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Anomalous charge and negative-charge-transfer insulating state in cuprate chain-compound $KCuO_2$

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Using a combination of X-ray absorption spectroscopy (XAS) experiments and first-principles calculations, we demonstrate that insulating $KCuO_2$ contains Cu in an unusually-high formal-3+ valence state, the ligand-to-metal (O to Cu) charge transfer energy is intriguingly negative ($\Delta \sim -1.5$ eV) and has a dominant ($\sim$60%) ligand-hole character in the ground state akin to the high Tc cuprate Zhang-Rice state. Unlike most other formal Cu^{3+} compounds, the Cu $2p$ XAS spectra of $KCuO_2$ exhibits pronounced $3d^8$ (Cu^{3+}) multiplet structures, which accounts for $\sim$40% of its ground state wave-function. $Ab\,initio$ calculations elucidate the origin of the band-gap in $KCuO_2$ as arising primarily from strong intra-cluster Cu $3d$ - O $2p$ hybridizations ($t_{\rm pd}$); the value of the band-gap decreases with reduced value of $t_{\rm pd}$. Further, unlike conventional negative charge-transfer insulators, the band-gap in $KCuO_2$ persists even for vanishing values of Coulomb repulsion U, underscoring the importance of single-particle band-structure effects connected to the one-dimensional nature of the compound.

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The electronic properties of strongly correlated transition metal (TM) oxides −which consist of partially filled TM d-orbitals hybridized with the ligand (oxygen) p-orbitals− are effectively categorized under the well known Zaanen-Sawatzky-Allen (ZSA) phase diagram [1–3], a guiding principle for materials scientists that takes into consideration the on-site d-d Coulomb interaction energy at the TM site (U) and the ligand-to-TM charge transfer energy (Δ). There is an intriguing region of the ZSA phase diagram of compounds with negative values of Δ that has been less explored [4–10]. In TM oxides the value of Δ decreases by increasing the valence (oxidation) state of the TM ion, and for unusual high valence states Δ can even become negative [8]. Such high-valence compounds are very unstable, and only a few pristine negative Δ compounds exist (see Table I). For such highly covalent compounds, it is energetically favorable to transfer an electron from the ligand to the metal ion, as the energy cost Δ for this process is negative, giving rise to a large $ligand$-$hole$ character and usually metallic nature of the ground state. However, there exists a very select number of compounds, which are insulating while having negative or extremely small values of Δ, driven by a combination of strong metal-ligand hybridization either with strong electronic correlations, as in the case of the correlated covalent insulators [4, 6, 15, 16], like in Sr_2CuO_3 [17], or describable within an effective single-particle band-structure, as in the case of $NaCuO_2$ [5, 7, 8, 15, 18, 19].

In this work, using X-ray absorption spectroscopy (XAS) experiments, model XAS and density functional theory (DFT) calculations, we have investigated the electronic structure of $KCuO_2$ [21], and have elucidated the nature of its experimentally observed insulating state. Our results suggest that $KCuO_2$ hosts Cu in a formal 3+ valence state, has a negative Δ and a dominant ligand-hole character on its ground state.

Table I. Coulomb repulsion U and charge-transfer Δ energies (in units of eV) for some transition metal oxides with unusually high formal-valence states for the B site (Fe, Co, Ni, Cu) cation.

Compound	Formal-valence	U	Δ	Transport	Ref.
$SrFeO_3$	(4+)	7.8	0.0	Metal	[2]
$BaFeO_3$	(4+)	7.1	−0.9	Insulator	[11]
$SrCoO_3$	(4+)	7.0	−5.0	Metal	[12]
$LaNiO_3$	(3+)	7.0	1.0	Metal	[13]
$LaCuO_3$	(3+)	7.0	−1.0	Metal	[14]
$NaCuO_2$	(3+)	8.0	−2.5	Insulator	[7]
$KCuO_2$	(3+)	8.0	−1.5	Insulator	this work

We find a charge band gap ($\sim$ 1.24 eV) with preponderance of O $2p$ states at the valence band and conduction band edges, which originates from strong intra-cluster Cu $3d$ - O $2p$ hybridization in this negative Δ compound and competes with point-charge Coulomb contributions to the crystal-field energies of the Cu $t_{2\rm g}$ orbitals. The chain-topology driven band-gap persists for vanishing U, which is distinct from the conventional picture of correlated covalent insulators [4, 6, 15], and also decreases with decreasing values of $t_{\rm pd}$. The inclusion of additional electron-electron correlations with the use of a non-negligible value of U is, however, necessary to account for the experimental value of the gap. Our work thus establishes that $KCuO_2$, similar to $NaCuO_2$, is a negative Δ insulator where the insulating behavior arises from single-particle band structure effects from the unique one-dimensional CuO_2 chain geometry and electron-electron correlations accounted for within an effective U term.

