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High-pressure Raman study of the Peierls distortion in linear-chain gold complexes AuX_2(dibenzylsulfide) ($X_2 = Cl_2, Br_2$)

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We have measured Raman spectra of the quasi-one-dimensional (1D) halogen-bridged mixed-valence gold complexes $AuCl_2$(DBS) and $AuBr_2$(DBS) (DBS, dibenzylsulfide) under hydrostatic pressure up to 7 GPa. The symmetric stretching vibration of the bridging halogens about the gold (III) ion (the Peierls mode) is found to decrease in frequency in the pressure range from zero to 3–5 GPa. This negative frequency shift is attributed to a reduction of the Peierls distortion under pressure. Results for the gold complexes are discussed in light of the high-pressure behavior of related 1D platinum complexes.

I. INTRODUCTION

Quasi-one-dimensional (1D) halogen-bridged mixed-valence metal complexes (HMMC's) are formed from linear chains of alternating metal and halogen ions with two different formal oxidation states of the metal ions within a single chain.[1] Linear-chain mixed-valence platinum complexes have been investigated extensively as 1D model compounds showing a Peierls-distorted ground state and strong electron-phonon coupling. The halogen-bridged mixed-valence *gold* complexes (HMGC's) $AuCl_2$(DBS), $AuBr_2$(DBS), and AuClBr(DBS) [DBS=dibenzylsulfide=$S(CH_2C_6H_5)_2$] also fall into this class of semiconducting 1D materials.[2,3] A schematic representation of the crystal structure[2] of $AuCl_2$(DBS) is shown in Fig. 1. The formal oxidation states of the gold ions are Au(I) and Au(III). The bridging halogens within the chains (hereafter denoted X) are positioned closer to the Au(III) ions, thus giving rise to the Peierls-distorted ground state. An important structural difference to the nearly ideal 1D system in related platinum complexes is the paired-chain structure. Both $AuBr_2$(DBS) and AuClBr(DBS) are suggested to have similar crystal structures.[2,3]

The HMGC's show *intrachain* charge-transfer absorption bands for light polarized parallel to the chain direction ($\mathbf{E} \| \mathbf{x}$), which is a characteristic property of many 1D HMMC's. The energies of the optical gaps in the gold complexes range from 1.8 to 2.2 eV and are in part determined by the large Peierls distortion and a correspondingly large charge-density wave (CDW) amplitude. In contrast to 1D platinum complexes, the HMGC's also show a visible absorption edge for $\mathbf{E} \perp \mathbf{x}$, with smaller oscillator strengths and at 0.2- to 0.4-eV higher energy compared to $\mathbf{E} \| \mathbf{x}$. This absorption has been interpreted[3] as an *interchain* charge-transfer transition arising from the paired-chain structure.

Due to the strong electron-phonon coupling, pressure studies of HMMC's are of particular interest. The high-pressure behavior of HMGC's has been investigated by electrical conductivity[4] and polarized optical-absorption measurements.[5] The conductivity increases by 3 to 6 orders of magnitude for pressures up to 20 GPa. The absorption edge energies of the visible charge-transfer tran-

