

LETTER TO THE EDITOR

Crystal Structure and Magnetic Properties of Na₉V₁₄O₃₅:
Sodium–Vanadium Bronze η -Na_xV₂O₅

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The crystal structure of η -Na_{1.3}V₂O₅, a member of Na_xV₂O₅ bronze family, has been determined by single-crystal X-ray study: its actual stoichiometric formula is denoted by Na₉V₁₄O₃₅. The monoclinic system *P2/c* was confirmed with $a = 15.209(8)$ Å, $b = 5.036(5)$ Å, $c = 20.786(6)$ Å, $\beta = 109.18(3)^\circ$ with $Z = 2$. The refinements converged to $R = 0.036$ and $R_w = 0.037$ for 3848 reflections with $I > 3\sigma(I)$. The structure is of a layer type consisting of V₂O₅ layers and interlayer Na atoms. The V₂O₅ layer adopts a novel framework built up with edge-sharing VO₅ square pyramids for five V atoms (four V⁴⁺ and one V^{4.5+}) and vertex-sharing VO₄ tetrahedra for two V atoms (V⁵⁺). Low-dimensional behavior with a spin gap was observed in the magnetic susceptibility but the structure is dissimilar to any structure type of low-dimensional spin-gap systems. The compound probably presents a new type of spin-gap system. © 1999 Academic Press

INTRODUCTION

In the sodium–vanadium bronze system Na_xV₂O₅, there exist seven phases denoted by α -, β -, δ -, τ -, α' -, η -, and κ -phases in the ascending order of x (1–3). They are mixed-valent compounds of V⁴⁺ (d^1 , $S = \frac{1}{2}$) and V⁵⁺ (d^0 , $S = 0$), among which α' -NaV₂O₅ ($x = 1.0$) has been studied most intensively for its anomalous phase transition like a spin-Peierls transition (4–7). The spin state of α' -NaV₂O₅ surely falls into spin singlet accompanied with the lattice distortion, despite various arguments on the origin of phase

transition (8). Low-dimensional spin systems with $S = \frac{1}{2}$ and singlet ground states are of great interest because of their fundamental quantum nature. The transitions to spin singlet without lattice distortion have been observed in layered vanadates of CaV₂O₅ (9), MgV₂O₅ (10), and CaV₄O₉ (11): the former two compounds whose intralayer structures are similar to that of α' -NaV₂O₅ (12) are considered to be two-leg spin-ladder systems and the latter one to be a plaquette spin-gap system.

Recently the η -phase Na_xV₂O₅ ($x = 1.3$) was reported to exhibit low-dimensional behavior of the magnetic susceptibility by two of the authors (M.I. and Y.U.) who also suggested a spin-singlet state since the magnetic susceptibility became very low values at low temperatures (6). To understand the observed spin-gap behavior of the η -phase, its crystal structure and thus the geometrical arrangement of magnetic V⁴⁺ ions have to be determined. In this study we have solved the crystal structure of the η -phase, thereby giving the stoichiometric formula Na₉V₁₄O₃₅ for the η -phase. A layered structure consisting of V₂O₅ layers and interlayer Na atoms is disclosed and the valence states of V atoms are clearly demonstrated.

EXPERIMENTAL

Sample Preparation

Powder samples were prepared by a solid state reaction of V₂O₃, V₂O₅, and NaVO₃ at appropriate molar ratios. The

details of the preparation were reported elsewhere (6). Small crystals were often found in powder samples. The composition range of the η -phase on the composition line of $\text{Na}_x\text{V}_2\text{O}_5$ was determined to be as narrow as $1.28 \leq x \leq 1.29$: a mixture of α' - and η -phase was obtained below $x = 1.28$ and that of η - and κ -phase above $x = 1.30$. Out of the composition line of $\text{Na}_x\text{V}_2\text{O}_5$ unknown phases were included. The composition of η -phase is thus tentatively denoted as $\text{Na}_{1.285}\text{V}_2\text{O}_5$.

