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THE ROLE OF ARSENIC IN THE IRREVERSIBLE PHOTOINDUCED TRANSFORMATIONS IN VACUUM DEPOSITED a-As_xS_{100-x} THIN FILMS[♣]

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The results from our recent studies on the optical changes induced by unpolarized and linearly polarized light in vacuum deposited a-As_xS_{100-x} ($15 \leq x \leq 42$) amorphous thin films are summarized. The observed compositional trend of the photoinduced changes in the optical constants of as-deposited samples with different As/S ratio is compared with their photographic behaviour, investigated previously. On this basis the active role of As atoms during the irreversible photostructural transformations in arsenic sulphide films is emphasized. Thus, new experimental evidence for the validity of the so-called light induced phase separation model in arsenic chalcogenides has been obtained. Further, the kinetics of photodarkening and photoinduced dichroism in the a-As_xS_{100-x} films studied is simultaneously followed and the existence of similar regularities in the compositional dependences of the both effects is established. On this ground the possibility to describe the mechanism of photoinduced scalar and vectorial effects in arsenic chalcogenides by one and the same model is discussed.

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1. Introduction

During the past four decades thin films of amorphous chalcogenide glasses have been a subject of intensive investigations from fundamental point of view and potential applications as well [1]. Basic research has been focused on the problems of glass forming ability, order-disorder, intrinsic defects and mainly on the phenomenon of the so-called "photostructural changes". As known, the latter include various irreversible and reversible on annealing near the glass transition temperature changes in the physical and chemical properties of glasses upon actinic irradiation [2]. As a rule, these photoinduced changes are invariably accompanied by the scalar effects of photodarkenig or photobleaching, which are manifested as absorption edge shift towards lower or higher energies, respectively [3]. When the exposure is performed with linearly polarized light, simultaneously with the photodarkening/photobleaching the so-called vector effects of photoinduced birefringence and dichroism also occur [4]. At present, the nature of these various photoinduced transformations remain still not quite clear, although numerous experimental studies were performed, so that the mechanism of the phenomena keeps on challenging a great number of scientists.

Up to now, a variety of models for the mechanism of photostructural changes in chalcogenide glasses have been published in the literature. The common feature of the most models is the assumption that the origins of irreversible and reversible changes are different [5]. The same

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opinion prevails also about the mechanism of photoinduced scalar and vectorial effects [6]. Simultaneously, in some models it is believed that the nature of the different kinds of photostructural changes is one and same [7,8]. One of these models supposes the existence of a similarity between the mechanism of photoinduced transformations in arsenic chalcogenides and the primary photographic process in silver halides [7]. On this basis it is assumed that the photodarkening effect, which invariably occurs in arsenic chalcogenides, is due to the nucleation and growth of arsenic clusters during irradiation. The reversibility of the induced changes upon heating is attributed to a thermal decomposition of the clusters and back bonding of As atoms into amorphous network. In comparison with the other models this hypothesis supplies the most reliable explanation of the photodarkenig phenomenon since it is evident that the formation of a new phase of metal As would undoubtedly lead to an enlargement of the absorption spectral region towards longer wavelengths. The formation of As_2O_3 crystallites on the surface of heavily exposed to light of As_2S_3 and As_2Se_3 films is regarded as a first experimental evidence for the validity of the model [7]. Later, it was found that the extent of photodarkening in As_xSe_{100-x} films increases with the As content [9]. In addition, this so-called light induced phase separation model is supported by the established density increase of the As-As and S-S bonds in illuminated As_2S_3 films [10,11]. However there was not any experimental evidence confirming the formation of As clusters in the early illumination stages of arsenic chalcogenide films.

Having in mind the valuable experience of silver halide photography in visualization of very small silver clusters, formed on illumination and called latent image, by photographic development [12], in the recent years we applied the same approach for a verification of the model for light induced phase separation in as-deposited thin films from the As-S system. We established that in a narrow exposure interval, a-As_2S_3 films show a negative photographic response, which confirmed the formation of a developable latent image under the action of light [13]. On the basis of a simulation of the light induced changes by vacuum deposition of metal As on the surface of the films, followed by physical photographic development we concluded that the latent image is built up by As atoms. This conclusion was further supported by the observed strong influence of the As content on the efficiency of the photographic process in a-As_xS_{100-x} films [14]. Thus, the photographic experiments performed supplied new experimental evidence for the active role of As atoms during the action of light and, therefore, for the validity of the light induced phase separation model.