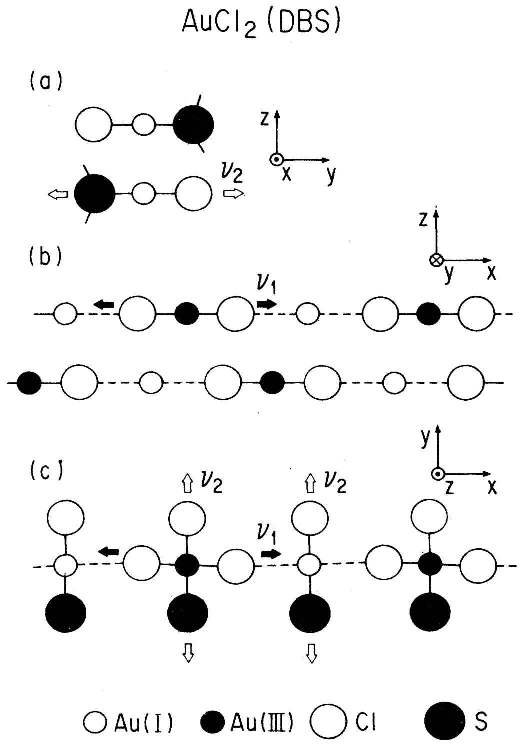

FIG. 1. Schematic representation of the crystal structure of $AuCl_2$(DBS) after Ref. 2. (a) Paired chains seen from the chain direction (x). (b) Relative arrangement of two chains seen from the y direction. (c) A view of one chain from the z direction. The symmetric stretching vibration of bridging halogens about Au(III), $\nu_1 = \nu_S$(Cl-Au(III)-Cl), and the symmetric stretching vibration of the halogen and DBS side ligands about Au(III) or Au(I), $\nu_2 = \nu_S$(S-Au-Cl), are indicated by arrows.

sitions were found to decrease monotonically with increasing pressure up to 5–6 GPa. The red shift for polarization **E**||**x** is found to be exceptionally large, e.g., −0.29 eV/GPa for $AuCl_2$(DBS). This large red shift has been attributed[5] to a significant reduction of the normalized Peierls distortion[6] under pressure.

In this paper we report on a high-pressure Raman investigation of $AuCl_2$(DBS) and $AuBr_2$(DBS) in the range up to about 7 GPa ($T=300$ K). The primary motivation for this Raman study is to find out whether the large red shift of the optical-absorption edges goes along with anomalous frequency shifts of vibrational modes related to the Peierls distortion. High-pressure Raman studies of the vibrational modes in HMMC's have been performed previously for several Pt compounds.[7–10] An interesting feature there is that some of these complexes show an initial decrease with pressure of the frequency of the Peierls mode ν_1, which is the symmetric stretching vibration of the bridging halogens X (X=Cl,Br) about Pt(IV), i.e., $\nu_S(X\text{-Pt(IV)-}X)$. For the gold complexes we find that the corresponding symmetric stretching vibration $\nu_S(X\text{-Au(III)-}X)$ also decreases for pressures up to about 3–5 GPa. This behavior not only supports a decrease of the normalized Peierls distortion under pressure, but in addition suggests an *increase* of the intrachain Au(III)—X bond length under pressure.

II. EXPERIMENTAL DETAILS

The preparation of samples of $AuCl_2$(DBS) and $AuBr_2$(DBS) has been described elsewhere.[2,3] The needle-shaped orange crystals obtained after recrystallization were about 0.05–0.2 mm thick. High-pressure measurements were performed at room temperature by using a gasketed diamond window cell[11] in combination with the ruby luminescence method for pressure measurement.[12] As a pressure medium we have used a 1:1 mixture of pentane and isopentane, which provides isotropic pressure conditions up to about 7 GPa.[13] Raman spectra were excited at 514.5 or 647.1 nm in a near-backscattering geometry. The gold complexes are sensitive to damage by laser radiation. Therefore, the total laser power which was focused on a spot of about 0.1-mm diameter was kept below 2 mW. Under these restricting conditions the weak Raman signal was detected using a multichannel detection system consisting of a 0.6-m grating spectrograph equipped with a subtractive grating prefilter stage and a resistive anode-type photomultiplier.[14] The spectral resolution was about 4 cm^{-1}.

III. EXPERIMENTAL RESULTS

Raman spectra of the two gold complexes at different pressures are shown in Figs. 2(a) and 2(b). Samples were excited in resonance with the broad intrachain charge-transfer absorption band,[3] i.e., at 2.41 eV for $AuCl_2$(DBS) and at 1.92 eV for $AuBr_2$(DBS). The Raman shifts do not change by changing the excitation energy from 2.41 to 1.92 eV. The pressure dependences of the mode frequencies in $AuCl_2$(DBS) and $AuBr_2$(DBS) are shown in Figs. 3(a) and 3(b), respectively.