Single-Crystal X-ray Diffraction

A single crystal with dimensions of $0.25 \times 0.15 \times 0.10$ mm was mounted on a Rigaku AFC-7R X-ray diffractometer with monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å). The monoclinic system was confirmed with unit cell parameters of $a = 15.209(8)$ Å, $b = 5.036(5)$ Å, $c = 20.786(6)$ Å, and $\beta = 109.18(3)^\circ$ determined from 25 reflections in a $43.6^\circ < 2\theta < 44.6^\circ$ range. The cell volume of $1504(2)$ Å³ and the formula weight of 211.42 for $\text{Na}_{1.285}\text{V}_2\text{O}_5$ yield $Z = 14$ which gives a proper calculated density of 3.269 g cm⁻³ by comparison with 3.470 g cm⁻³ for α' - NaV_2O_5 (12). Now the composition of η -phase can be rewritten by using integers as $\text{Na}_9\text{V}_{14}\text{O}_{35}$ ($Z = 2$). Data collection was performed by a ω - 2θ scanning method with a scanning width $\Delta\omega = (1.31 + 0.30 \tan \theta)^\circ$ up to $2\theta = 70^\circ$, where no significant intensity decay (-0.4%) was observed in three standard reflections monitored every 150 reflections. A total of 7437 reflections were collected of which 3848 reflections with $I > 3\sigma(I)$ were used in the structure determination. An empirical absorption correction of the ψ scan method was applied with transmission factors of 0.523–0.650. Crystallographic data and experimental parameters are listed in Table 1. All the calculations for data processing and structure determination were carried out by

TABLE 1
Crystallographic Data and Experimental Parameters
for $\text{Na}_9\text{V}_{14}\text{O}_{35}$

Space group	$P2_1/c$
a (Å)	15.209(8)
b (Å)	5.036(5)
c (Å)	20.786(6)
V (Å ³)	1504(2)
Z	2
D_c (g cm ⁻³)	3.269
μ (cm ⁻¹)	43.84
No. of total reflections	7437
No. of unique reflections	7225 ($R_{\text{int}} = 0.046$)
No. of observed reflections	3848 ($I > 3\sigma(I)$)
No. of variables	263
R	0.036
R_w	0.037
$\rho_{\text{max/min}}$ (e/Å ³)	0.58/–0.68

TABLE 2
Atomic Coordinates and Equivalent Temperature Factors
for $\text{Na}_9\text{V}_{14}\text{O}_{35}$

Atom	x	y	z	B_{eq} (Å ²)
V(1)	0.51232(4)	0.40093(12)	0.43570(2)	0.608(9)
V(2)	0.72446(4)	0.40048(12)	0.39381(2)	0.627(9)
V(3)	0.93649(4)	0.41358(12)	0.34980(2)	0.583(9)
V(4)	0.14464(4)	0.41964(12)	0.31797(2)	0.751(9)
V(5)	0.90708(4)	0.61662(13)	0.47777(3)	0.751(9)
V(6)	0.30126(4)	0.39856(12)	0.47716(2)	0.604(9)
V(7)	0.40307(4)	0.35629(11)	0.26866(2)	0.595(8)
Na(1)	0.43267(10)	0.1268(3)	0.65415(7)	1.21(3)
Na(2)	0.21830(10)	0.1169(3)	0.70023(7)	1.47(3)
Na(3)	0.65342(11)	0.1255(8)	0.61784(7)	1.41(3)
Na(4)	0.87103(10)	0.1418(3)	0.57538(7)	1.60(3)
Na(5)	0	0.1002(5)	0.75	1.55(4)
Na(1)	0.43267(10)	0.1268(3)	0.65415(7)	1.21(3)
O(1)	0.58407(15)	0.4610(5)	0.53209(10)	0.70(4)
O(2)	0.50071(17)	0.0845(5)	0.42066(12)	1.21(5)
O(3)	0.37294(14)	0.4673(5)	0.57357(10)	0.76(4)
O(4)	0.79812(15)	0.4697(5)	0.49050(10)	0.83(4)
O(5)	0.29159(17)	0.0814(5)	0.46526(12)	1.21(5)
O(6)	0.71330(17)	0.0838(5)	0.37860(12)	1.22(5)
O(7)	0.16230(15)	0.4657(5)	0.61633(10)	0.73(4)
O(8)	0.55327(16)	0.4521(5)	0.65945(10)	0.89(4)
O(9)	0.5	0.1907(7)	0.25	0.88(6)
O(10)	0.1408(2)	0.0919(5)	0.32027(12)	1.40(5)
O(11)	0.93789(18)	0.0914(5)	0.34483(12)	1.33(5)
O(12)	0.14505(18)	0.4667(5)	0.73876(10)	0.89(4)
O(13)	0.34730(16)	0.4498(5)	0.69915(11)	0.96(4)
O(14)	0.76361(15)	0.4572(5)	0.61472(10)	0.84(4)
O(15)	0.33564(16)	0.1200(6)	0.28055(11)	1.20(5)
O(16)	0.95713(16)	0.4598(5)	0.67227(11)	0.97(4)
O(17)	0.09797(18)	0.0694(6)	0.51118(12)	1.34(5)
O(18)	0.99172(15)	0.4680(5)	0.55730(10)	0.88(4)