As a next step in our investigations on the role of As during the photostructural transformations in the As-S system studied, the photoinduced changes in the optical properties of as-deposited a-As_xS_{100-x} thin films were followed [15,16]. Besides, attention was also paid to the microstructure of samples with different As/S ratio [17], since it is well known that the thin film growth morphology may influence substantially the occurrence of the irreversible photostructural changes [18]. In the present work the results from these studies are summarized and discussed in terms of the contemporary ideas for the mechanism of the photostructural phenomena in arsenic chalcogenides.

2. Experimental details

The experiments were performed with as-deposited thin films obtained by thermal evaporation of synthesized As_xS_{100-x} ($15 \le x \le 42$) compounds onto planetary rotating substrates in a standard high-vacuum unit maintaining 5×10^{-4} Pa residual pressure. A resistively heated Ta crucible with a special design [19] was used as an evaporation source. It allowed the sublimation and evaporation of the bulk material without local overheating, thus preventing non-desirable effects of thermal decomposition. The substrates used were BK-7 optical glass plates, the latter exhibiting a negligible absorption in the visible and near IR wavelength region. The deposition rate was about 0.3 nm/s and the thickness of the films was between 100 and 1500 nm. The microstructure of the samples was inspected under a TEM microscope JEOL, JEM 100 B.

The photoinduced changes in the optical constants were followed in As-S films with thickness and composition similar to that of the samples used in the photographic experiments. For the purpose 100 nm a-As_xS_{100-x} ($29 \le x \le 42$) films were illuminated till saturation by a 200 W mercury lamp having light intensity on the specimen surface 25 mW/cm^2. The transmission and reflection spectra of as-deposited and illuminated samples were recorded by a high-precision Cary 5E spectrophotometer in the wavelength region 400-1300 nm. On their basis the optical constants and physical thickness of the films were determined using the Marquardt - Levenberg method for non-linear minimization as well as the more flexible and refined Simplex method [20]. Because of the small film thickness ($d \le 100$ nm $\le \lambda/5$) the goal function was defined as a cumulative product of experimental data vector elements. The uncertainties of the optical parameters are sufficiently low, for instance Δn, $\Delta d \approx 1\%$.

The optical changes induced by linearly polarized light were followed in a-As_xS_{100-x} ($15 \le x \le 42$) films with thickness 1500 nm. The kinetics of photodarkening and photoinduced anisotropy was studied by a computerised polarimetric system [21], which measures the Stokes parameters of light in real time. On this basis the change in the average optical density, which is a measure for the photodarkenig and photoinduced dichroism are evaluated simultaneously. Optical irradiation was performed using an Ar$^+$ laser (λ = 488 nm) with light intensity on the film surface 33 mW/cm^2. The kinetics of photoinduced effects, both vectorial and scalar, was monitored by a probe Ar$^+$ laser beam with very low intensity.

3. Results and discussion

Fig. 1 presents TEM micrographs of Pt/C replicas from the surface of 100 nm a-As_xS_{100-x} ($29 \le x \le 45$) films deposited on glass substrates [17]. The SAD patterns show that the films are amorphous between x = 29 and 40 at. % As, while the $As_{45}S_{55}$ sample is polycrystalline. This result is not surprising having in mind that the glass forming region in the As-S system is between 5 and 43 at. % As [22]. Besides, it is seen that all samples studied are characterized by a granular surface morphology as it has been already demonstrated for films with stoichiometric As/S ratio in our previous investigations [23]. Simultaneously, the micrographs in Fig. 1 show that the grain size is slightly influenced by the As content which gives the reason to expect that the photoresponse of As_xS_{100-x} films will be mainly governed by the composition. This was an important prerequisite to perform further experiments on studying the optical behaviour of As_xS_{100-x} thin films during their interaction with actinic light [16].