$Methods\,(experimental).-$ Single-phase polycrystalline $KCuO_2$ was synthesized in an orthorhombic $Cmcm$ space

group by mixing KO_2 and CuO powders in a 1:1 ratio in an Ar-filled glovebox followed by sintering under a dry O_2 atmosphere for 2.5 days at 450^{o}C [22]. XA measurements at Cu $L_{2,3}$- and O K-edges were performed on the 4-ID-C beam line of the Advanced Photon Source (APS) at Argonne National Laboratory, USA. The sample powder was mounted on the holder using carbon-tape under a nitrogen gas atmosphere to ensure minimum exposure to air, and XAS measurements in total-electron-yield (TEY), total-fluorescence-yield (TFY), and in the inverse-partial-fluorescence-yield (IPFY) modes were performed at room temperature without any additional surface preparation. The probing depth in case of the TEY ($\sim$5 nm) is much smaller than that of TFY or IPFY ($\sim$100 nm)[23], and thus, while TEY studies the under-coordinated surface electronic-structure of a solid, the TFY and IPFY are well-suited to investigate the bulk electronic-structure. The non-resonant O K-edge was monitored during IPFY measurements: these IPFY measurements are further free from any self-absorption effects that may still be present in the TFY spectra [24].

Methods (theory).– We have performed three sets of complementary calculations. To act as a reference XAS spectra, calculations of the Cu $L_{2,3}$ XA spectrum on a orthorhombic $Cmcm$ space-group lattice of $KCuO_2$ [25] (e.g., Figs. 1(a-b)) were performed using the Finite Difference Method Near-Edge Structure (FDMNES) code [26]. The FDMNES calculations were performed using the full-multiple-scattering theory with a cluster radius of 6 Å around the absorbing Cu atom and an on-site Coulomb energy (U) of 8 eV.

In order to determine the relative TM-O covalencies, cluster calculations for simulating the Cu $L_{2,3}$ XA spectrum of a single CuO_2 planar-cluster with a D_{4h} symmetry [27] were performed using the Charge Transfer Multiplet program for X-ray Absorption Spectroscopy (CTM4XAS) [28]. The charge transfer energy Δ between Cu $3d$ and O $2p$ orbitals is defined as $E(d^{n+1}\underline{L}) - E(d^n)$, where $E(d^n)$ is the multiplet-averaged energy for n-electron occupancy on Cu $3d$ levels and $E(d^{n+1}\underline{L})$ denotes the multiplet-averaged energy obtained after transferring one electron from an O $2p$ level to the Cu $3d$ level having n=8 electrons, corresponding to the formal (3+) valence state of Cu. For the CTM4XAS calculations, the basis size was restricted up to one electron charge-transfer from O $2p$ to Cu $3d$.

To determine the density of states (DOS) of $KCuO_2$ and $NaCuO_2$, the rotationally invariant LDA+U scheme of Dudarev *et al.* [29] was employed in DFT electronic structure calculations. Calculations were carried out with the *Vienna Ab initio Simulation Package* (VASP) [30] using projector-augmented wave pseudopotentials [31, 32]. The first Brillouin zone was sampled using a 12×12×6 Monkhorst-Pack set of k-points and a 400 eV energy cutoff.

Results and discussion.– Two distinct groups of experimentally-observed XAS peaks, one around 930 eV (L_3 region) and another group around 950 eV (L_2 region) can be clearly identified for the Cu $L_{2,3}$-edge of $KCuO_2$ (c.f., Fig. 1(c)). While the spectral features for the L_3 and L_2 regions are nearly identical, they are separated by about 20 eV due to the 3/2 × Cu $2p$ core-spin-orbit coupling. Looking around the Cu L_3 region closely, we observe two intense peaks at 930.3 eV and 932.3 eV, which correspond to the Cu d^9 and the Cu $d^9\underline{L}$ initial states, respectively [33–35].

