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Interrelation of vibrational spectra of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ single crystals: A consequence of trivalent cation and anion substitutions

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ABSTRACT

Silver gallium (indium) ternary selenides (tellurides) single crystals were studied through infrared reflection in the frequency range of 80–500 cm^{-1}. These spectra presented four infrared-active modes for studied crystals. Spectral dependencies of optical constants were computed from reflectivity spectra. The frequencies of transverse and longitudinal optical modes, damping constants and oscillator strengths were also evaluated. By replacing light selenium anions by heavier tellurium ones in $Ag_3Ga_5Se_9$ crystal and by substitution of light gallium cations by heavier indium ones in $Ag_3Ga_5Te_9$ crystal all the bands shift towards low frequencies. The bands observed in IR spectra of studied crystals were assigned to various vibration types (valence and valence-deformation). Crystal structure and atomic composition ratio of the constituent elements in $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals were revealed by structural characterization techniques of X-ray diffraction and energy dispersive spectroscopy.

1. Introduction

$Ag_3B_5C_9$ ternary semiconductors, where B = Ga or In and C = Se or Te, have potentials as photo-absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells [1–5]. They are visible-light-active crystals with high-absorption coefficients, suitable band gaps, and easy conversion between *n*- and *p*-type carrier types which permits a variety of potentially low-cost homo- and hetero-junction [6–8].

$Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ compounds are the representatives of above-mentioned materials. The minute state diagrams of the $AgGaSe_2$–Ga_2Se_3, $AgGaTe_2$–Ga_2Te_3 and $AgInTe_2$–In_2Te_3 systems have been investigated in Refs. [9,10]. It has been found that at 25 mol % Ga_2Se_3, Ga_2Te_3 and In_2Te_3, the $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ compounds, melting congruently at 884, 720 and 710 °C, respectively, are formed.

The electrical and optical properties of $Ag_3Ga_5Se_9$ crystals have been studied in Ref. [11]. The band gap of $Ag_3Ga_5Se_9$ crystals deduced from the temperature dependence of conductivity and Hall effect was found to be 1.70 eV. The energy band gap for the direct optical transitions was established as 1.76 eV at $T = 300$ K, with the rate of direct band gap change with temperature of $\gamma = -3.2 \times 10^{-4}$ eV/K. The electrical resistivity and Hall mobility of $Ag_3Ga_5Te_9$ crystals were investigated in the temperature range of 65–480 K [10]. The value of conductivity at room temperature was identified as 4.3×10^{-4} $(\Omega\,cm)^{-1}$. The activation energies of impurity states 0.15, 0.26 and 0.63 eV were obtained from the dependence of conductivity on temperature. The room temperature mobility was found to be lower than 1 $cm^2/V\,s$. The optical and electrical properties of $Ag_3In_5Te_9$ crystals have been studied in Ref. [12]. The energy band gaps for the direct optical transitions were established as 0.96 and 1.01 eV at 300 and 77 K, respectively. IR reflectivity spectra, registered in 50–500 cm^{-1} frequency range for isostructural chalcogenide crystals $Ag_3Ga_5S_9$ and $Ag_3In_5S_9$ [13] and $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ [14] were reported recently. The inversion of LO- and TO-mode frequencies was revealed for latter two crystals.

Information about the spectral dependencies of optical parameters such as refractive index, dielectric constant, reflectivity and absorption coefficients, the frequencies of transverse and longitudinal phonons are essential in the characterization of materials that are used in the fabrication of optoelectronic devices. The present paper reports the results of the study of optical constants in silver gallium (indium) ternary selenides (tellurides) by infrared reflection method in the $80-500$ cm^{-1} frequency range.

2. Experimental details

$Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ polycrystals were synthesized in evacuated (10^{-5} Torr) quartz tubes using individual elements taken

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Fig. 1. The photograph of the $Ag_3In_5Te_9$, $Ag_3Ga_5Te_9$ and $Ag_3Ga_5Se_9$ grown crystals.

in stoichiometric proportions. The single crystals were grown by the Bridgman method in our crystal growth laboratory (Middle East Technical University). The resulting ingots appeared gray in color. Fig. 1 shows the photograph of the grown crystals.

To carry out the reflectivity measurements, the obtained ingots were cut and the surfaces produced were ground precisely. Before the reflectivity measurements, the samples were mechanically polished with 0.5 μm Al_2O_3 powder. IR reflection spectra of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals were registered in the frequency range between 80 and 500 cm^{-1} handling the diffraction IR spectrometers FIS-21 with a resolution of 1 cm^{-1}.

