Intrinsic Origins of Crack Generation in Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Layered Oxide Cathode Material

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Ni-rich LiNi$_x$Co$_{y}$Mn$_{1-x-y}$O$_2$ layered oxide cathodes have been highlighted for large-scale energy applications due to their high energy density. Although its specific capacity is enhanced at higher voltages as Ni ratio increases, its structural degradation due to phase transformations and lattice distortions during cycling becomes severe. For these reasons, we focused on the origins of crack generation from phase transformations and structural distortions in Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ using multiscale approaches, from first-principles to meso-scale phase-field model. Atomic-scale structure analysis demonstrated that opposite changes in the lattice parameters are observed until the inverse Li content $x = 0.75$; then, structure collapses due to complete extraction of Li from between transition metal layers. Combined-phase investigations represent the highest phase barrier and steepest chemical potential after $x = 0.75$, leading to phase transformations to highly Li-deficient phases with an inactive character. Abrupt phase transformations with heterogeneous structural collapse after $x = 0.81$ (~220 mAh g$^{-1}$) were identified in the nanodomain. Further, meso-scale strain distributions show around 5% of anisotropic contraction with lower critical energy release rates, which cause not only micro-crack generations of secondary particles on the interfaces between the contracted primary particles, but also mechanical instability of primary particles from heterogeneous strain changes.

Ni-rich transition metal layered oxides (LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$, with $x > 0.5$, Ni-rich NCM) have been spotlighted during the past decade as the most promising candidates for high capacity cathode materials in Li-ion batteries (LIBs) due to their high energy densities (>$200$ mAh g$^{-1}$ until ~4.6 V vs. Li/Li$^+$)1–3. Although LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111) has been successfully commercialized, in order to meet the demand for large-scale energy storage applications such as electric vehicles (EVs) and energy storage systems (ESSs), further NCM research and development have been directed toward enhancing its specific capacity by increasing the ratio of the Ni component toward LiNi$_{x}$Co$_{y}$Mn$_{1-x-y}$O$_2$ (NCM811)4–6.

While the increase of the Ni ratio in NCM contributes to an enhanced specific discharge capacity, it also results in severe capacity degradation caused by cation mixing, surface side reactions, and crack propagation with structural instability1. To better understand these challenges, Jung et al. investigated the degradation mechanism of the phase transformation induced by cation mixing from the surface to bulk using ex situ structural analysis7. Similarly, Lin et al. described the surface reconstruction and chemical evolution of the rhombohedral layered structure to a cubic spinel structure using high-throughput X-ray absorption spectroscopy8. As theoretical approaches, electronic correlations for the redox reactions between the multivalent transition metals in the Ni-rich NCM9 and stability analysis with respect to the various ratios of the Ni, Co, and Mn components in the NCM10 have been performed through first-principles calculations. On the bases of these fundamental data, many researchers have suggested solutions to resolve the cyclic degradation problem. Along with diverse approaches such as morphology control11, elemental doping12–17 and surface coating18–20, Sun et al. have suggested various effective ways to reduce cyclic degradation and improve electrochemical performance through the design of core-shell11, gradient core-shell12,21, and full concentration gradient structures2,21,24 for Ni-rich NCM cathodes.

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Nevertheless, micro-crack propagation in the secondary particle related to structural instability remains problematic, although cation mixing and surface deterioration can be prevented through the above-mentioned approaches. Among the promising Ni-rich compounds, severe structural changes and crack propagation have been reported experimentally in LiNi₁₋ₓCoₓAlₓO₂ (NCA) cathodes. Although, Meng et al. recently reported the experimental observation of micro-crack generation of NCM811 with severe cyclic degradation and suggested surface coating with Li₂TiO₃ to mitigate the crack propagation, the fundamental origin has not been adequately addressed for the Ni-rich NCM cathodes. Moreover, the underlying mechanism for the phase transformation and structural changes in NCM811 is not fully understood. For these reasons, we focused on the study of intrinsic characteristics of the phase transformation and structural changes of NCM811 to elucidate its inherent structural instability regardless of cation mixing and surface deterioration.

