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Synthesis and X-ray diffraction study of graphite intercalation compounds with multilayered metallic packages

I. A. Udod, M. V. Gnatenko and S. P. Sirotinkin
Moscow State University, Department of Chemistry, 119899 Moscow, (Russia)

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Abstract

New quaternary graphite intercalation compounds (GICs) were synthesized by intercalation of lithium and sodium into ternary potassium–mercury GICs. X-ray diffraction showed that quaternary compounds have five-layer structures Li–K–Hg–K–Li (in the case of lithium) and K–Hg–Na–Hg–K (in the case of sodium). The compounds were synthesized under non-equilibrium conditions.

The interaction of ternary potassium–sodium–mercury alloys with graphite was investigated. The thermodynamical approach suggested shows that the third component of the alloy (in this case mercury) can determine the method of intercalation of binary alkali metal alloys in graphite. Moreover, a quaternary GIC with a five-layer structure of intercalant was synthesized by direct interaction of potassium–sodium–mercury alloy with graphite under equilibrium conditions.

1. Introduction

Binary alkali metal alloy and graphite intercalation compounds (GICs) obtained by the usual (from gaseous or liquid phase) technique have a monolayer structure of intercalant [1–3]. The large values of negative volume effects of intercalation of alkali metals in graphite, and the low values of average compressibilities of the GICs, show that the graphite matrix strongly "compresses" the metallic layer [4, 5].

The interaction of some binary alloys (heavy alkali metal and d^{10} metal) and alkali metal hydrides with graphite produces ternary GICs with a multilayer structure of intercalant [6, 7]. In this case the influence of the graphite matrix is essentially small [8]. Thus, these GICs partially keep the properties of the initial intermetallic compounds.

In the present work different methods of synthesis of GICs with multilayered metallic packages and their chemical properties in the unusual two-dimensional state are discussed.

2. Experimental details

Highly oriented pyrolitic graphite with a disorientation angle along the *c*-axis of about 1° in the form of quasi-single-crystal plates was used. During

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intercalation into graphite powder, thermodynamic equilibrium was established very rapidly and intermediate compounds were not formed.

The chemical reactions took place at the intimate contact of the lamellar phase (initial graphite or GIC) with the melting metallic phase. It is therefore necessary to underline a peculiarity of the liquid phase reaction: the sample contains a minimum of three phases after the final reaction (free metal phase, alloy in the intercrystalline fields and strictly GIC). The free metallic surplus can be separated by a mechanical method, but it is very difficult to eliminate the alloy in the intercrystalline fields. Thus really we have two-phase samples.

This fact limits the application of chemical analysis in the investigation of new compounds. Chemical analysis was considered only as a qualitative and approximate method.

In a reflection survey of the plates of GICs, the 001 intensities of the layered phase are found to be some orders higher than the possible intensities from the highly dispersive metallic admixture. So X-ray analysis of GICs is a useful technique not only for the identification of known phases, but also for investigation of the structures of new compounds.

The X-ray study of the new compounds synthesized was carried out in three steps.

(1) The reflection survey allows us to obtain the family of 001 lines. The value of the identity period I_c is characteristic of the GICs and may indicate the novelty of the studied compounds. The identity period I_c is connected with the interplanar distance d_i and the number of stages s by the following expression [9]:

$$I_c = d_i + (n-1)3.35 \tag{1}$$

where the stage number is understood to mean the number of graphite layers separating the intercalant layers. The stage number and the order of alternation of layers along the c axis was determined from a study of the 001 intensities. Experimental values of the structure factors $|F_{001}^{\text{exp}}|$ were calculated from the following expression [10]:

$$|F_{001}^{\text{exp}}| = \left(\frac{I_{001}^{\text{exp}}}{KLPA}\right)^{1/2} \tag{2}$$

I_{001}^{exp} is the value of the integrated intensity of the 001 line, K is a scale factor, L, P and A are angle-dependent Lorenz, polarization and absorption factors respectively. The Debye–Waller temperature factor was neglected. The central symmetry of layered packages was assumed [11]. So in this case we have the following correlation:

$$F_{001} = \sum_{j=1}^{m} N_j f_j \cos(2\pi l z_j) \tag{3}$$

where m is the number of planes in the cell, f_j is the atomic scattering factor, N_j is the atomic density and z_j is the position of the atomic layer. The intensity of the 001 line is usually distorted, so it was not used in the calculations. The reliability of the model used was estimated by the residual index R_f:

$$R_f = \frac{\sum_l \left| |F^{exp}_{001}| - |F^{cal}_{001}| \right|}{\sum_l |F^{exp}_{001}|} \tag{4}$$