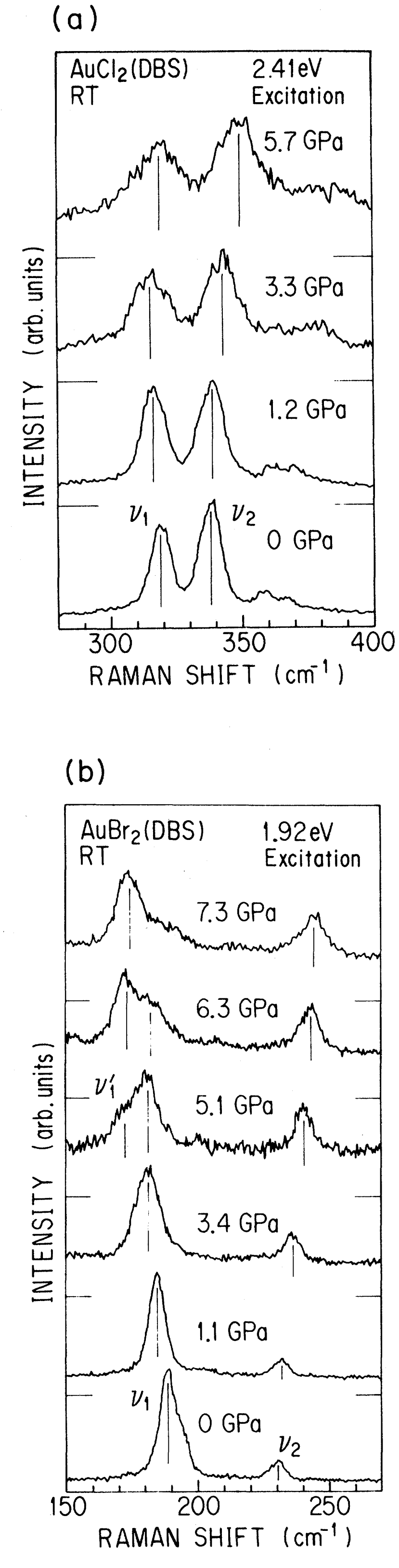

FIG. 2. Raman spectra of (a) $AuCl_2$(DBS) and (b) $AuBr_2$(DBS) at different pressures ($T=300$ K).

For both complexes we observe two modes, ν_1 and ν_2. A characteristic feature of the ν_1 mode is a negative frequency shift in the range up to ~ 3 GPa for $AuCl_2(DBS)$ and up to ~ 5 GPa for $AuBr_2(DBS)$, followed by a positive frequency shift at higher pressures. In $AuBr_2(DBS)$ we find a new mode ν_1' near 5 GPa, with frequency (172 cm^{-1}) about 9 cm^{-1} below the ν_1 mode. The intensity of the ν_1' mode increases at higher pressures, while that of ν_1 decreases, such that at 7.3 GPa the ν_1 mode is only seen as a high-frequency shoulder of ν_1'. The frequencies of the ν_2 modes increase monotonically with pressure. A notable feature is that the pressure dependence of the ν_2 mode is superlinear in $AuCl_2(DBS)$ and almost linear in $AuBr_2(DBS)$.