using the software SDP for Windows (13) and teXsan for Windows (14).

Structure Determination

Possible space groups Pc and $P2_1/c$ were chosen and the space group $P2_1/c$ was adopted since the intensity statistics strongly suggested the centrosymmetric option. Positions of V atoms were determined by a direct method provided by SDP for Windows (13) and subsequently those of Na atoms and O atoms were located in differential Fourier maps. This procedure successfully gave seven V atoms, five Na atoms and eighteen O atoms, being inconsistent with the formula $\text{Na}_9\text{V}_{14}\text{O}_{35}$ and $Z = 2$. The refinements using anisotropic displacement parameters converged to $R = 0.036$ and $R_w = 0.037$. Full occupancies of V and Na sites were confirmed and thus their occupancies were fixed to unity. The atomic coordinates and equivalent temperature factors are listed in Table 2.

RESULTS AND DISCUSSION

Description of the Structure

The structure of $\text{Na}_9\text{V}_{14}\text{O}_{35}$ or $\eta\text{-Na}_{1.3}\text{V}_2\text{O}_5$ takes a layer type consisting of V_2O_5 layers and interlayer Na atoms as depicted in Fig. 1. The V_2O_5 layer adopts a novel framework structure built of VO_5 square pyramids for V(1), V(2), V(3), V(5), and V(6) and VO_4 tetrahedra for V(4) and V(7). Table 3 lists V–O bond distances for these V–O polyhedra. The VO_5 square pyramids are joined by edge sharing with their apical oxygens pointing up and down alternately to form a zigzag chain running along [100]. The zigzag chain is structurally similar to that of the V_2O_5 layer of $\alpha'\text{-NaV}_2\text{O}_5$ (12). It is interesting to note that the zigzag chain exhibits a crystallographic shear or step at every five edge-sharing $\text{VO}_5\text{-VO}_5$ units: the shear operation is in the [001] direction and by two-edge length of VO_5 square pyramid. The zigzag chains are bridged by the VO_4 tetrahedra to

form the V_2O_5 layer. Interlayer Na atoms are coordinated by six oxygens except for the Na(5) atom of 7-coordination; Na–O bond distances are listed in Table 4 for Na–O < 2.9 Å. The Na atoms are bonded to both apical and bridging oxygens of the V_2O_5 layered framework, which is just like those in $\alpha'\text{-NaV}_2\text{O}_5$ (12) but is different from those in $\delta\text{-Na}_{0.5}\text{V}_2\text{O}_5$ (15) that are bonded solely to apical oxygens.

The structure of $\text{Na}_9\text{V}_{14}\text{O}_{35}$ could be regarded as a kind of shear structure derived from the mother structure whose layer structure is formed by infinite zigzag chains of VO_5 square pyramids bridged by VO_4 tetrahedra. This structural viewpoint anticipates the existence of homologous compounds.