The c-axis charge density ρ_z can be calculated from the Fourier transform of the structure factors as calculated F^{cal}_{001}, or experimental $|F^{exp}_{001}|$ [11]:

$$\rho_z = \frac{1}{I_c} \sum_l F_{001} \cos\left(\frac{2\pi l z}{I_c}\right) \tag{5}$$

In the latter case the magnitude $|F^{exp}_{001}|$ is determined directly from the data I^{exp}_{001}, but the sign must be extracted from a structural model.

(2) The family of $hk0$ lines can be obtained from a transmission survey on the plates of GICs. It allows us to determine the parameters of the two-dimensional sub-lattice, as a rule epitaxed with the initial graphite matrix. A similar approach was widely used for investigating ternary GICs with multilayer intercalant structure [12–15]. However, in some cases it is necessary to correlate the data obtained from 001 and $hk0$ analyses.

(3) To determine the coordinates of every atom, correct data for all hkl families should be obtained. However, single crystals of the GICs investigated were not synthesized, so the closest ball package of metal atoms was assumed for estimation of interatomic distances.

3. Results and discussion

It was established earlier [16], that the interaction of ternary potassium–mercury GICs with alkali metals under hard conditions led to the decomposition of the initial three-layer package of intercalant. In fact, the increase in alkali metal concentration in the intercrystalline fields displaces the chemical equilibrium to form GICs with monolayer intercalant [6]. However, the formation of intermediate compounds was observed on (C_4KHg + Li, Na) and (C_8KHg + Na) systems by X-ray analysis. The rise in intensity of 001 lines of the new GIC with larger interplanar distance was followed by a decrease in quantity of alkali metal (a decrease in alkali metal melting peak square on DTA curves). This proves that the intercalation of lithium or sodium into the potassium–mercury matrix took place. It is difficult to obtain new quaternary compounds in a pure phase since the process depends on several parameters such as synthesis temperature, length of interaction time, type of graphite, etc. A decrease in synthesis temperature and control of the length of reaction time were needed for essential separation of two processes: the relatively fast intercalation of alkali metals into the potassium–mercury GIC from the slower decomposition of new compounds. Immediate contact of the solid phase with the melting metal evidently promoted decomposition, which is why quaternary compounds on powder of C_4KHg and C_8KHg have not been obtained. However, in the case of quasi-single-crystal plates we succeeded in isolating new quaternary compounds C_4KLi_xHg, C_4KNa_xHg and C_8KNa_xHg. The absence of admixtural traces on X-ray diffractograms of the new GICs allowed us to analyse the 001 intensities (Fig. 1).

Lagrange *et al.* [17] established using X-ray analysis that the layered package in C_4KHg and C_8KHg consists of two superimposed potassium layers, which are in octal epitaxy with respect to adjacent carbon layers. Potassium atoms build triangular prismatic sites, which are entirely occupied by mercury atoms. An insignificant shift of mercury atoms from the medium plane of the layered package was also assumed (Fig. 2).

An increase in interplanar distance from 10.20 Å to 10.80 Å was observed in the case of lithium intercalation in C_4KHg. The Fourier transforms of the 001 structure factors showed that the initial KHg fragment did not change,

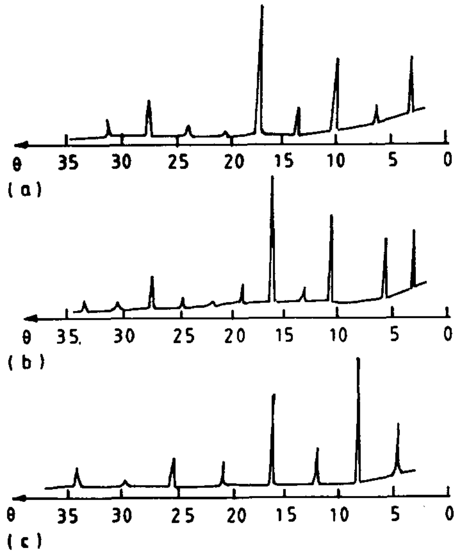


Fig. 1. 001 diffraction patterns of (a) C_4KNa_xHg (1st stage), (b) C_8KNa_xHg (2nd stage), and (c) C_4KLi_xHg (1st stage); emission of Cu $K\alpha$.