3. Results and discussion

The chemical compositions of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals were determined by energy dispersive spectroscopic analysis using JSM-6400 electron microscope. Fig. 2 shows the resulting spectra obtained from the measurements carried out in 0–10 keV energy range. Since every element has unique energy levels, each element produces characteristic X-rays that make it possible to determine the elemental composition of the sample by analyzing the spectra. The atomic compositions of the studied samples (Ag: Ga: Se), (Ag: Ga: Te) and (Ag: In: Te) were found to be 17.8: 29.6: 52.5, 18.0: 29.6: 52.4 and 17.7: 29.7: 52.6, respectively. The atomic weight ratios of the constituent elements in the crystals show slight changes from that of initial ratios (17.7: 29.4: 52.9) in the growth process. In the grown crystal, some deficiency occurs in the compositions of chalcogenes. The slight deficiency of these elements in the grown crystals can be explained with the higher

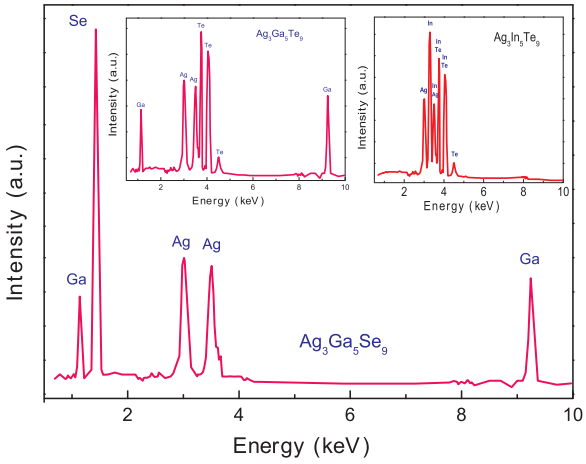

Fig. 2. Energy dispersive spectroscopic analysis of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals.

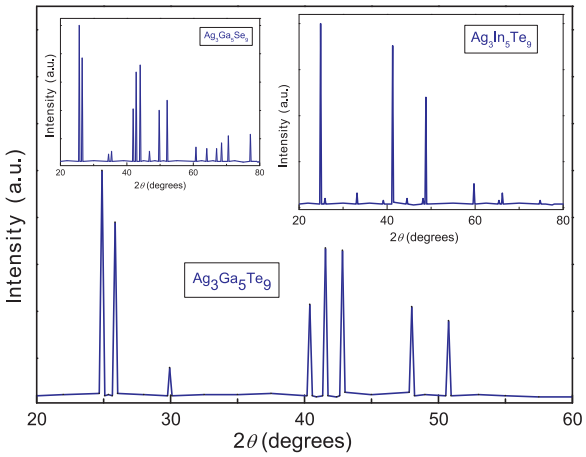

Fig. 3. X-ray diffraction patterns of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals.

volatility of them as compared to the silver, gallium and indium.

XRD technique was used to obtain the structural parameters of the $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals. The crystal system and lattice parameters were evaluated using a least-squares computer program "DICVOL 04". Fig. 3 presents the X-ray diffractograms of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals. The sharp diffraction peaks are the indication of the well crystallinity of the samples. The lattice parameters of the orthorhombic unit cells were found to be $a = 0.9767$, $b = 0.9225$, $c = 0.5257$ nm and $a = 1.594$, $b = 0.7164$, $c = 0.4512$ nm for $Ag_3Ga_5Se_9$ and $Ag_3Ga_5Te_9$, respectively, whereas $Ag_3In_5Te_9$ is crystallized in tetragonal structure with the parameters $a = 0.8738$ and $c = 0.7147$ nm. In ICSD database the lattice parameters are available only for $Ag_3Ga_5Te_9$ crystal (ICSD Card no.: 00-056-1284) [15]. Therefore, we could compare the lattice parameters of the evaluated ones and the ones in ICSD database only for $Ag_3Ga_5Te_9$ crystal, which are fairly well correlated with each other.

