Cu 3d 와 4p 궤도함수의 혼성과 리간드의 Spin-Orbit Coupling 이 Tetragonally 일그러진 CuCl₄²⁻ 착물의 Zero-Field Splitting 에 미치는 영향*

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(1989. 9. 22 접수)

The Effect of Ligand's Spin–Orbit Coupling and the Intermixing of |3d> and |4p> Cu Atomic Orbitals on Zero–Field Splitting in the Tetragonally Distorted Tetrahedral CuCl₄²⁻ Complex*

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(Received September 22, 1989)

요 약. D_{2d} 점군에 속하는 강결정장의 tetragonally 일그러진 사면체 $3d^9$ 전자계 착물의 바닥상태에 대한 리간드 궤도함수의 spin-orbit coupling 과 중심 금속의 3d 와 4p 궤도함수의 intermixing 이 미치는 영향에 대하여 중첩 섭동론을 사용하여 연구하였다. 단결정 Cs_2CuCl_4의 tetragonally 일그러진 $CuCl_4^{2-}$에 대한 d-d 전이의 실험값을 사용한 LCAO-MO 분석은 구리이온과 리간드 사이의 공유결합성은 Cu 4p orbital 의 기여가 증가하므로서 급격히 감소하고 리간드 Cl 3p 궤도함수의 spin-orbit coupling 상호작용에 의한 바닥상태의 에너지 준위 분리에 대한 효과는 $\Gamma_7(E) \to \Gamma_6(E) > \Gamma_7(B_2) \to \Gamma_6(E) > \Gamma_7(B_2) \to \Gamma_7(E)$의 순서로 감소하였다.

ABSTRACT. An effect of the spin–orbit coupling interaction of ligand orbitals and the intermixing |3d> and |4p> transition metal atomic orbitals on the ground state for a $3d^9$ system in a strong crystal field of tetragonally distorted tetrahedral symmetry that belongs to the D_{2d} point group has been investigated in this work, applying the degenerate pertubation theory. An LCAO–MO analysis in terms of the known energies of the d–d transitions for the tetragonally distorted $CuCl_4^{2-}$ ion in a single crystal of Cs_2CuCl_4 shows that the covalent mixing of Cu 3d and ligand Cl 3p orbitals decreases dramatically with increasing Cu 4p contribution. The extent of effect on the energy level splitting for the ground state by the spin–orbit coupling interaction of ligand orbitals decreases significantly in order $\Gamma_7(E) \to \Gamma_6(E) > \Gamma_7(B_2) \to \Gamma_6(E) > \Gamma_7(B_2) \to \Gamma_7(E)$.

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INTRODUCTION

Copper(II) is one of the most commonly investigated transition metals.[1-4, 10, 11] This is due to the fact that copper(II) binds a large variety of ligands and gives rise to numbers of geometries and stoichiometries. Because chlorocuprates are comparatively simple and exhibit a wide range of stereochemistries, they have frequently been used to test theoretical models of the bonding in metal complexes.[3, 9] They have been the subject of numerous spectroscopic investigations,[1, 5 10, 11, 14] and the $CuCl_4^{2-}$ ion has recently acted as a simple model of the active site in copper compounds of the general formula $(cation)_2CuCl_4$ that show a particularly rich stereochemistry. In some of these, 4-coordinate $CuCl_4^{2-}$ ions with flattended tetrahedral geometries are present. The extent of the observed distortion will depend on the degree to which these ligand field effects are opposed by interligand repulsions and loss of metal-ligand bonding through the Cu $4p$ orbitals. Structural studies of the $CuCl_4^{2-}$ ion have shown a range of geometries between tetrahedral and square planar,[2, 10] but in most cases the deformation is probably best described by D_{2d} distortion coordinate.[15, 25] The flattended geometry is energetically favored for the d^9 count, and this preference is classified as a first-order Jahn-Teller distortion; however, it has been shown that the orbital degeneracy of the tetrahedral $CuCl_4^{2-}$ is removed by spin-orbit coupling without recourse to distortion from T_d symmetry.[9]

Sharnoff's general eigenvalue equations for the ordering of d energy levels in *Fig.* 1 has often used to explain the $d-d$ transition[3, 6, 8, 13] but Sharnoff's equations may not show the correct pattern of the d-d energy splitting by the distortion without the spin-orbit coupling.