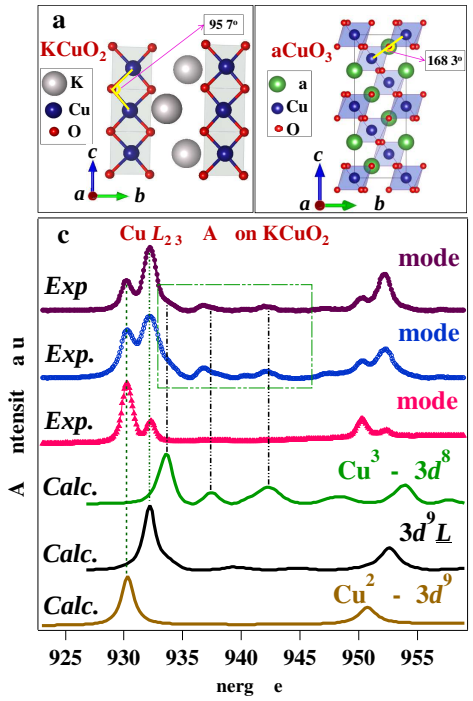

Figure 1. (Color online) Schematic crystal structures showing (a) edge-sharing of CuO_4 units in $KCuO_2$ and (b) corner-sharing of CuO_6 clusters for $LaCuO_3$. (c) Cu $L_{2,3}$ X-ray absorption (XA) spectra of $KCuO_2$ collected in the inverse-partial-fluorescence-yield (IPFY), the total-fluorescence-yield (TFY) and the total-electron-yield (TEY) modes. Calculated XA spectra (solid lines) of $KCuO_2$ with the FDMNES code for $3d^9$, $3d^8$ and $3d^9\underline{L}$ configurations are also shown.

The d^9 (Cu^{2+}) peak intensity increases significantly in the TEY mode as compared to the TFY and IPFY modes, indicating an abundance of Cu^{2+} valence states on the surface (see Methods section). This Cu^{2+} presence is believed to arise due to the presence of surface impurity phases rich in Cu^{2+}. Note that similar peaks of d^9 (Cu^{2+}) have been observed for other formally Cu^{3+} compounds in the XA spectrum (e.g., $NaCuO_2$ [5, 8, 33], $CaCu_3Co_4O_{12}$ [35] and Cs_2KCuF_6 [36]). Cu^{2+} impurity phases on the surfaces of these metastable compounds arises due to the loss of superficial anionic atoms during XAS experiments in ultra-high vacuum which effectively reduces the valence of surrounding Cu ions [8]. Further, we observed that $KCuO_2$ on exposure to air decomposes into CuO within five to ten minutes. Thus, given these constraints, it is impossible for us to avoid the Cu^{2+} related impurity peak in the XAS experiments. Within the bulk, $KCuO_2$ is not expected to suffer from such anionic losses and, accordingly, much lower intensity Cu^{2+} peaks in the bulk-sensitive TFY and IPFY XAS spectra are observed in Fig. 1(c). Some per-

centage of the TFY and IPFY signals are also contributed from the surface and near-surface region of the sample, which is dominant due to powder nature of $KCuO_2$ sample as compared to scraped bulk-polycrystalline pellet of $NaCuO_2$ [33], that still provides significant contributions of the d^9 peak. The differences in relative spectral weights among IPFY and TFY data [37] are assigned to known self-absorption effects [24] on the TFY spectra.

Focussing henceforth on the IPFY spectrum, as it is both bulk-sensitive and free from self-absorption effects, the main peak given by the $d^9\underline{L}$ state arises due to the charge transfer of an electron from the surrounding O atoms into formally Cu $3d^8$ (Cu^{3+}) state [33–35]. Furthermore, distinct multiplet-structures –that are considered to provide clear evidence for the presence of an ionic Cu^{3+} (d^8) state [33–35]– are observed around 940 eV. The presence of significant $d^9\underline{L}$ and d^8 intensities suggests that a coherent superposition of both states constitutes the ground state of formal Cu^{3+} ions in $KCuO_2$, similar to that of $NaCuO_2$ [33]. It is important to note that on a Cu $2p$-$3d$ XAS process it is difficult to detect contributions from the $d^{10}\underline{L}^2$ level to the ground-state. However, such contributions are usually small, as determined by X-ray photo-electron spectroscopy on related systems [8].