Through multiscale phase-transformation mechanics based on first-principles calculations, here, we investigated the fundamental reaction mechanism, structural distortions, thermodynamic combined-phase (CP) behaviours, and meso-scale phase-separation kinetics for NCM811 with respect to varying Li concentration. Since the redox reactions during cycling mainly involve the Ni and O ions, the Co and Mn ions would retain similar electronic structures before and after delithiation. Anisotropic structural changes are observed between the ab plane and c axis, which result in anisotropic shrinkage of the entire structure. In particular, an abrupt collapse of the structure is observed for an inverse Li content x = 0.75–1.0 in Li₁₋ₓNi₀.₈₅Co₀.₆₅Mn₀.₆₅O₂. The CP behaviour shows generally one-phase reactions with lower phase barriers below x = 0.75. However, a two-phase region with a remarkably higher phase barrier is presented after x = 0.75 and inactive phases are formed, which not only agrees well with the experiments of Ozhukov et al. but also correlates with the collapse of the structure after x = 0.75. Based on these first-principles calculation results, meso-scale phase separation simulations were performed, which reveals heterogeneous phase transformations and structural changes at different Li concentrations. Therefore, an intrinsic limitation of NCM811 exists in the region x = 0.75–0.81 (~220 mAh g⁻¹) due to the inactive phase separation and abrupt structural changes. Around 5% of the anisotropic contraction was observed in the nanodomain, which induces the contractions of the primary particles. In addition, very low critical energy release rates for crack generation of fully-lithiated and delithiated NCM811 were calculated. Such large volume reduction and low critical energy release rate could be the reason of causing the micro-crack generations in the secondary particles on the interfaces between the contracted primary particles. Further, the heterogeneous strain changes cause severe mechanical instability within the primary particles, which could be the reason of the generation of nano-cracks as a seed of the micro-cracks. These findings should provide helpful insights for the development of Ni-rich NCM cathode materials in the Li-ion battery research community.

**Results and Discussion**

**Redox Mechanism and Structural distortion.** Figure 1a and b show the atomic model used for the first-principles calculations projected on the bc and ab planes, respectively. The atomic model was developed based on the rhombohedral layered oxide structure (R-3m) of LiNiO₂ (Inorganic Crystal Structure Database (ICSD) ID: 10499). To represent the stoichiometry of NCM811, supercells of 2 x 2 x 1 with 12 f.u. were used; the exact stoichiometry of the supercell in this study is LiNi₀.₈₃Co₀.₀₈₃Mn₀.₀₈₃O₂ (Li₁₂Ni₁₀Co₁Mn₁O₂₄). The model was developed using high-throughput calculations based on previously described schemes. As shown in Fig. 1a, Co and Mn are located separately in the Ni-rich environment of the layered oxide structure, which would be thermodynamically related to d-electronic stability of the crystal field. To understand the thermodynamic phase transformations, the CP redox reaction of NCM811 consists of two one-phase reactions and the volumetric collapse (0.75 < x < 1.0) due to the rapid volume reduction, as shown in Fig. 3b, which is caused by the complete extraction of Li ions from between the transition metal layers. Therefore, the structural changes of NCM811 during electrochemical reactions are likely to be harmful to the cyclic performance due to the lattice distortions in opposing directions (0.0 < x < 0.75) and the volumetric collapse (0.75 < x < 1.0).

**Heterogeneous Phase Transformation.** To understand the thermodynamic phase transformations, the phase behaviours were investigated by calculating the DFT mixing enthalpies H_{mix}(x) with respect to normalized inverse Li content x using Eq. (1), as presented in Fig. 4a. Seven ground states are observed, including the initial (x = 0) and final (x = 1) states. The CP redox reaction of NCM811 consists of two one-phase reactions (0.0 < x < 0.1667; 0.3333 < x < 0.4167) and three two-phase reactions (0.1667 < x < 0.3333; 0.4167 < x < 0.75; 0.75 < x < 1.0). To predict the electrochemical behaviour, Fig. 4b presents the OCVs based on the ground states
in Fig. 4a, the shape of the curve is similar to the experimental OCV values for LiNiO2 estimated previously by the galvanostatic intermittent titration technique (GITT). By considering the configurational entropy at a finite temperature (300 K), more general phase behaviours can be understood using the CP free energy $f_{CP}(x)$ and the CP chemical potential $\mu_{CP}$ of Eqs (2) and (3), as shown in Fig. 5. Spinodal regions, where two-phase reactions occur, are indicated as green shaded regions in Fig. 5. Figure 5a shows that the first and second phase barriers from $x = 0.21$ to $0.30$ and from $x = 0.50$ to $0.67$ are low, but the third phase barrier from $x = 0.81$ to $0.93$ is remarkably steep and higher than the others. This means that phase separations are likely to be impeded due to the low phase barriers and the low slopes of the chemical potentials before $x = 0.75$, such that relatively smooth reactions similar to the one-phase reaction can be generated, rather than the two-phase reaction. In contrast, after $x = 0.75$, rapid phase separation by a two-phase reaction is likely to occur as indicated by the higher phase barrier in Fig. 5a and the sharp slope of the chemical potential in Fig. 5b. More importantly, the strong phase separation after $x = 0.75$ results in a highly Li-deficient phase ($Li_{0.8}Ni_{0.1}Co_{0.1}O_2$), leading to severe structural transformations to inactive phases such as the NiO rock salt phase previously observed by ex situ transmission electron microscopy in Ni-rich NCM.