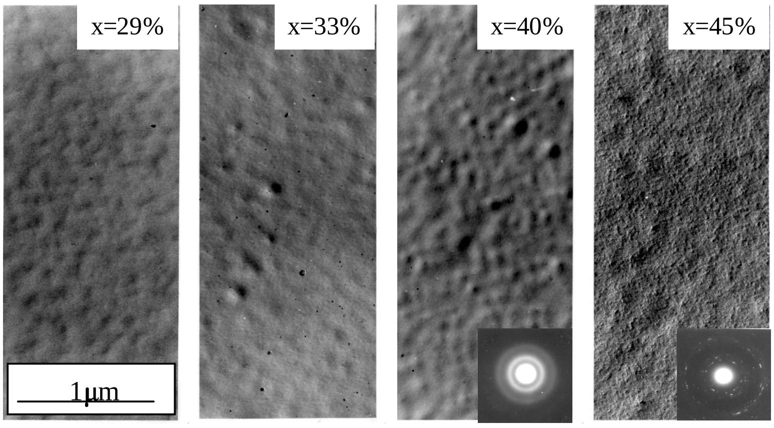

Fig. 1. TEM micrographs of Pt/C replicas from the surface of 100 nm As_xS_{100-x} films deposited on glass substrates.

Fig. 2 shows the dependence of the refractive indices n for 100 nm as-deposited and illuminated till saturation a-As_xS_{100-x} films on the As content, at λ = 633 nm. As can be seen from the figure n increases with the quantity of As and has the maximal value for the film with the stoichiometric As/S ratio. Besides, in all samples studied the refractive indices increase as a result of illumination. The results presented in Fig. 2 are in agreement with numerous published data on the optical properties and their photoinduced changes of evaporated as-deposited [24] and annealed films with higher thickness [25]. The dependence of the light induced refractive index change *Δn* on the composition of the films studied is shown in Fig. 3. It is clearly seen that *Δn* increases with the amount of As and reaches a maximum value in the film with the highest As content. Thus, one more experimental confirmation for the active role of As atoms in the scalar effect of photorefraction, observed invariably in arsenic chalcogenides [9], was obtained.

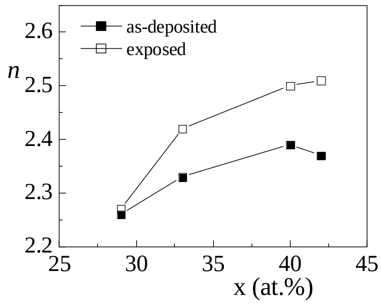

Fig. 2. Dependence of refractive indices *n* of 100 nm as-deposited and exposed a-As_xS_{100-x} films on the As content, at λ=633 nm.

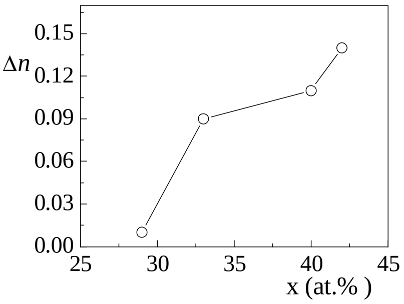

Fig. 3. Dependence of photoinduced refractive index change *Δn* in a-As_xS_{100-x} films on the As content, at λ=633 nm.

On the other hand it should be reminded here that similar trend was observed in the compositional dependence of the photographic response of the same a-As_xS_{100-x} films, although in a narrow interval between x = 29 and 40 at. % As [14]. Therefore, it can be concluded that there is a correlation between the influences of As content on the irreversible light induced changes in the optical properties of a-As_xS_{100-x} films and their photographic behavior, at least in the range $29 \leq x \leq 40$.

Further, in order to obtain some information about the photoinduced structural transformations in the studied samples the refractive index dispersions of exposed and unexposed a-As_xS_{100-x} were fitted by the Wemple-Didomenico [26] relation:

$$n^2 = 1 + \left(E_d E_0 \big/ (E_0^2 - (\hbar\omega)^2) \right), \tag{1}$$

where $(\hbar\omega)$ is the photon energy and E_0 and E_d are single oscillator fitting constants that measure the oscillator energy and strength, respectively. By plotting $(n^2–1)^{-1}$ against $(\hbar\omega)^2$ and fitting a straight line, E_d and E_0 were determined for all non-illuminated and illuminated As-S films. A special attention was given to the dispersion energy E_d, whose variation is assumed [25] to be due to the change of nearest neighbour atomic configurations. It has been pointed out that E_d obeys the simple empirical relation [26]:

$$E_d = \beta N_c Z_a N_e, \tag{2}$$

where β is a constant, N_c is the coordination number of the cation nearest neighbour of the anion, Z_a is the formal chemical valence of the anion and N_e is the total number of the valence electrons per anion.