Fig. 4 demonstrates the IR reflectivity spectra of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals in the frequency range of 80–500 cm^{-1}. Four IR-active optical modes were observed in the spectra. By replacing light selenium anions by heavier tellurium ones in $Ag_3Ga_5Se_9$ crystal, all the bands of $Ag_3Ga_5Te_9$ crystal shift towards low frequencies compared with $Ag_3Ga_5Se_9$ crystal. Accordingly, the substitution of light gallium cations by heavier indium ones in $Ag_3Ga_5Te_9$ crystal also results in shifting the bands of $Ag_3In_5Te_9$ crystal to low frequencies relatively to $Ag_3Ga_5Te_9$ crystal.

The analysis of reflectivity (R) was carried out employing the coming next dispersion relations [16]:

$$\varepsilon_1 = \varepsilon_\infty + \sum_{i=1}^{4} \frac{S_i \nu_{Ti}^2 (\nu_{Ti}^2 - \nu^2)}{(\nu_{Ti}^2 - \nu^2)^2 + \gamma_i^2 \nu^2},$$

$$\varepsilon_2 = \sum_{i=1}^{4} \frac{S_i \nu_{Ti}^2 \nu \gamma_i}{(\nu_{Ti}^2 - \nu^2)^2 + \gamma_i^2 \nu^2},$$

$$R = \frac{(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} - \left(2\left((\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1\right)\right)^{\frac{1}{2}} + 1}{(\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \left(2\left((\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}} + \varepsilon_1\right)\right)^{\frac{1}{2}} + 1}.$$

Here, ε_1 and ε_2 are the real and imaginary parts of dielectric constant, respectively, ε_∞ is the high-frequency dielectric constant, ν_T is the transverse mode frequency, γ is the damping constant and S is the oscillator strength.

The parameters of the IR-active modes in studied crystals, established by best agreement between the calculated reflectivity spectra with those measured experimentally, are presented in Table 1. The dependencies of ε_2 and Im $(1/\varepsilon)$ versus frequency for $Ag_3Ga_5Se_9$,

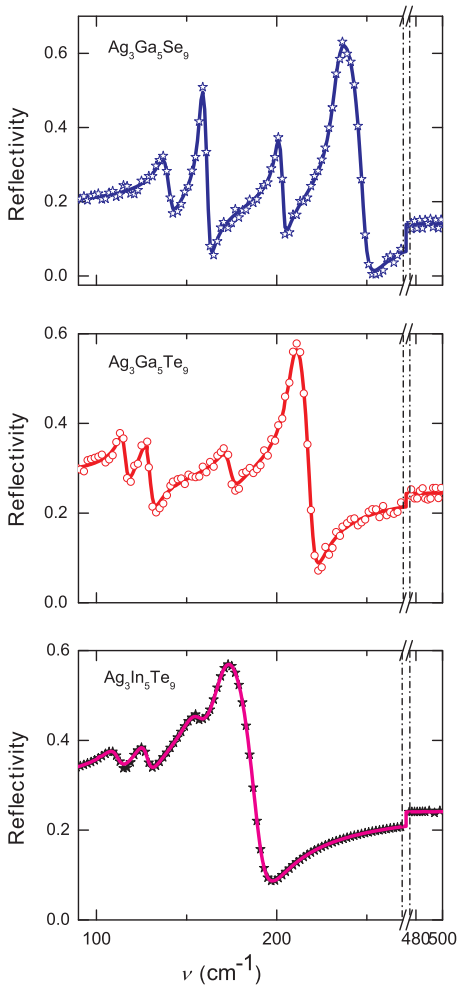

Fig. 4. Reflectivity spectra of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals. Stars and open circles are experimental data; Solid curves are calculated data. (Note the break in the range of 350–475 cm^{-1}).

Table 1
Transverse (ν_T) and longitudinal (ν_L) optical mode frequencies, damping constants (γ) and oscillator strengths (S) of $Ag_3Ga_5Se_9$, $Ag_3In_5Se_9$ and $Ag_3In_5Te_9$ single crystals.