To further establish the origin of the various features in the experimental XAS spectra, we simulated the Cu $L_{2,3}$ XAS spectra of $KCuO_2$ that corresponds to the d^8, d^9 and $d^9\underline{L}$ initial state configurations using the FDMNES code. As shown by the vertical guide lines in Fig. 1(c), the calculated XAS spectra corresponds to the d^9 and $d^9\underline{L}$ features in the experimental spectra, and the observed ionic d^8- experimental features can be broadly understood with the calculated spectrum for the d^8 ionic Cu^{3+} state.

We now compare the L_3 energy region for $KCuO_2$ with other systems that host unusual valence states of Cu, such as the optimally-doped $YBa_2Cu_3O_{7-\delta}$ (YBCO) [35], $LaCuO_3$ [35], and $NaCuO_2$ [33] in Fig. 2(a), after subtraction of the surface Cu^{2+} impurity peak [38, 39]. It is interesting to note that the Zhang-Rice spin-singlet-state, $d^9\underline{L}$ [40, 41], which arises due to external hole-doping in YBCO by chemical routes [33], naturally becomes the dominant state in formally Cu^{3+} compounds. This hole-doping mechanism is akin to a self-doping effect [20]. Judging from the intensity ratios shown in Fig. 2, the $d^9\underline{L}$ charge-transfer state appears dominant over the ionic d^8 state for $KCuO_2$, $NaCuO_2$ and $LaCuO_3$, thus suggesting that the associated charge transfer energies Δ for all of these compounds are unusually *negative*. We note that negative values of Δ have been already proposed for insulating $NaCuO_2$ [5, 7, 8] and metallic $LaCuO_3$ [14].

A closer analysis of the XA shapes on Fig. 2(a) points to spectral differences within several formal Cu^{3+} compounds. Let us focus on the differences in the XA spectral features related to the $d^9\underline{L}$ state first: The $d^9\underline{L}$ peak for $LaCuO_3$ is broad and can be well described using two peaks, one centered at 930.8 eV and another at 932.2 eV. This splitting occurs from the delocalization of the ligand-hole, due to inter-cluster hybridization effects that are aided by the corner-sharing geometry of the CuO_6 clusters with Cu-O-Cu bond angle of 168.3° in $LaCuO_3$ [14] (c.f., Fig. 1(b)). For $KCuO_2$ and $NaCuO_2$, on the other hand, such inter-cluster hybridization effects are negligible due to the near-orthogonal Cu-O-Cu bond-angle (95.7°) between neighboring CuO_4 clusters (c.f., Fig. 1(a)) and a single $d^9\underline{L}$ peak is observed.

