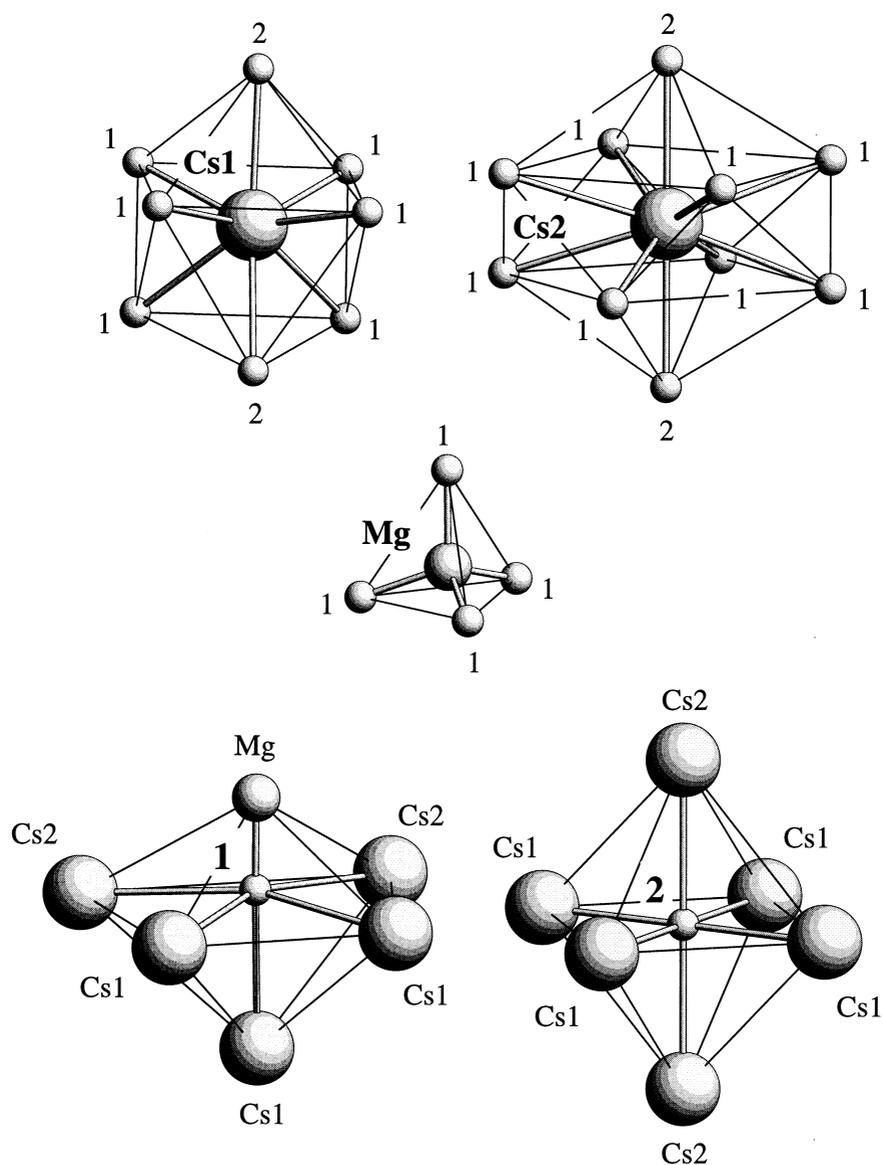


Fig. 4. Metal and deuterium co-ordinations in Cs_3MgD_5 ; D sites numbered; site symmetries $m.2m$ (Cs1), 422 (Cs2), $-42m$ (Mg), m (D1) and $4/m$ (D2).

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