Valence States of Vanadium Atoms

$\text{Na}_9\text{V}_{14}\text{O}_{35}$ is a mixed-valent compound with an average vanadium valence of 4.357. The valence state of each V atom

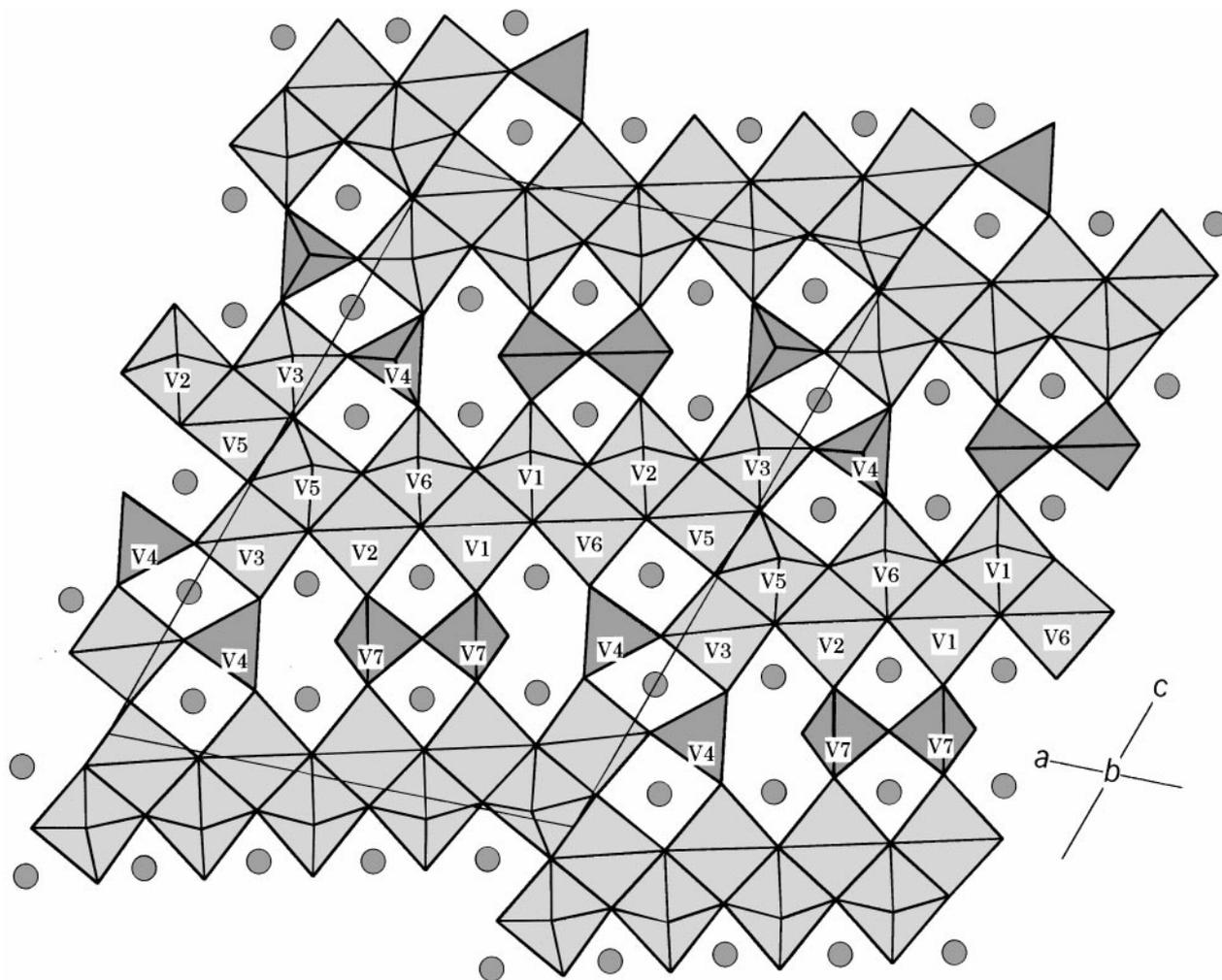


FIG. 1. Crystal structure of $\text{Na}_9\text{V}_{14}\text{O}_{35}$ viewed along the b axis. VO_5 square pyramids and VO_4 tetrahedra are drawn by light and heavy shades, respectively and interlayer Na atoms by dark circles.