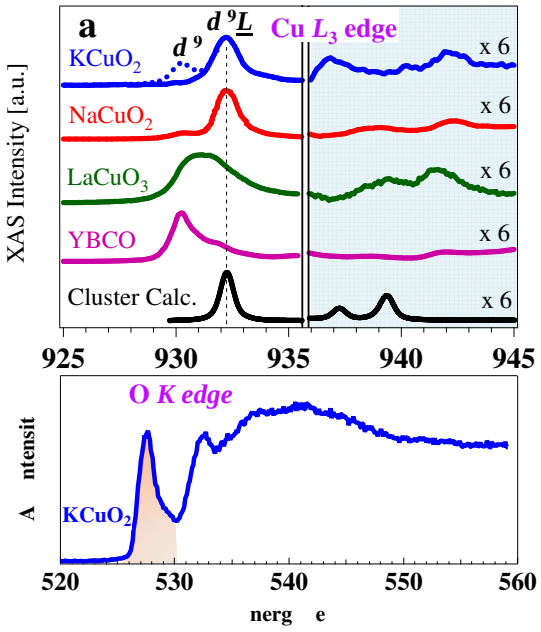

Figure 2. (Color online) (a) Cu L_3 X-ray absorption (XA) spectra of $KCuO_2$, $NaCuO_2$ [33], $LaCuO_3$ and $YBa_2Cu_3O_{7-\delta}$ (YBCO). The main Cu L_3 peak in $KCuO_2$ and $NaCuO_2$, and the shoulder in YBCO around 932 eV correspond to the $d^9\underline{L}$ Zhang-Rice singlet state. The d^8 multiplet structures six-fold-increased for easier observation are also shown. The calculated XAS spectrum for a single undistorted CuO_4 cluster of D_{4h} symmetry and corresponding to Δ = -1.5 eV is also shown. (b) The O K-edge XA spectrum of $KCuO_2$ consists of a pronounced pre-peak around 527.6 eV (shaded area) suggesting a large ligand-hole character of its ground state.

The d^8 multiplet region of formally Cu^{3+} compounds shown by the shaded area in Fig. 2(a) is discussed next. Covalency and Δ are not independent, since the relative intensities between the d^8 multiplets to the $d^9\underline{L}$ peak usually increase with decreasing covalency, and their energy separation increases with larger negative values of Δ [36]. $KCuO_2$ has stronger multiplet intensities than iso-structural $NaCuO_2$, which suggests a larger contribution of the ionic d^8 state to its ground state. Further, the average energy difference between the d^8 multiplets and the $d^9\underline{L}$ peak is 5.9 eV and 8.2 eV for $KCuO_2$ and $NaCuO_2$, respectively, thus showing a smaller negative Δ for $KCuO_2$.

For the calculated Cu $L_{2,3}$ XA spectra on a single CuO_4 cluster with planar D_{4h} symmetry [42], we optimized the parameter values to match the calculated energy separations between the average d^8 multiplets and the $d^9\underline{L}$ main peak with energy differences obtained from experiment (Fig. 2(a)). The estimated Δ, thus obtained, turned out to be -1.5 eV

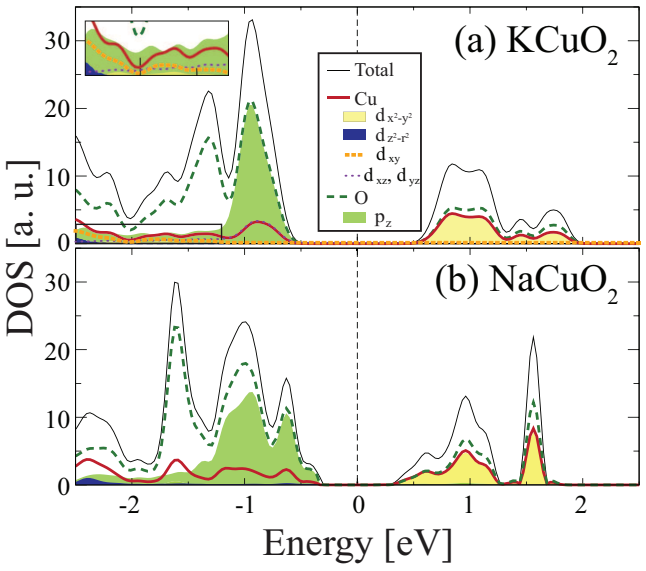

Figure 3. (Color online) Density of states for (a) $KCuO_2$ and (b) $NaCuO_2$; the total contributions from a given atomic species are indicated by trendlines and the orbital projections are shown by colored area plots. A U of 8 eV was used for these calculations. $KCuO_2$ is found to exhibit a larger bandgap than $NaCuO_2$.

and -2.5 eV for $KCuO_2$ and $NaCuO_2$ respectively. Furthermore, both the resultant ground states have dominant $d^9\underline{L}$ characters, $39\%d^8 + 61\%d^9\underline{L}$ ($36\%d^8 + 64\%d^9\underline{L}$) for $KCuO_2$ ($NaCuO_2$), with a higher ionic character for the ground state of $KCuO_2$, as suggested earlier.

The O K-edge XA spectrum $-$which probes the ligand hole-states$-$ exhibits a pronounced pre-peak for $KCuO_2$ at 527.6 eV, as seen in Fig. 2(b). The intensity of the O K-edge pre-peak correlates directly with the amount of ligand-hole character in the ground state [36], thus the strong pre-peak in $KCuO_2$ further establishes a large $d^9\underline{L}$ character of its ground state.