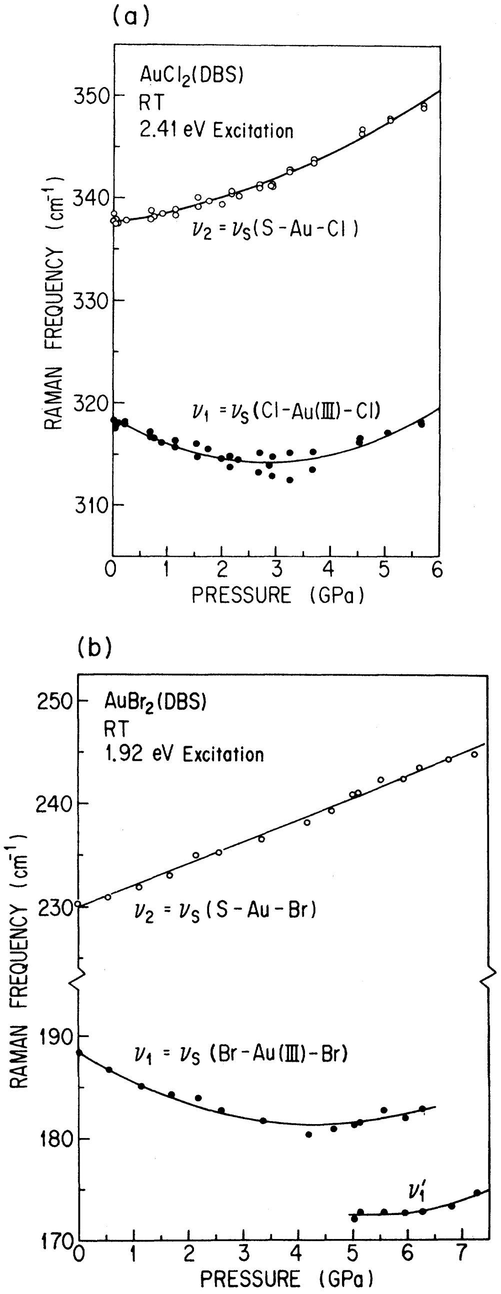

FIG. 3. Raman shifts of the ν_1 and ν_2 modes of (a) $AuCl_2(DBS)$ and (b) $AuBr_2(DBS)$ as a function of pressure. Solid lines for ν_1 and ν_2 correspond to the result of a least-squares fit to the experimental data using Eq. (1).

The Raman frequencies ω_0 of $AuCl_2(DBS)$ and $AuBr_2(DBS)$ measured at ambient pressure ($T=300$ K) and the corresponding mode assignments are summarized in Table I. The assignment is straightforward in both complexes, if one takes into account (i) the polarization characteristics of Raman modes in HMGC's reported earlier,[3] (ii) a comparison of Raman frequencies of HMGC's with those observed for reference compounds with gold in either Au(I) or Au(III) oxidation states (see Table I), and (iii) the pressure dependence reported here. The ν_1 modes are the symmetric stretching vibrations $\nu_S(X\text{-Au(III)-}X)$ of bridging halogens about the Au(III) ions (see Fig. 1). These vibrations are closely related to the Peierls distortion. The ν_2 modes oscillate perpendicular to the chain direction[3] and are assigned to the symmetric stretching vibrations $\nu_S(S\text{-Au-}X')$ of the DBS and halogen side ligands X' about Au(III) or Au(I) (see Fig. 1).

The solid lines in Fig. 3 correspond to the results of least-squares fits of the quadratic relation

$$\omega(P)=\omega_0+bP+cP^2 \tag{1}$$

to the experimental Raman frequencies as a function of pressure P. First- and second-order coefficients b and c are summarized in Table II, which also lists the maximum total shifts $\Delta\omega$ to lower frequency and the pressure P_m corresponding to the minimum in frequency of the ν_1 modes. We note from Table II that the linear coefficients $b(\nu_1)$ of HMGC's are smaller than those of 1D platinum complexes, but the negative frequency shift extends to higher pressures as compared to the platinum complexes.

The Raman intensities of the ν_1 modes in HMMC's are commonly observed to resonate strongly with the intrachain charge-transfer absorption band. In the case of the 1D gold complexes, also the ν_2 modes show resonance behavior with visible excitation, for polarization directions $\mathbf{E}\parallel\mathbf{x}$ as well as $\mathbf{E}\perp\mathbf{x}$ (Ref. 3). The Raman intensities are found to decrease with increasing pressure, presumably because the charge-transfer absorption bands move out of resonance with the laser excitation energy. Within the accuracy of the present experiment this effect is similar

TABLE I. Raman frequencies of $AuCl_2(DBS)$, $AuBr_2(DBS)$, and related gold complexes at ambient pressure ($T=300$ K).

Sample	$\nu_S(X\text{-Au(III)-}X)$	$\nu_S(S\text{-Au-}X')$
$AuCl_2(DBS)$	318	338
$AuBr_2(DBS)$	188	230
$Au(III)Cl_3(DBS)$	325	349
$Au(III)Cl_3L$ [a]	315[a]	340[a]
$Au(I)Cl(DBS)$		333
$Au(III)Br_3(DBS)$	203	231
$Au(I)Br(DBS)$		226

[a] $L=S(CH_3)_2$, $S(C_2H_5)_2$; data after Ref. 15. (The mode assignment given here is different from that of Ref. 15.)