The effect of covalence on the spin-orbit coupling constant has received relatively little attention, although it is well known that ζ is generally reduc-ed below its free ion value. Neverthless Jorgensen[19] has postulated that this parameter may be influenced by two types of covalence, namely central field covalence, and symmetry restricted covalence. The former relates to the screening effect of the ligand on the central field of the cation which results in a decreased effective positive charge on the metal expansion of the radial function, whereas, in the case of O_h symmetry, the latter is due to the respective involvement of the e_g and t_{2g} metal orbitals in molecular orbital formation with appropriate symetry adopted ligand combinations.[20] R. Al-Mobarak and D. Warren[21] have showed that the fulfillment of the cusp condition of wavefunctions was an over stringent requirement for the use of wavefunctions to calculate the spin-orbit coupling constant, ζ, for a series of $3d$ transition metal ions, and that the reduction of ζ below the free-ion value on complex formation should be due dominantly to symmetry restricted covalency rather than to central field effects by determining the distance dependence of the spin-orbit coupling constant.

It is the purpose of this work, firstly, to derive the general equation for the order of d orbital state energy levels due to either the distortion alone or both the distortion and the spin-orbit coupling, and secondly to investigate an effect of the spin-orbit coupling interaction of ligand orbitals and the intermixing of $|3d\rangle$ and $|4p\rangle$ transition metal atomic orbitals on the ground state for a $3d^9$ system in a strong crystal field of tetragonally distorted tetrahedral symmetry that belongs to the D_{2d} point group, applying the degenerate perturbation theory. The $d-d$ transition energies are analyzed in terms of an LCAO-MO theory whose orbitals contain $3d$, $4p$ characters of Cu and ligand Cl $3p$ character.

THEORY

The halmiltonian representing the various interac-

tions may be expressed as

$$\hat{H}=\Sigma_{i=1}^{n}\ \{-\frac{\hbar^{2}}{2m}\nabla_{i}-\frac{ze^{2}}{4\pi\epsilon r_{i}}+V(r)+\zeta\underline{l}_{i}\cdot\underline{s}_{i}$$

$$+\delta(\underline{l}_{iz}^{2}-2)\}+\Sigma\Sigma_{i<j}\frac{e^{2}}{4\pi\epsilon r_{ij}},\qquad(1)$$

where

$$V(\underline{r}_{i})=A_{32}r_{i}^{3}\ \{Y_{32}(\theta,\phi)-Y_{3-2}(\theta,\phi)\}$$

$$+A_{40}r_{i}^{4}\ [\ Y_{40}(\theta,\phi)+(5/14)^{1/2}\ \{Y_{4-4}(\theta,\phi)$$

$$+Y_{44}(\theta,\phi)\}\ ].\qquad(2)$$

Here $\underline{r}_i$ is the electron radius vector about the electron-bearing atom, $V(\underline{r}_i)$ the crystal field potential of tetrahedral symmetry, and A_{32} and A_{40} crystal field parameters. By using the complementary relation between the $(10-N)$ electron system of $t_2{}^{6-n}\ e^{4-m}\ (n+m=N)$ and N-electron system of $t_2{}^n\ e^m$ whose the t_2 and e functions are the δ -functions, we choose the hamiltonian as

$$\hat{H}=-\frac{\hbar^{2}}{2m}\nabla^{2}-\frac{Ze^{2}}{4\pi\epsilon r_{i}}+V(\underline{r})+\zeta\underline{l}\cdot\underline{s}+\delta(\underline{l}_{z}^{2}-2)\}$$

$$(3)$$

Here the distortion in tetrahedral complex is the tetragonal distortion corresponding to a flattening of the tetrahedron as indicated by the arrows in *Fig.* 1.

A qualitative diagram of the term splittings in a compressed D_{2d} geometry and with the inclusion of spin-orbit coupling is given in *Fig.* 2.