Fig. 3 shows the density of states (DOS) projected onto orbital contributions for $KCuO_2$ and $NaCuO_2$, which were found to have insulating gaps of 1.24 eV and 0.62 eV respectively for the U value of 8 eV. The band-gaps in $KCuO_2$ and $NaCuO_2$, however, exist even for $U = 0$ eV, in agreement with previous observations on $NaCuO_2$ [7, 15, 18], highlighting the role of single-particle band-structure effects due to the chain topology in giving rise to the insulating state in $KCuO_2$. The inclusion of correlations, however, is essential in increasing the band-gap value as compared to $U = 0$ eV and bringing it to the agreement with the experimental value [8]. Furthermore, the projected DOS shows a strong O character in both valence and conduction band edges [43]. The Cu t_{2g} levels occur between the lower-lying $3d_{3z^2-r^2}$ and higher-lying $3d_{x^2-y^2}$ levels, as usually observed for one-dimensional CuO_2 chains due to point charge (Coulomb) contribution [44]. However, the t_{2g} levels is intriguingly seen to have Cu (d_{xz}) and Cu(d_{yz}) character immediately below E_F and Cu d_{xy} character only at further lower energies, which is different from a point charge (Coulomb) contribution to crystal-field splitting. Similar effect has been observed in $Cs_2Au_2Cl_6$, and arises from a dominant pd covalency contribution in case of negative Δ compounds [10]; the inversion of the t_{2g} orbitals thus further confirms the negative Δ in $KCuO_2$.

We also performed a Bader analysis [45] to understand the charge density distribution over electronic orbitals. The total occupation of Cu $3d$-shell in both systems is 8.8, which represents a mixture of d^8 and d^9 states, in qualitative agreement with cluster calculations and establishing the superposition of both contributions to the ground state of formally Cu^{3+} ions in $KCuO_2$ and $NaCuO_2$, as discussed earlier.

Conclusions.– We have described the presence of the anomalous charge state of Cu in $KCuO_2$ from experiment and theory. We established the negative charge transfer energy of the $KCuO_2$ ground state and its dominant ligand-hole character, which arise due to large intra-cluster hybridization effects and remain localized due to weak inter-cluster hybridizations. Localized cuprate like Zhang-Rice singlet state thus occur at every unit cell, which consequently gives rise to the experimentally observed insulating and diamagnetic character of $KCuO_2$ [20, 21]. Moreover, $KCuO_2$ exhibits strong d^8 related multiplet structures, resulting from the large ionic Cu^{3+} character of its ground-state. $KCuO_2$ is shown to belong to the unusual class of covalency driven negative charge transfer with the correlated gap that is adiabatically connected to the single-particle gap arising the chain geometry of the compound.

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[37] The d^9 peak in the TFY spectra does not suffer from self-absorption effects as the impurity phases containing Cu^{2+} ions lie only over the sample surfaces. However, self-absorption effects affect the $d^9\underline{L}$ TFY peak intensity, since it arises from formal Cu^{3+} ions present in high concentrations and spread over the bulk of the sample.

[38] An arc-tangent background function was subtracted from the spectra first, followed by multi-peak-fitting analysis of the L_3 edge; the peak corresponding to Cu^{2+} (shown with the dashed line in Fig. 2(a)) was subtracted subsequently.

[39] The XA spectrum of $NaCuO_2$ in Fig. 2(a) is taken from Ref. [33].

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[42] D_{4h} effective ligand field parameters: $10D_q$ = 2.5 eV, D_t = 0.24 eV, D_s = 0.19 eV; and Coulomb correlations U_{dd}=8.0 eV and U_{pd} = 10.5 eV were used. The metal-ligand mixing interaction (T_{B1g}) optimized to -2.42 eV and -3.46 eV was used for $KCuO_2$ and $NaCuO_2$, respectively.

[43] Due to the extended nature of the O p orbitals, the decomposition of the total DOS by projecting on the LAPW spheres is known to underestimate the O p character [18], thus the valence and conduction bands have larger O p character than that obtained under the LDA+U scheme.

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