Crystal	Mode	ν_T (cm^{-1})	ν_L (cm^{-1})	γ (cm^{-1})	S
$Ag_3Ga_5Se_9$	ν_1	138 ± 1	141 ± 1	7 ± 0.6	0.33 ± 0.03
	ν_2	158 ± 1	162 ± 1	3 ± 0.2	0.33 ± 0.03
	ν_3	201 ± 1	204 ± 1	4 ± 0.3	0.20 ± 0.02
	ν_4	234 ± 1	249 ± 1	6 ± 0.5	0.61 ± 0.05
$Ag_3Ga_5Te_9$	ν_1'	115 ± 1	117 ± 1	5 ± 0.4	0.30 ± 0.03
	ν_2'	128 ± 1	130 ± 1	6 ± 0.5	0.35 ± 0.03
	ν_3'	173 ± 1	175 ± 1	8 ± 0.7	0.21 ± 0.02
	ν_4'	208 ± 1	220 ± 1	7 ± 0.6	0.88 ± 0.08
$Ag_3In_5Te_9$	ν_1''	111 ± 1	113 ± 1	10 ± 0.8	0.38 ± 0.03
	ν_2''	127 ± 1	129 ± 1	8 ± 0.7	0.39 ± 0.03
	ν_3''	157 ± 1	160 ± 1	15 ± 1.2	1.34 ± 0.12
	ν_4''	179 ± 1	191 ± 1	14 ± 1.1	1.88 ± 0.17

$Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ are displayed in Fig. 5. The longitudinal mode frequencies ν_L were calculated from the maxima of the function of energy losses $Im(1/\varepsilon) = \varepsilon_2 / (\varepsilon_1^2 + \varepsilon_2^2)$ (Table 1). The high-frequency dielectric constant ε_∞ = 5.1 ± 0.2, 9.0 ± 0.2 and 8.1 ± 0.4 for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$, respectively, were established from the high-frequency reflection coefficients R_∞ (ν = 500 cm^{-1}). The low-frequency dielectric constants ε_0, determined from relation $\varepsilon_0 = \varepsilon_\infty + \sum_1^4 S$, were found to be 6.6 ± 0.3, 10.8 ± 0.4 and 12.1 ± 0.5 for

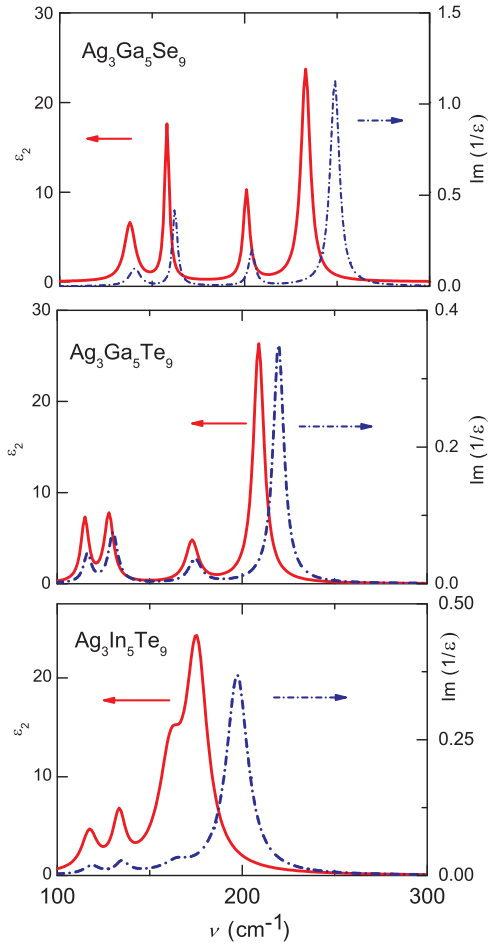

Fig. 5. The imaginary part of the dielectric constant ε_2 and the function of energy losses Im ($1/\varepsilon$) versus frequency for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals.

$Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals, respectively.

The first three modes in the spectra of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals (see Table 1) may be attributed to IR-active modes, in which only the tetrahedral coordinated Ag and Ga(In) atoms are displaced strictly along the coordinate axes, while the octahedral coordinated Ga(In) and Se(Te) atoms accomplish deformation vibrations [17]. Hence, the detected in the IR spectra of silver gallium (indium) ternary selenides (tellurides) modes, having small LO − TO splitting, are the mixed valence-deformation modes. The high-intensity modes with frequencies ν_4 = 234 cm^{-1} ($AgGa_5Se_9$), ν_4' = 208 cm^{-1} ($Ag_3In_5Se_9$) and ν_4'' = 179 cm^{-1} ($Ag_3In_5Te_9$) are associated with antiphase vibration of cation and anion sublattices [18,19].