Here Δ_t is defined as the separation between the orbital levels of $^2T_2$ created by the axial field component in the absence of spin-orbit coupling. A crystal structure analysis Cs_2CuCl_4 has revealed flattening tetrahedral $CuCl_4{}^{2-}$ ion assumed with D_{2d} symmetry. A point-charge electrostatic crystal-field model would predict, therefore, the least stable orbital to be the d_{xy} (ground state B_2). In this compound the distortion, Δ_t, was chosen about 5,000 cm^{-1} by B.N. Figgis and others.[5, 8, 24]

If the rotatory-reflections S_4 axis is taken to be the axis of quantization, we may write the t_2 correct $3d$ wavefunctions in a strong crystal field of tetrahedral symmetry as
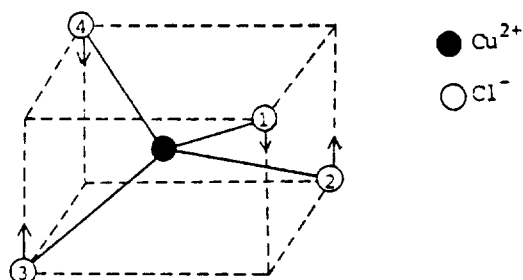
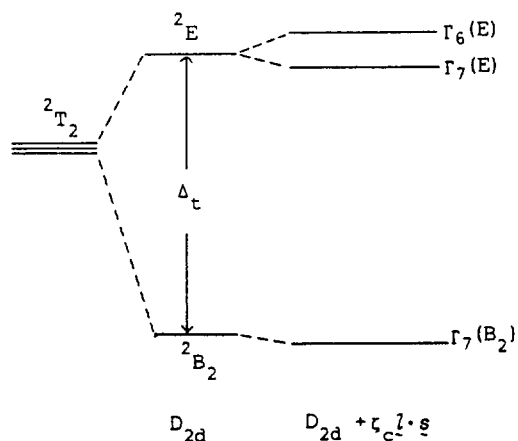*Fig.* 1. Coordinate and numbering system for $CuCl_4{}^{2-}$ with a tetragonal distortion.

Fig. 2. Term diagram of $CuCl_4{}^{2-}$ in a compressed, D_{2d} geometry and with the inclusion of distortion and spin orbit coupling.

$$\phi_1\ (|\psi_{xy}>)=a(\alpha|3d_{xy}>-\beta|4p_z>)+L/2|\chi_z>,$$

$$\phi_2\ (|\psi_{xz}>)=a(\alpha|3d_{xz}>-\beta|4p_y>)+L/2|\chi_y>,$$

$$\phi_3\ (|\psi_{yz}>)=a(\alpha|3d_{yz}>-\beta|4p_x>)+L/2|\chi_x>.$$

$$(4)$$

In this case, the coefficient a and L must be of opposite sign because we assume that the unpaired electron is in an antibonding orbital in transition metal complex. Here the wavefunctions are defined as follows

$$d_{xy}=i/\sqrt{2}\ (|d_{-2}>-|d_2>),$$

$$d_{xz}=1/\sqrt{2}\ (|d_{-1}>-|d_1>),$$

$$d_{yz}=i/\sqrt{2}\ (|d_{-1}>+|d_1>),\qquad(5)$$

$$p_z=|p_0>,$$

$$p_x=1/\sqrt{2}\ (|p_{-1}>-|p_1>),$$

Table 1. The Spin Orbit coupling and the tetragonal distortion matrix when the rotatory-reflection S_4 axis is chosen to be our axis of quantization

$\delta(l_z-2)+\zeta_c l \cdot s$	$|\Phi_1^+\rangle$	$|\Phi_2^-\rangle$	$|\Phi_3^+\rangle$	$|\Phi_3^-\rangle$	$|\Phi_2^+\rangle$	$|\Phi_1^-\rangle$
$\langle\Phi_1^+|$	$\zeta_c/2-\delta$	$-\zeta_c/\sqrt{2}$				
$\langle\Phi_2^-|$	$-\zeta_c/\sqrt{2}$	2δ				
$\langle\Phi_3^+|$			$-\zeta_c/2-\delta$			
$\langle\Phi_3^-|$				$\zeta_c/2-\delta$	$-\zeta_c/\sqrt{2}$	
$\langle\Phi_2^+|$				$-\zeta_c/\sqrt{2}$	2δ	
$\langle\Phi_1^-|$						$-\zeta_c/2-\delta$