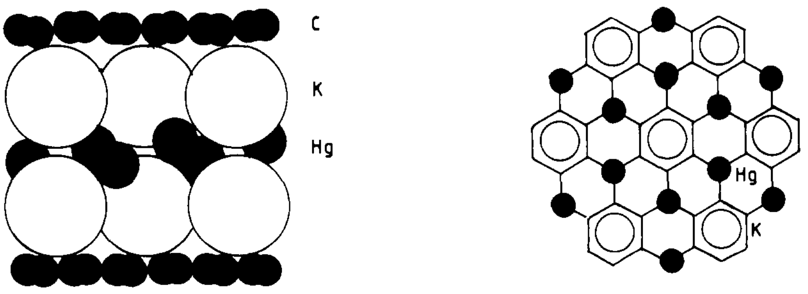


Fig. 2. Structure of initial C_4KHg [17].

but the distance between the potassium and carbon layers increased (Fig. 3). *hk*0 lines were identified by the supposition of a planar hexagonal sublattice with $a = 4.95$ Å, the lack of change of the KHg fragment was thus confirmed. The residual index for the suggested package Li–K–Hg–K–Li, R_f is equal to 0.058, the chemical formula is C_4KLiHg.

The quaternary GIC C_4KLiHg oxidized rapidly in air, 001 lines of initial C_4KHg appeared simultaneously with the disappearance of quaternary GIC 001 lines. The high mobility of lithium atoms can be explained from the suggested model. Lithium atoms contact with graphite and with potassium layers. The intercalation of one lithium layer into graphite enlarged the interplanar distance to 0.35 Å [9] and, in this case, the intercalation of two lithium layers enlarged the interplanar distance to 0.60 Å.

The Fourier transforms of the 001 structure factors for the first stage sodium quaternary compound showed that the initial crimped mercury layer broke into two layers and the sodium layer was placed between them (Fig. 4). The residual index in this case is $R_f = 0.071$, and the chemical formula is $C_4KNa_{0.5}Hg$. The shortest interatomic distances for the suggested model (assuming closest ball package of metal atoms) and also those for C_4KHg and $NaHg_2$ are given in Table 1. In contrast to quaternary lithium GIC, in this case potassium and sodium layers immediately contact with mercury layers in the five-layer package K–Hg–Na–Hg–K. That is why the chemical stability of the last compounds in air is close to that of the initial potassium–mercury GIC: 001 lines of the binary GIC C_8K disappear completely after several minutes, while 001 lines of C_4KHg and $C_4KNa_{0.5}Hg$ were observed during one day and longer.

For quaternary GICs $C_8KNa_{0.5}Hg$ (second stage), Fourier transforms of 001 structure factors ($R_f = 0.0102$) showed a five-layer package K–Hg–Na–Hg–K, as for the first-stage compound. Thus, intercalation of sodium in empty interplanar space in graphite under usual conditions is very difficult, unlike lithium [16].

The interaction of C_4RbHg with sodium also began with an increase in interplanar distance of $13.83 - 10.79 = 3.04$ Å. However, because the metallic

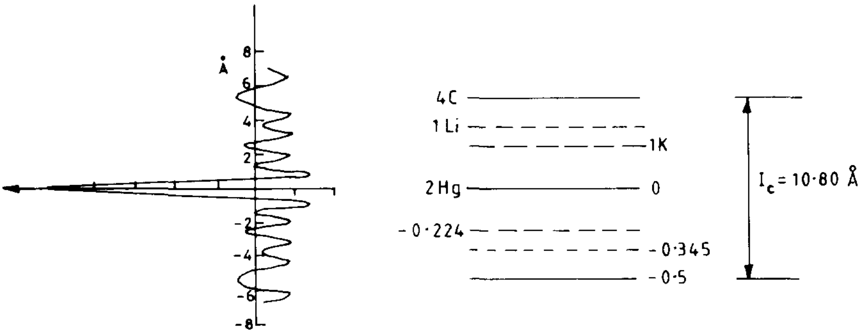


Fig. 3. Quaternary potassium–lithium–mercury GIC. Fourier transform of the 001 structure factors (– – – calculated, —— experimental). Model for the intercalated metallic package.