Assuming that the change of E_d is primarily a coordination number effect [25], we calculated the effective As coordination number N_c^e in illuminated and non-illuminated a-As_xS_{100-x} films. It was established that N_c^e for all samples studied by us increases as a result of irradiation, which is obviously due to changes in the nearest atomic configurations and, therefore, to the bond transformations in the amorphous network. Taking into account the results from Raman [10] and IR

[11] spectroscopy of illuminated As_2S_3 films it can be supposed that part of the As-S bonds in the exposed samples are converted into As-As bonds. These transformations would lead to changes in the atomic configurations and most probably to the creation of some coordination defects. Having in mind the analysis of the possible combinations of defects associated with the formation of homopolar As-As bonds in arsenic chalcogenides [27] it can be supposed that the increase of the effective As coordination number is due to the formation of $As_4^+S_1^-$ defect pairs.

The dependence of photoinduced change of N_c^e on the As content in the As_xS_{100-x} films studied by us is shown in Fig. 4. The existence of two extrema at x = 33 and 40 at. % of As is clearly seen. The maximum value of ΔN_c^e in $As_{40}S_{60}$ film shows that the As-S bonds, which characterize the stoichiometric composition could play an important role in the photoinduced transformations.

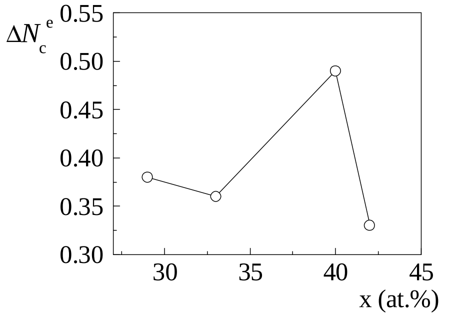

Fig. 4. Dependence of ΔN_c^e on the As content in 100 nm as-deposited As_xS_{100-x} films.

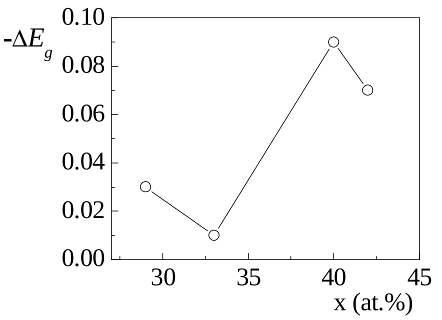

Fig. 5. Dependence of ΔE_g on the As content in 100 nm as-deposited As_xS_{100-x} films.

Simultaneously, the composition $As_{33}S_{67}$ is of a particular interest, because it appears as a characteristic point transition in many physical properties of As-S glassy system [28]. If we accept the Tanaka's idea that the homopolar S-S bonds, which do exist in S-rich samples together with the main As-S bonds, also play some role in the photostructural changes [25] it may be supposed that the minimum at x=33at. % is due to a change of the dominant type of bonds involved in the transformations. A speculation could be also made about some influence of the excess As-As bonds on the evaluated value of ΔN_c^e for $As_{42}S_{58}$ sample. These suggestions seem to be confirmed by the compositional dependence of photoinduced change in the optical band gap energy E_g, determined for all samples studied by using the Tauc's procedure [29], which is presented in fig. 5. As seen the reduction of E_g under the action of light is maximal for $As_{40}S_{60}$ film and is minimal for $As_{33}S_{67}$ one. According to the simple model of Yamaguchi [30] the photoinduced changes in E_g are determined mainly by the strength of the created bonds, which decreases in the row S-S, As-S, As-As. In terms of this approach the maximal value of ΔE_g for $As_{40}S_{60}$ films means that the number of the photo created As-As homopolar bonds is greatest at this composition. Simultaneously, from this point of view the smallest value of ΔE_g for $As_{33}S_{67}$ films sugests that the quantity of generated As-As bonds is minimal. However, the results from our photographic experiments show that these films are characterized by a considerable photographic response [14], which indicates that during irradiation As-As bonds must be created leading to the formation of developable As clusters. Obviously, the dependence of ΔE_g on the composition of a-As_xS_{100-x} films could not be explained only by the influence of the strength of the created homopolar bonds under the action of light. It can be supposed that some part in the E_g modification is due to the formation of the so-called "intimate" valence alteration defect pairs [2], which would lead to the creation of new localized states in the forbidden gap of arsenic sulfide.