$$p_y=i/\sqrt{2}\,(|p_{-1}\rangle+|p_1\rangle), \qquad (6)$$

the wavefunctions χ_n $(n=x, y\ z)$ are real, normalized linear combinations of ligand orbitals

$$\chi_x=1/2\,(\sigma_1-\sigma_2-\sigma_3+\sigma_4),$$
$$\chi_y=1/2\,(\sigma_1-\sigma_2+\sigma_3-\sigma_4),$$
$$\chi_z=1/2\,(\sigma_1+\sigma_2-\sigma_3-\sigma_4), \qquad (7)$$

where σ_i $(i=1,2,3,4)$ is a σ orbital, attached to the ith Cl ion whose positive lobe points towords the Cu ion.

Since these wave functions are degenerate, we may choose any orthogonal set of linear combinations, so we take the basis set of wavefunctions as

$$\Phi_1^\pm=1/\sqrt{2}\,(\phi_2+i\phi_3)^\pm,$$
$$\Phi_2^\pm=i\phi_1^\pm,$$
$$\Phi_3^\pm=1/\sqrt{2}\,(\phi_2-i\phi_3)^\pm, \qquad (8)$$

When the rotatory-reflection S_4 axis is taken to be our axis of quantization, the spin-orbit coupling and the tetragonal distortion matrix for a $3d^9$ system in a strong crystal field of tetragonally distorted tetrahedral symmetry that belongs to the D_{2d} point group is represented in *Table* 1.

The $^2T_2$ ground state, arising in the first three terms in equation (3) is seperated into three kramer's doublets by the spin-orbit coupling interaction and the tetragonal field components with the following eigenvalues and the corresponding eigen functions,

$$\varepsilon_1=\zeta_c/4+\delta/2+X/2, \qquad (9)$$

$$\psi_1^+=A|\Phi_1^+\rangle+B|\Phi_2^-\rangle,$$
$$\psi_1^-=A|\Phi_3^-\rangle+B|\Phi_2^+\rangle, \qquad (10)$$

$$\varepsilon_2=\zeta_c/4+\delta/2-X/2, \qquad (11)$$

$$\psi_2^+=B|\Phi_1^+\rangle-A|\Phi_2^-\rangle,$$
$$\psi_2^-=B|\Phi_3^-\rangle-A|\Phi_2^+\rangle, \qquad (12)$$

$$\varepsilon_3=-\zeta_c/2-\delta,$$
$$\psi_3^+=|\Phi_3^+\rangle, \qquad (13)$$

$$\psi_3^-=|\Phi_1^-\rangle, \qquad (14)$$

where

$$A^2=1/2+1/2\,(\zeta_c/2-3\delta)/X,$$
$$B^2=1/2-1/2\,(\zeta_c/2-3\delta)/X, \qquad (15)$$
$$AB=-(\zeta_c/\sqrt{2})/X, \text{ and}$$

$$X^2=(9/4)\,\zeta_c^2-3\delta\zeta_c+9\delta^2. \qquad (16)$$

The number ζ_c is given by

$$\zeta_c=a^2\,(\alpha^2\zeta_{3d}-\beta^2\zeta_{4p})+(L^2/2)\,\zeta_{3p}, \qquad (17)$$

where ζ_{3d} and ζ_{4p} are spin-orbit coupling constant[16, 23] for an electron in the 3d and 4p orbital of free Cu^{2+} and have the values -827.7 cm^{-1} and -925.0 cm^{-1} respectively. The spin-orbit coupling constant[22] for Cl$^-$ 3p orbital is -580.0 cm^{-1}. The sign of the spin-orbit coupling constant is negative because the shell to which it refers is more than half full. Here the distortion parameter δ as $\Delta_t/3$ is 1700 cm^{-1}.