TABLE 3
Bond Distances (Å) for V–O Polyhedra in Na₉V₁₄O₃₅

V(1)O ₅ square pyramid					
V(1)–O(1)	1.965(3)	V(1)–O(1) ⁱ	1.930(3)	V(1)–O(2)	1.622(4)
V(1)–O(3) ⁱ	1.935(3)	V(1)–O(8) ⁱ	2.039(3)		
V(2)O ₅ square pyramid					
V(2)–O(3) ⁱ	1.938(3)	V(2)–O(4)	1.984(3)	V(2)–O(6)	1.624(4)
V(2)–O(7) ⁱ	1.925(3)	V(2)–O(13) ⁱ	2.027(3)		
V(3)O ₅ square pyramid					
V(3)–O(7) ⁱ	1.954(3)	V(3)–O(11)	1.626(4)	V(3)–O(12) ⁱ	1.947(3)
V(3)–O(16) ⁱⁱ	1.929(3)	V(3)–O(18) ⁱⁱ	1.973(3)		
V(4)O ₄ tetrahedron					
V(4)–O(10)	1.653(4)	V(4)–O(12) ⁱⁱⁱ	1.745(3)	V(4)–O(14) ⁱ	1.734(3)
V(4)–O(16) ⁱ	1.736(3)				
V(5)O ₅ square pyramid					
V(5)–O(4)	1.911(3)	V(5)–O(7) ⁱ	1.938(3)	V(5)–O(17) ⁱ	1.603(4)
V(5)–O(18)	1.885(3)	V(5)–O(18) ⁱⁱ	1.954(3)		
V(6)O ₅ square pyramid					
V(6)–O(1) ⁱ	1.949(3)	V(6)–O(3)	1.972(3)	V(6)–O(4) ⁱ	1.961(3)
V(6)–O(5)	1.616(4)	V(6)–O(14) ⁱ	1.977(3)		
V(7)O ₄ tetrahedron					
V(7)–O(8) ⁱ	1.719(3)	V(7)–O(9)	1.843(2)	V(7)–O(13) ^{iv}	1.719(3)
V(7)–O(15)	1.642(3)				

Note. Symmetry codes: ⁱ1 – x, 1 – y, 1 – z; ⁱⁱ2 – x, 1 – y, 1 – z; ⁱⁱⁱx, y + 1, z – 1; ^{iv}x, 1 – y, z – ½.

was estimated by bond valence calculations. The results are given in Table 5 where equations proposed for V^{IV}–O and V^V–O by Brown *et al.* (16) and that for V–O by Waltersson (17) are used for comparison. It is clear that the tetrahedral V(4) and V(7) atoms are pentavalent and the square-pyr-

TABLE 4
Bond Distances (Å) for Na–O Polyhedra in Na₉V₁₄O₃₅

Na(1)–O(2) ⁱ	2.369(3)	Na(2)–O(6) ⁱ	2.431(3)	Na(3)–O(1)	2.431(3)
Na(1)–O(3)	2.360(4)	Na(2)–O(7)	2.424(4)	Na(3)–O(2) ⁱ	2.454(4)
Na(1)–O(6) ⁱ	2.350(4)	Na(2)–O(11) ⁱ	2.482(4)	Na(3)–O(5) ⁱ	2.391(3)
Na(1)–O(8)	2.435(4)	Na(2)–O(12)	2.361(4)	Na(3)–O(8)	2.577(4)
Na(1)–O(9) ⁱ	2.497(3)	Na(2)–O(13)	2.586(4)	Na(3)–O(2) ⁱ	2.454(4)
Na(1)–O(13)	2.369(3)	Na(2)–O(15) ⁱⁱ	2.369(3)	Na(3)–O(5) ⁱ	2.391(3)
Na(4)–O(4)	2.442(4)	Na(5)–O(10) ⁱⁱⁱ	2.367(3)		
Na(4)–O(5) ⁱ	2.594(4)	Na(5)–O(10) ⁱⁱⁱ	2.367(3)		
Na(4)–O(10) ⁱ	2.471(4)	Na(5)–O(11) ^{iv}	2.633(3)		
Na(4)–O(14)	2.564(4)	Na(5)–O(11) ⁱ	2.633(3)		
Na(4)–O(16)	2.532(4)	Na(5)–O(16) ^v	2.371(4)		
Na(4)–O(17) ⁱ	2.323(3)	Na(5)–O(16) ^{vi}	2.371(4)		
Na(4)–O(18)	2.606(4)				

Note. Symmetry codes: ⁱ1 – x, – y, 1 – z; ⁱⁱx, – y, ½ + z; ⁱⁱⁱ– x, – y, 1 – z; ^{iv}x – 1, – y, z + ½; ^vx – 1, y, z; ^{vi}1 – x, y, ½ – z.