Further, in order to study the role of As on the occurrence of both scalar and vectorial effects, the optical changes in 1500 nm As_xS_{100-x} ($15 \le x \le 42$), induced by linearly polarized light were followed [15]. Fig. 6 presents the kinetics of the scalar effect of photodarkening, expressed as a change of average optical density $\Delta D_{av} = (D_{II} + D_{\perp})/2$, for the stoichiometric a-$As_{40}S_{60}$ film. D_{II} and $D_{\perp}$ are the optical densities in parallel and perpendicular directions to the polarization plane of exciting Ar^+ beam, respectively. As seen from the figure the saturated value of the photodarkening in the stoichiometric film is about 0.4. Similar kinetic curves were recorded for other non-stoichiometric films, which showed the occurrence of photodarkening in all samples except for the film with composition $As_{15}S_{85}$ where a negligible photobleaching effect was observed. The dependence of the achieved saturated values of ΔD_{av} on the As content in the As-S films studied is shown in Fig. 7. As seen the increasing of the As quantity leads to a considerable change of the ΔD_{av} from -0.03 at x = 15 at. % to 0.8 at x = 42 at. %. As. Additionally, the analysis of the kinetic curves showed that the time for achieving the saturation level of ΔD_{av} diminishes significantly with increasing the As content in the films.

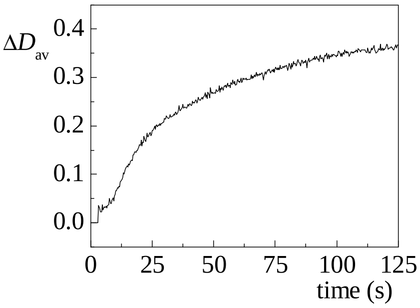

Fig. 6. Kinetics of ΔD_{av} of 1500 nm as-deposited a-$As_{40}S_{60}$ film.

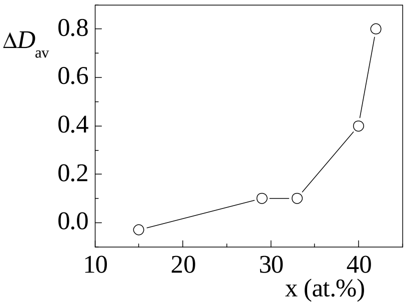

Fig. 7. Dependence of ΔD_{av} on the As content in 1500 nm as-deposited a-As_xS_{100-x} films.

Therefore, it can be concluded that the photoinduced transformations associated with the scalar effect of photodarkening proceed with a higher efficiency in As-rich samples. Thus, similar to some other literature data [9] the results obtained demonstrate the active role of As in the irreversible optical changes in arsenic chalcogenides.

Simultaneously, it is found that there is a difference between the intensity of the transmitted actinic light polarized parallel and perpendicular to the polarization of the pumped Ar^+ beam. Taking into account that the measurements are at a wavelength situated in the range of strong absorption of As_2S_3 and that there are practically no multiple reflections within the thin film, it can be assumed that the observed anisotropy is mainly due to the changes of absorption coefficient and can be regarded as a measure for the photoinduced dichroism.

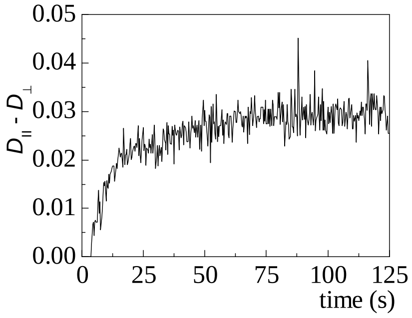

Fig. 8. Kinetics of photoinduced dichroism in 1500 nm as-deposited a-$As_{40}S_{60}$ film.