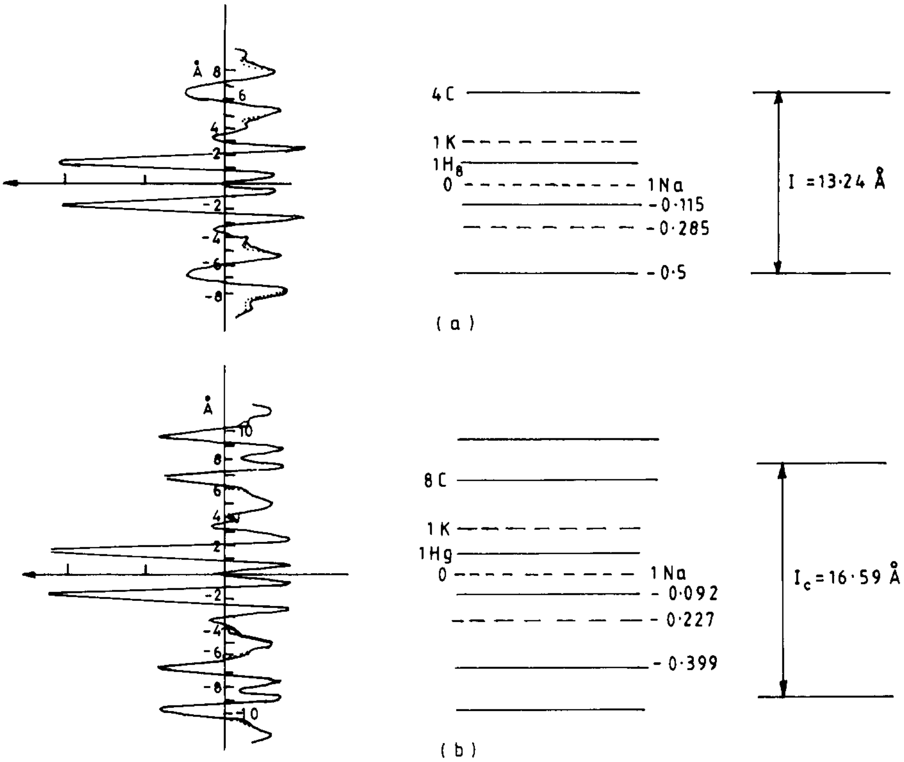


Fig. 4. Quaternary potassium–sodium–mercury GICs. Fourier transform of the 001 structure factors (– – – calculated, —— experimental). Model for the intercalated metallic package, (a) first stage and (b) second stage.

TABLE 1

Comparison of the shortest distances in $C_4KNa_{0.5}Hg$, C_4KHg and $NaHg_2$

Type of bond	Substance	Bond length (Å)
K–Hg	C_4KHg	3.53
K–Hg	$C_4KNa_{0.5}Hg$	3.62
Na–Hg	$NaHg_2$	3.30
Na–Hg	$C_4KNa_{0.5}Hg$	3.22

package Rb–Hg–Na–Hg–Rb is less stable, the quaternary compound was not isolated. The stability decreases because rubidium possesses (unlike potassium) stronger affinity to graphite and a weaker affinity to mercury, in comparison with potassium.

The quaternary compounds described above were synthesized under non-equilibrium conditions. It would be interesting to perform these reactions where the quaternary sodium first-stage GIC, for example, was the final product. For this purpose the interaction of potassium–sodium–mercury alloys of different compositions with graphite was investigated.