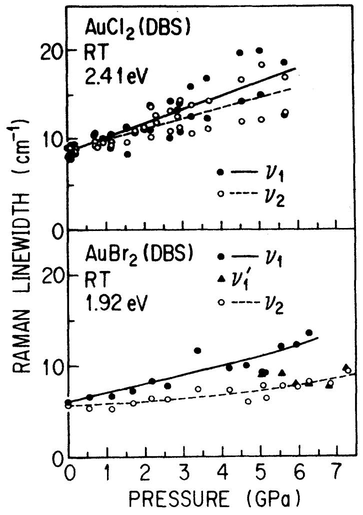

FIG. 4. Linewidth of Raman modes of (a) $AuCl_2$(DBS) and (b) $AuBr_2$(DBS) as a function of pressure.

for ν_1 and ν_2 modes and independent of the polarization direction. The Raman linewidths of the ν_1 and ν_2 modes increase with pressure by roughly a factor of 2 in 6 GPa, as shown in Fig. 4. We note that all pressure effects described here are fully reversible.

IV. DISCUSSION

The most notable result from the present Raman study is the initial decrease of the frequency of the ν_1 modes with pressure. In first approximation the frequency ω of the ν_1 mode may be written in terms of the two stretching force constants f_1 and f_2 for the Au(III)—X and Au(I)—X bond, respectively,

$$\omega=[(f_1+f_2)/m_X]^{1/2} . \tag{2}$$

Here, m_X is the mass of the bridging halogen X. At ambient pressure, the interaction between Au(I) and X is weak, and X is more strongly bound to Au(III). This picture corresponds to a separated mixed-valence system, i.e., the alternate arrangement of the molecules of Au(I)X(DBS) and Au(III)X_3(DBS), which are weakly coupled to each other. Thus, the distance $d_2=d$(Au(I)-X) is larger compared to $d_1=d$(Au(III)-X), and accordingly, we have $f_1>f_2$. The negative pressure shift of the ν_1 modes indicates a decrease of the dominant force constant f_1 which is explained as follows: The Au(III)-Au(I) distance along the chain is expected to decrease under pressure so that the bridging halogens X couple more strongly to Au(I). Thus, the X ions will be pulled in the direction towards Au(I), thus reducing the strength of the Au(III)—X bond. In other words, the negative pressure coefficient $b(\nu_1)$ not only indicates a decrease of the Peierls distortion due to a compression of the Au(I)—X bond, but in addition an *increase* of the Au(III)—X bond length during the initial compression. This simple qualitative picture is quite similar to the double-well potential model used in the standard description of hydrogen bonding.[11]

The above explanation for the negative sign of $b(\nu_1)$ is supported by the fact that the distance of d(Au(III)-Cl) is shorter in trivalent Au(III)Cl_3(DBS) compared to mixed valence $AuCl_2$(DBS).[2,16] In some 1D platinum complexes one finds an increase of the intrachain Pt-Pt distance with decreasing temperature which has been explained by a similar mechanism.[17,18] With decreasing Peierls distortion we can expect a corresponding decrease of the amplitude of the CDW, i.e., of the charge ρ in the notation $-\mathrm{Au}^{2-\rho}-X-\mathrm{Au}^{2+\rho}-X-$, resulting in a decrease of the Peierls gap energy and an anomalously strong red shift of the absorption edge for $\mathbf{E}\|\mathbf{x}$ as is experimentally observed.[5]

The appearance of the ν_1' mode in $AuBr_2$(DBS) at 5 GPa is attributed to the onset of a sluggish structural phase transition. This phase transition does not result in a breakdown of the linear-chain structure, because the dichromatic character and polarization directions are preserved in the optical-absorption spectra.[3,5]

The energy of the ν_1 (ν_1') modes in $AuCl_2$(DBS) and

TABLE II. Raman frequencies of $AuCl_2$(DBS) and $AuBr_2$(DBS) and their first- and second-order pressure coefficients b and c at $T=300$ K. The quantities $\Delta\omega$ and P_m refer to the maximum shift of the ν_1 modes to lower frequency and to the pressure at the frequency minimum, respectively. Data given for related platinum compounds are from Ref. 8 and refer to $\nu_1=\nu_S$(X-Pt(IV)-X). With the exception of $AuCl_2$(DBS), only data up to P_m have been used to determine pressure coefficients b and c.