Furthermore, the dependencies of refractive index n and absorption index k versus frequency were computed from reflectivity spectra for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ utilizing the following relations [16]:

$$n = [(\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}) / 2]^{1/2}, \quad (1)$$

$$k = [(-\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}) / 2]^{1/2}. \quad (2)$$

The spectral dependencies of refractive index n for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ are shown in Fig. 6. The high- and low-frequency refractive indices were determined as 2.56 ± 0.03, 3.28 ± 0.04 and 2.75 ± 0.03 (ν = 500 cm^{-1}) and 2.59 ± 0.03, 3.31 ± 0.04 and 3.69 ± 0.04 (ν = 80 cm^{-1}), respectively, with maximum magnitudes of n = 4.33, 4.88 and 4.67 corresponding to the frequencies ν = 231, 207 and 157 cm^{-1} for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$, respectively. Taking account of the values of absorption index k, it was possible to estimate the absorption coefficient (α) employing the

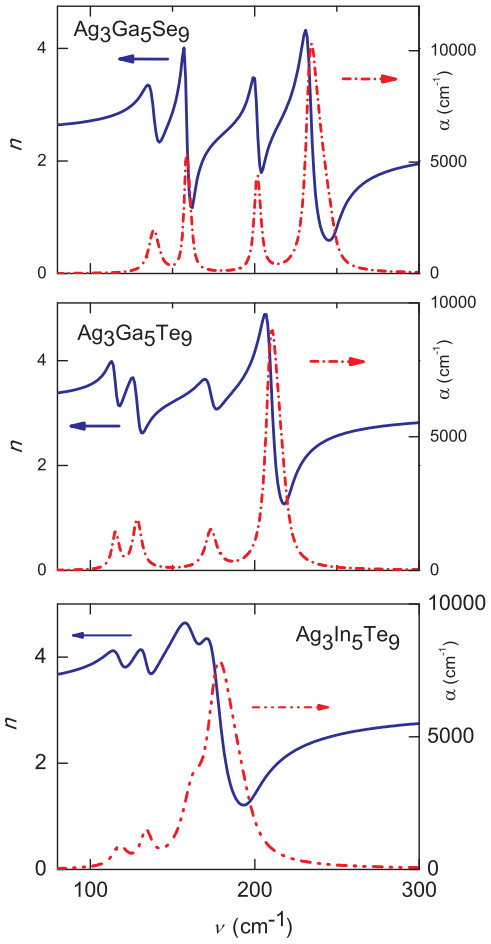

Fig. 6. The dependencies of refractive indices n and absorption coefficients α on frequency for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals.

relationship $\alpha = 4\pi k/\lambda$, where λ is the wavelength [16]. The computed spectral dependencies of absorption coefficients of $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$ crystals are presented in Fig. 6. Maximum magnitudes of α, 10,300, 8960 and 7884 cm^{-1}, are occurred at the frequencies of 235, 211 and 179 cm^{-1} for $Ag_3Ga_5Se_9$, $Ag_3Ga_5Te_9$ and $Ag_3In_5Te_9$, respectively.

4. Conclusions

Silver gallium (indium) ternary selenides (tellurides) single crystals grown by Bridgman method were characterized by X-ray powder diffraction and energy dispersive spectroscopy analysis. The lattice parameters of the orthorhombic unit cells were found to be $a = 0.9767$, $b = 0.9225$, $c = 0.5257$ nm and $a = 1.594$, $b = 0.7164$, $c = 0.4512$ nm for $Ag_3Ga_5Se_9$ and $Ag_3Ga_5Te_9$, respectively, whereas $Ag_3In_5Te_9$ is crystallized in tetragonal structure with the parameters $a = 0.8738$ and $c = 0.7147$ nm. The atomic compositions of studied samples (Ag: Ga: Se), (Ag: Ga: Te) and (Ag: In: Te) were found from energy dispersive spectroscopy analysis to be 17.8: 29.6: 52.5, 18.0: 29.6: 52.4 and 17.7: 29.7: 52.6, respectively. IR spectra, registered in the frequency range of 80–500 cm^{-1}, revealed four modes for all studied crystals. Spectral dependencies of optical constants: refractive index, absorption index and absorption coefficient were computed from registered reflectivity. The frequencies of transverse and longitudinal optical modes, oscillator strengths and damping constants were also evaluated. By replacing light selenium anions by heavier tellurium ones in $Ag_3Ga_5Se_9$ crystal and by substitution of light gallium cations by heavier indium ones in $Ag_3Ga_5Te_9$ crystal all the observed bands shift towards low frequencies. The bands revealed in infrared spectra of studied crystals were ascribed to various vibration types (valence and valence-deformation).

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