To continue the investigation of the C–K–Na–Hg system, it would be useful to consider the mechanism of interaction of alloys and hydrides with graphite more carefully. These chemical reactions may be conditionally divided into two processes: real intercalation of atoms into interplanar spaces of graphite and filling of the intercrystalline fields by alloy. As a rule the second process is slower. The first step of the reaction is non-equilibrium and may be characterized as a quasi-gas phase step (single particles in the intercrystalline fields), as a rule binary GICs of alkali metals are formed at this step [6]. As the intercrystalline fields become filled, the next chain of chemical equilibria begins to proceed:

$$\text{free alloy} \rightleftharpoons \text{alloy in the intercrystalline fields} \rightleftharpoons \text{alloy in GIC} \qquad (6)$$

Thus, the second step is a liquid phase step. Using this model, the formation of intermediate compounds in our case as well as peculiarities in the behaviour of sodium hydride and Cs–As, Cs–Sb alloys in relation to graphite may be explained [18, 19].

In Table 2 equilibrium products of reactions of graphite with potassium–sodium–mercury alloys of different compositions are gathered. Reactions were performed as follows: graphite with a large excess of ternary alloy of well defined composition was kept for several days at a temperature of 250–300 °C in glass tubes sealed under vacuum. Only the relative quantity of mercury was changed in the initial alloys (relation of potassium to sodium was unity).

When the mercury content was insignificant the formation of a ternary potassium–sodium GIC with monolayer structure of intercalant was observed. Similar compounds of variable composition $C_8K_xNa_{1-x}$ can be synthesized by direct interaction of K–Na alloys with graphite, the interplanar distance d_i depending on x [20]. From the data of ref. 20, $d_i = 5.20–5.24$ Å in our case corresponds to the composition $C_8K_xNa_{1-x}$, $x = 0.7–0.75$.

An increase in mercury concentration in the ternary alloy increases its enthalpy and results in the formation of a thermodynamically more stable GIC, according to eqn. (6). This may be achieved by the substitution of sodium for potassium forming binary GIC C_8K (Table 2). It should be noted

TABLE 2

The dependence of equilibrium GICs on composition of K–Na–Hg alloys

N	Initial alloy	Colour	I_c (Å)	Number stage	a (Å)	GIC
1	$KNaHg_{0.25}$	Yellow	5.20–5.24	1	4.95	$C_8K_xNa_{1-x}$
2	$KNaHg_{0.5}$	Yellow	5.40	1	4.95	C_8K
3	KNaHg	Red	8.45–8.50	1	4.95	$C_4K_xNa_{1-x}$
4	$KNaHg_2$	Grey–yellow	13.18–13.20	1	4.95	$C_4KNa_{0.5}Hg$

that the substitution of atoms in the layer is too slow because of dimensional obstacles. So the enthalpy of the GIC may increase in this case by increasing the number of metallic layers in the interlayer spacing of graphite. We succeeded in synthesizing a GIC of red colour with identity period $I_c = 8.45$–8.50 Å; the 001 lines and *hk*0 lines are shown in Fig. 5. The lack of change of the parameter $a = 4.95$ Å of the planar hexagonal sublattice shows the octal structure of the metallic layer, as for C_8K.

Fourier transforms of the 001 structure factors (Fig. 6) show that the last compound is the first stage compound with a two-layer structure of intercalant. Chemical analysis showed that the mercury content in the plate was less than 5%, and so testified that mercury was contained in the

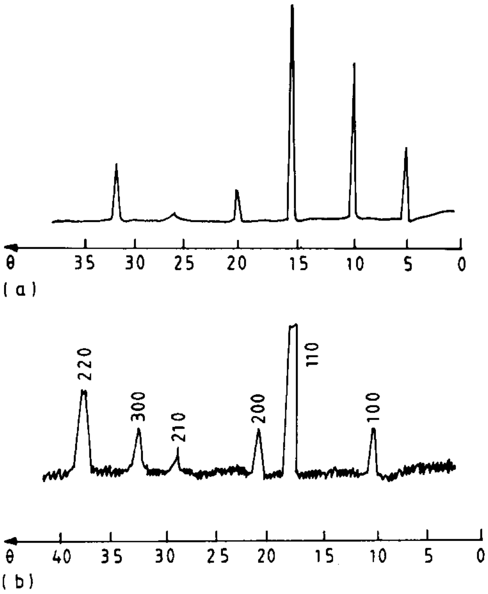


Fig. 5. (a) 001 and (b) *hk*0 diffraction patterns of ternary potassium–sodium GIC of first stage; emission of Cu Kα.