Sample	Mode	ω_0 (cm^{-1})	b (cm^{-1}/GPa)	c (cm^{-1}/GPa^2)	$\Delta\omega$ (cm^{-1})	P_m (GPa)
$AuCl_2$(DBS)	ν_1	318	−2.9(2)	0.52(4)	−4	3
	ν_2	338	0.7(1)	0.24(2)		
$AuBr_2$(DBS)	ν_1	188	−2.8(3)	0.25(6)	−8	5
	ν_2	230	2.0(2)	0.01(2)		
WRS[a]	ν_1	315			−7	0.2−2
Pt(en)Cl[b]	ν_1	313	−6		−13	2.5
RGS[c]	ν_1	184	−8		−8	1

[a] Wolffram's red salt $[Pt(II)(EA)_4][Pt(IV)Cl_2(EA)_4]Cl_4\cdot 4H_2O$, where EA denotes ethylamine.
[b] $[Pt(II)(en)_2][Pt(IV)Cl_2(en)_2](ClO_4)_4$, where en denotes 1,2-diaminoethane.
[c] Reihlen's green salt $[Pt(II)(EA)_4][Pt(IV)Br_2(EA)_4]Br_4\cdot 4H_2O$.

$AuBr_2$(DBS) start to increase again above 3 and 5 GPa, respectively (see Fig. 3). Within the local picture of a weakly coupled mixed-valence system this behavior can be attributed to increasing repulsive interactions between molecular units. On the other hand, with increasing pressure the HMGC's change from the limiting case of a weakly coupled mixed-valence system towards a condition where a Peierls-Hubbard model with extended electronic states may be an appropriate description of the electron-phonon system. Within a 1D Peierls-Hubbard model it is the relative strengths of repulsive Coulomb, electron-transfer, and electron-phonon interactions, which self-consistently determine the equilibrium state.[19]

The pressure P_m at which the frequencies of the ν_1 (ν_1') modes start to increase again is larger for $AuCl_2$(DBS) and $AuBr_2$(DBS) as compared to the platinum complexes listed in Table II. This may be related to a stronger interchain coupling in the Au compounds as compared to the Pt compounds. Another important difference between 1D Au and Pt complexes is the strength of the intrachain charge-transfer coupling of the metal orbitals, which is weaker for the $d_{x^2-y^2}$ orbitals of Au as compared to the d_{z^2} orbitals of Pt compounds.

The phonon energies of the ν_2 modes show an increase under pressure as it would be expected for increasing repulsive interchain interactions. However, a superlinear increase of the energy of ν_2 in $AuCl_2$(DBS) and the unusual linear increase in the case of $AuBr_2$(DBS) is observed in the same pressure range where also the anomalous behavior of the frequency of the ν_1 (ν_1') modes is observed. Thus, we suggest that the ν_2 modes couple to the change of the Peierls distortion and that there is a significant hybridization between the ν_1 and ν_2 modes.

An increase of Raman linewidths under pressure (see Fig. 4) is also observed in some platinum complexes,[20] and thus appears to be a common phenomenon in HMMC's. We cannot rule out the possibility that local internal stresses due to crystalline imperfections are responsible for a change in Raman linewidth in these somewhat delicate gold complexes. On the other hand, as the coupling between Au(I) and X increases with pressure, the Peierls phonon will develop an extended character with respect to the more localized mode at ambient pressure. Thus, interaction with defects on the chains is expected to cause increasing line broadening with increasing pressure. In addition, the pressure-induced change of resonance conditions may affect the linewidth.

In summary, Raman measurements for the linear-chain mixed-valent gold complexes $AuCl_2$(DBS) and $AuBr_2$(DBS) under pressure show an initial decrease in frequency of the Peierls mode. This behavior is qualitatively understood in terms of a double-well potential picture for the intrachain three-atom system Au(I)-X-Au(III). An increase of the distance between Au(III) and bridging halogen X is suggested for the pressure range up to about 3 to 5 GPa. A linear or even superlinear increase of the frequency of symmetric ligand vibrations in $AuCl_2$(DBS) and $AuBr_2$(DBS), which oscillate perpendicular to the chain direction, indicates a coupling of these vibrations to the Peierls mode. The appearance of a new Raman line in $AuBr_2$(DBS) near 5 GPa is interpreted as the onset of a sluggish structural phase change, where the Peierls mode is reduced in frequency. For a quantitative determination of the pressure dependence of the Peierls distortion by single-crystal x-ray diffraction one has to overcome the problem of twinning in these crystals.

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