The reduction factor[7], k, has been refered to as an electron delocalization factor and a measure of covalence, and it has been used to account for the time spent by an unpaired t_{2g} electron on the ligands. The real-valued parameters a, α, β and L in wavefunctions (4) are constrained by the normalization condition,
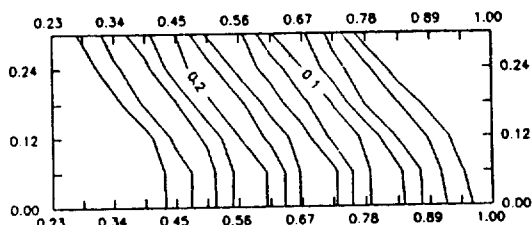
Fig. 3. Values for reduction factor, k, as a function of the intermixing of $3d$ and $4p$ Cu orbitals at each point of variations of ligand character.

$$1 = (aa)^2 + 2(aa)L<3d_M|3p_L>$$
$$+ 2(a\beta)L<4p_M|3p_L> + (a\beta)^2 + L^2,$$
$$\tag{18}$$

$$x = (aa)^2 - 2(aa)L<3d_M|3p_L> + 2(a\beta)$$
$$L<4p_M|3p_L> - (a\beta)^2 + L^2\gamma/2. \tag{19}$$

Here γ is chosen as a zero because the contributions ligand's $3s$ orbitals to σ -ligands are not considered. The values of reduction factor for variation of orbital character are represented as a contour diagram in *Fig.* 3.

RESULTS AND DISCUSSION

In this work we have derived the general equations (9)–(16), the order of d state energy levels due to either the distortion alone or both the distortion and the spin–orbit coupling, and investgated an effect of the spin–orbit coupling interaction of ligand orbitals and the intermixing of $|3d>$ and $|4p>$ transition metal atomic orbitals on the ground state for a $3d^9$ system in a strong crystal field environment of tetragonally distorted tetrahedral symmetry that belongs to the D_{2d} point group, applying the degenerate perturbation theory. The qualitative diagram for this term splitting is as shown in *Fig.* 2. Here, the measurement of E term splitting can be calculated as $3\zeta_c/4 + 3\delta/2 - 1/2$ $(9/4 \cdot \zeta_c^2 - 3\delta \zeta_c + 9\delta^2)^{1/2}$.

We use Eq. (19) to draw a section of the contour map of values for reduction factor, k, as a function of the intermixing Cu $3d$ and Cu $4p$ or-
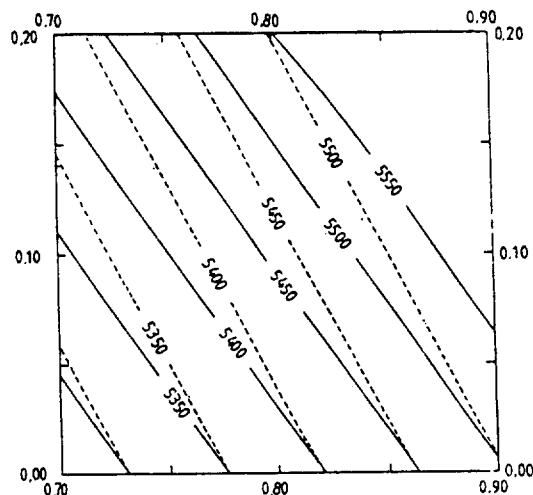

Fig. 4. Variations of $\Gamma_7(B_2) - \Gamma_6(E)$ dependent on each Cu $3d$ and ligand character. The dotted lines indicate the values without the ligand's spin orbit coupling effect.

Fig. 5. Variations or $\Gamma_7(E) - \Gamma_6(E)$ dependent on each Cu $3d$ and ligand character. The dotted lines indicate the values without the ligand's spin orbit coupling effect.
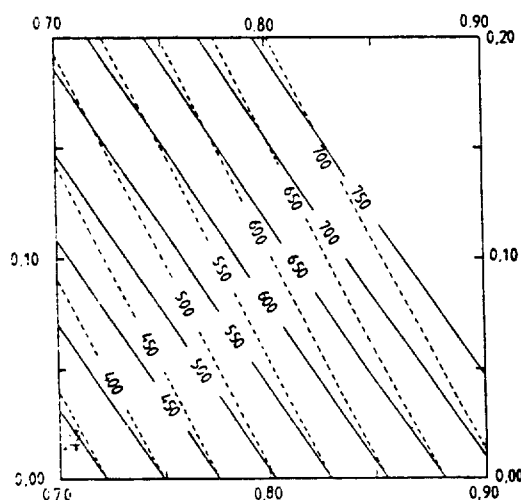
bitals at each point of variation of ligand character as shown in *Fig.* 3. This contour in *Fig.* 3 shows the qualitative scheme between the covalence and the orbital reduction factor, k.