TABLE 5
Bond Valence Calculations for V Atoms of Na₉V₁₄O₃₅

	V ^{IVa}	V ^{Vb}	V ^c
V(1)	3.90	4.15	4.04
V(2)	3.88	4.13	4.02
V(3)	3.97	4.23	4.12
V(4)	4.72	5.00	5.14
V(5)	4.29	4.56	4.50
V(6)	3.93	4.19	4.08
V(7)	4.62	4.89	5.01

^aCalculated with the equation in Ref. (16) for V^{IV}–O.

^bCalculated with the equation in Ref. (16) for V^V–O.

^cCalculated with the equation in Ref. (17) for V–O.

amidal V atoms except for V(5) are tetravalent. The valence of V(5) atom is doubtless judged to be 4.5. Consequently an average valence of the V atom from bond valence calculations yields 4.357 in agreement with that from the formula Na₉V₁₄O₃₅. The V(5) site where a crystallographic shear takes place is, therefore, occupied evenly by V⁴⁺ and V⁵⁺.

Magnetic Properties and Their Relation to the Structure

Figure 2 shows temperature dependence of magnetic susceptibility measured up to 700 K. It shows low-dimensional behavior, namely a broad maximum around 100 K, and decreases toward zero at the lowest temperature suggesting a spin-singlet state as a ground state. The μ SR experiments revealed the absence of a long-range magnetic order down to the lowest temperature (18). Therefore such behavior of the susceptibility is attributable to low-dimensional systems with spin gaps, for example an alternate chain system, a spin-ladder system, a dimer system and a plaquette system; however, the susceptibility curve cannot be fitted by

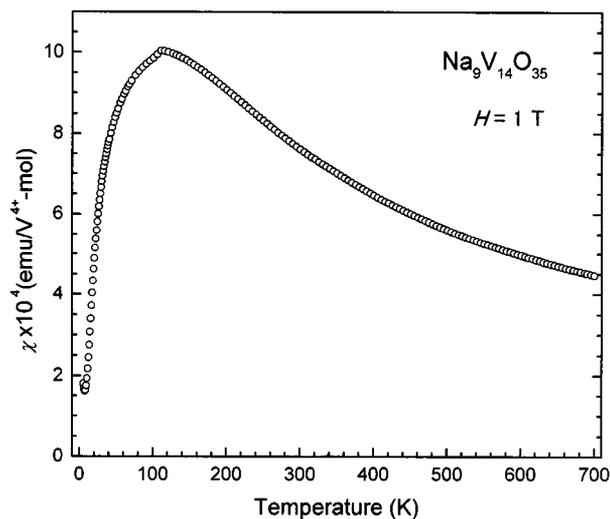


FIG. 2. Magnetic susceptibility of Na₉V₁₄O₃₅ measured in a field of 1 T.

theoretical equations for a spin-ladder or a dimer system. Moreover the structure, especially the geometrical arrangement of magnetic V^{4+} ions, is related to none of the above systems. It is noted here that our preliminary low-temperature powder X-ray diffraction study has detected no sign of structural transition down to 10 K. Consequently $Na_9V_{14}O_{35}$ is regarded as a new type of low-dimensional system. It is presumed from the intralayer structure that V(1), V(2), V(3), V(5), and V(6) can form a spin-singlet state in the zigzag chain because even numbers of magnetic V^{4+} ions (d^1 , $S = \frac{1}{2}$) are included in the chain. However, somewhat special consideration should be paid to the electronic state of V(5) atom with the valence of 4.5. Statistical distribution of V^{4+} over V(5) sites must produce finite magnetic susceptibility originated from free spins, which is expected to obey the Curie-(Weiss) law. Instead distributions of $V^{4+}-V^{4+}$ and $V^{5+}-V^{5+}$ pairs on V(5) sites should be taken into account to explain the spin-gap behavior. Though we have no idea of the spin-gap mechanism of $Na_9V_{14}O_{35}$ at present, it is said that $Na_9V_{14}O_{35}$ is a new type of spin-gap system.

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