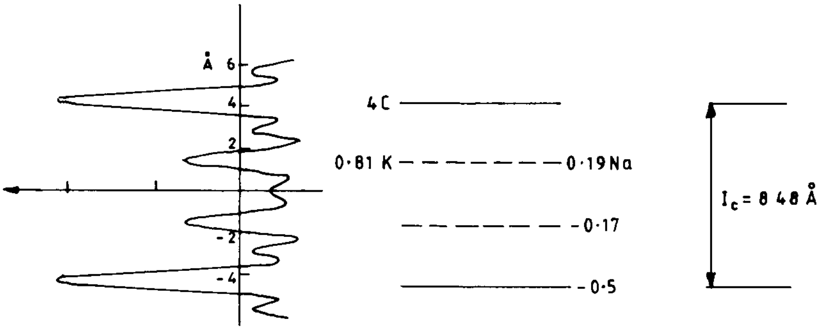
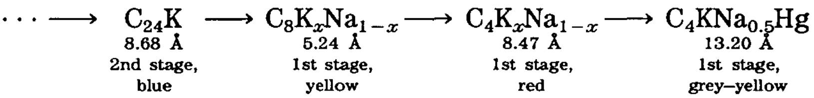


Fig. 6. Ternary potassium–sodium GIC. Fourier transform of the 001 structure factors (– – – calculated, —— experimental). Model for the intercalated metallic package.

intercrystalline alloy only. Thus, for the first time we succeeded in synthesizing a ternary GIC of potassium and sodium of the first stage with a two-layer package of intercalant. The composition of the metallic layer in $C_4K_xNa_{1-x}$ fluctuated from 0.75 to 0.82 (for potassium) from the Fourier transform data ($R_f = 0.07\text{–}0.08$).

This compound looks like the binary GIC of sodium ($d_i = 7.99\text{–}8.03$ Å), synthesized under high pressure and possessing the two-layer structure of intercalant [21].

The alloy with composition $KNaHg_2$ reacts with graphite (at a temperature of 350–370 °C) according to the following:



$$\cdots \longrightarrow \underset{\substack{8.68\ \text{Å}\\ \text{2nd stage,}\\ \text{blue}}}{C_{24}K} \longrightarrow \underset{\substack{5.24\ \text{Å}\\ \text{1st stage,}\\ \text{yellow}}}{C_8K_xNa_{1-x}} \longrightarrow \underset{\substack{8.47\ \text{Å}\\ \text{1st stage,}\\ \text{red}}}{C_4K_xNa_{1-x}} \longrightarrow \underset{\substack{13.20\ \text{Å}\\ \text{1st stage,}\\ \text{grey–yellow}}}{C_4KNa_{0.5}Hg}$$

The final product in this case is a quaternary potassium–sodium–mercury GIC of the first stage with interplanar distance $d_i = 13.18\text{–}13.24$ Å, similar to the GICs formed by sodium intercalation in C_4KHg. The quaternary GIC obtained by the interaction of the ternary alloy with graphite may contain admixtural sodium in potassium layers and admixtural potassium in sodium layers. This explains the narrowness of the 001 lines, observed on X-ray diffractograms.

4. Conclusions

(1) Sodium and lithium intercalations in a potassium–mercury matrix, as well as their interaction with graphite are distinct. A quaternary potassium–lithium–mercury GIC of the first stage has a five-layer package Li–K–Hg–K–Li with a very mobile lithium layer. A quaternary potassium–sodium–mercury GIC of the first and second stages has a five-layer package K–Hg–Na–Hg–K and is considerably more stable at air.

(2) The final equilibrium product of the interaction of graphite with potassium–sodium–mercury alloys depends on the mercury content. When the mercury content is small a GIC with monolayer intercalant is formed. The increase in mercury content in the ternary alloy leads to the formation of the ternary potassium–sodium GIC of the first stage with two-layer structure of intercalant. The thermodynamical approach suggested shows that the third component of the alloy (in this case mercury) can determine the method of well known intercalation of binary alkali metal alloys in graphite. Moreover, we succeeded in synthesizing a quaternary GIC with five-layer structure of intercalant by the direct interaction of potassium–sodium–mercury alloy with graphite under equilibrium conditions.

It should be noted that the formation of the well known KHg package at the interaction of ternary potassium–sodium–mercury alloys with graphite was not observed.

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