As shown in *Fig.* 4 and 5, the contour maps of the LCAO-MO analysis in terms of the known energies of the $d-d$ transitions for the tetragonally distorted $CuCl_4^{2-}$ ion in a single crystal of Cs_2

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Table 2. The effect of the ligand's spin-orbit coupling on the intermixing of $3d$ and $4p$ Cu atomic orbitals on the energies of the d–d transitions of $CuCl_4{}^{2-}$ belong to the point group D_{2d} Unit: cm^{-1}

			Spin–orbit Coupling Effect of Ligand				
Character(%)			When neglected		When included		Exp.
$3d$	$4p$	Ligand	$\Gamma_7(B_2)-\Gamma_6(E)$	$\Gamma_7(E)-\Gamma_6(E)$	$\Gamma_7(B_2)-\Gamma_6(E)$	$\Gamma_7(E)-\Gamma_6(E)$	Values
No overlap	70.3	11.7	18.0[23]	5445	453	5546	469	$\Gamma_7(B_2)-\Gamma_6(E)$
	89.4	5.0	6.6	5538	731	5550	750	5550
	91.3	5.0	3.7	5550	750	5558	762	$\Gamma_7(E)-\Gamma_6(E)$
Overlap	70.9	13.3	15.8[23]	5475	484	5486	499	750
	80.6	5.1	14.3[9]	5535	582	5559	616	
	88.6	5.1	6.3	5534	726	5550	750	
	88.9	5.3	5.8	5550	750	5564	772	

$CuCl_4$ show that the covalent mixing of Cu $3d$ and ligand Cl $3p$ orbitals decreases dramatically with increasing Cu $4p$ contribution. *Fig.* 4 and 5 show almost linear relation between the Cu $3d$ state and the ligand Cl $3p$ state because of neglecting the overlap between Cu $3d$ orbital and ligand $3p$ orbital, while including the overlap between the Cu $3d$ orbital and the ligand $3p$ orbital show somewhat complicated contour lines related to the covalence between the Cu $3d$ orbital and the ligand Cl $3p$ orbital.[28] The effects of ligand's spin–orbit coupling on the intermixing of $3d$ and $4p$ Cu atomic orbitals on the energies of the d–d transition of $CuCl_4{}^{2-}$ that belongs to the point group D_{2d} are in *Table* 2 and are qualitatively shown in *Fig.* 4 and 5. When the overlap integral and effects of ligand's spin–orbit coupling are included, an LCAO–MO analysis in terms of the known energies of the d–d transition for the tetragonally distorted $CuCl_4{}^{2-}$ ion in a strong crystal field shows that the unpaired electron spends 88.6% of its time in a Cu $3d$ state with 5.1% of its time in a Cu $4p$ state. This is somewhat more ionic that the results of other spectroscopic methods (g-value, 71% Cu $3d$; hyperfine, 69% Cu $3d$; superhyperfine, 75% Cu $3d$; core level XPS, 64% Cu $3d$).[26,27] The calculated pattern of each orbital character are almost consistent with the EPR hyperfine splitting and the polarized crystal absorption spectra, but $3d$ orbital character of Cu is increased about 18.6% but $4p$(Cu) and $3p$(Cl) character are decreased about 6.9% and 13.4%, respectively, compared with the LCAO–MO analysis of the g-values of the known energies of the d–d transitions.[23] The d–d transition energies with the ligand's spin–orbit coupling effect are greater than those without the effects of ligand's spin–orbit coupling. This difference is 24 cm^{-1} in $\Gamma_7(E) \rightarrow \Gamma_6(E)$, and 16 cm^{-1} in $\Gamma_7(B_2) \rightarrow \Gamma_6(E)$.

In the above results, when we do the LCAO–MO analysis in terms of the known d–d transition energies, we may be conclude that consideration for the overlap between the Cu $3d$ orbital and the ligand Cl $3p$ orbital should be cared, the covalent mixing of Cu $3d$ and ligand $3p$ orbitals decreases dramatically with increasing Cu $4p$ contribution and finally the extent of effect on the d–d energy level splitting for the ground state by the spin–orbit coupling interaction of ligand orbitals is small but significant.

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