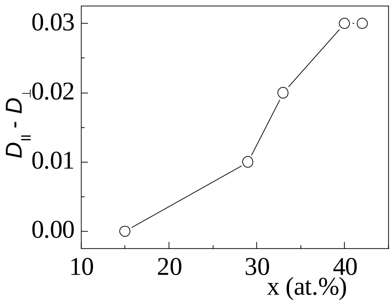

Fig. 9. Dependence of photoinduced dichroism on the As content in 1500 nm a-As_xS_{100-x} films.

The kinetics of this vectorial effect, expressed as (D_{II} -- $D_{\perp}$) for the stoichiometric $As_{40}S_{60}$ film is presented in Fig. 8. As seen, the saturated value of the dichroism is about 3×10^{-2}, which is one order of magnitude lower than the scalar effect of photodarkening, in agreement with literature data [6]. Similar kinetic curves were obtained for other samples of the As_xS_{100-x} system studied. The achieved saturation values of the photoinduced dichroism, as dependent on the As content in the films, are plotted in Fig. 9. As can be seen, this photoinduced vectorial effect is almost negligible in the samples with low As content and is practically measurable only in the As-rich films. On this basis some active role of As atoms in the production of optical anisotropy in arsenic sulphide can be assumed. This statement seems to be confirmed by the data obtained from the transmission spectra of samples with different As/S ratio, recorded in linearly polarised light before and after irradiation to saturation by the Ar^+ laser. From these spectra the differences between photoinduced absorption edge shift ($\Delta\lambda$) for light polarized in parallel and perpendicular direction to the induced optical axis at a given transmittance (T=10%) were determined. The data obtained are presented in Fig. 10 in dependence on the As content. As seen from the figure, the anisotropy in the photoinduced absorption edge shift is negative for films with low As content, practically zero for x = 33 at. % As and increases gradually to 4 nm for As-rich samples.

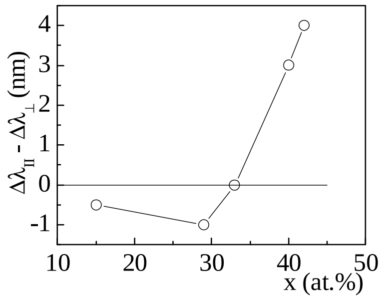

Fig. 10. Dependence of $\Delta\lambda_{/\!/}$ - $\Delta\lambda_{\perp}$ on the As content in 1500 nm a-As_xS_{100-x} films.

The results presented in Fig. 10 not only show the influence of As content on the value of $\Delta\lambda_{/\!/}$ - $\Delta\lambda_{\perp}$, but demonstrate once again the specific behaviour of the thin films with composition $As_{33}S_{67}$ at which the photoinduced anisotropy in the absorption edge shift changes its sign passing through zero. Therefore, it may be concluded that there are some similar regularities in the optical changes in As-S films studied, induced by unpolarized and linearly polarized light. On this basis the existence of a similarity in the nature of photoinduced scalar and vectorial effects in arsenic chalcogenides can be supposed. Moreover, in our opinion the results from the studies of photoinduced transformations in a-As_xS_{100-x} films by photographic and optical methods allow us to advance the hypothesis that the mechanism of both effects may be described by the model for light induced phase separation. The main grounds for this is the possibility for explanation of the photodarkening by the formation of As clusters and on the other hand the supposition that these clusters may play the role of the anisotropic crystalline structures [31] which suppose the occurrence of photoinduced dichroism during irradiation with linearly polarized light. Evidently, the expressed hypothesis requires further experimental confirmation.

4. Conclusions

The results summarized in the present work show that there is a correlation between the compositional trends of the irreversible photoinduced optical changes in vacuum deposited a-As_xS_{100-x} thin films and their photographic behavior, investigated previously. In this way the conclusion for the active role of As atoms during the interaction of arsenic sulfide with light, drawn on the basis of the photographic experiments receives one more confirmation. Moreover, the established similar regularities in the dependences of scalar end vector effects on the composition of films with different As/S ratio give the reason to suppose that As atoms play an essential role not only in the occurrence of the photodarkening but also in the photoinduced dichroism. On this basis a hypothesis is advanced, according to which, it is very probably the both types of photoinduced effects in arsenic chalcogenides obey one and the same mechanism.

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