**Origins of Crack Generation.** To describe the meso-scale phase transformations of LiNi0.8Co0.1Mn0.1O2 in a nanodomain with dimensions of 31.36 nm $\times$ 31.36 nm at 300 K, a phase-field model analysis was conducted by solving Eqs (9) and (10). As simulation parameters, we set $D$ as $10^{-8}$ cm$^2$ s$^{-1}$ based on an experimental value, $\lambda$ as 0.49 nm from the interlayer distance of the atomic model, and the $\varepsilon_{ij}$ values as $\varepsilon_{0,1667} = 128.66$ eV, $\varepsilon_{0,4167} = 7.85$ eV, and $\varepsilon_{0,77} = 169.95$ eV. The phase transformation simulations were carried out on the ac plane during relaxation from the solid solution at $x = 0.65$ (Fig. 6a) with a theoretical charge capacity of $\sim 179$ mAh g$^{-1}$ and $x = 0.85$ (Fig. 6e) with a theoretical charge capacity of $\sim 234$ mAh g$^{-1}$. The $a$, $c$, and volumetric strains (denoted as $\varepsilon_a$, $\varepsilon_c$, and $\varepsilon_V$, respectively) are displayed in Fig. 6b ($x = 0.65$) and f ($x = 0.85$), 6c ($x = 0.65$) and 6d ($x = 0.85$), and 6g ($x = 0.85$), respectively. The strains are defined as $\varepsilon_a = \Delta a/a_{x=0}$, $\varepsilon_c = \Delta c/c_{x=0}$, and $\varepsilon_V = \Delta V/V_{x=0}$, where $a$ and $c$ are the lattice parameters and $V$ is the volume, respectively. Finally, 2D diffusion in the $a$ and $b$ directions was applied, and the phase separation was triggered by random noise.

From the distribution of the inverse Li concentration, distinct phase separation is observed in Fig. 6e at $x = 0.85$, correlated with the sharp slope of the chemical potential in Fig. 5b, but only slight phase separation is observed in Fig. 6a at $x = 0.65$. For this reason, smooth electrochemical reactions may be possible until $x = 0.65$ ($\sim 179$ mAh g$^{-1}$), but phase separation to an inactive phase ($Li_{0.8}Ni_{0.1}Co_{0.1}Mn_{0.1}O_2$) should occur at $x = 0.85$ ($\sim 234$ mAh g$^{-1}$), meaning that the third spinodal region from $x = 0.81$ to 0.93 induces intrinsically irreversible
**Figure 2.** (a,b,c,d) Partial density of states (PDOSs) of (a) Ni d- (gray solid line), (b) Co d- (blue solid line), (c) Mn d- (purple solid line), and (d) O p- (red solid line) orbitals in LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}. (e,f,g,h) PDOSs of (e) Ni d- (gray dashed line), (f) Co d- (blue dashed line), (g) Mn d- (purple dashed line), and (h) O p- (red dashed line) orbitals in Li_{0.0}Ni_{0.8}Co_{0.1}Mn_{0.1}O_{2}. The Fermi level is 0.0 eV (green dotted line).

**Figure 3.** (a) Calculated a (blue inverse triangles and solid line, left axis) and c lattice parameters (red triangles and solid line, right axis), and (b) volume of cell (black circles and solid line) with respect to the inverse Li content x in Li_{1-x}Ni_{0.8}Co_{0.1}Mn_{0.1}O_{2}. 
characteristics. Furthermore, from a structural perspective, at $x = 0.65$, not only are contraction strains of $\varepsilon_1$ and $\varepsilon_3$ observed, but also slight differences occur between $\varepsilon_1 (-6 \times 10^{-6} < \varepsilon_1 < -6 \times 10^{-7})$ and $\varepsilon_3 (0.027 < \varepsilon_3 < 0.028)$, as shown in Fig. 6b and c. Fortunately, the extent of structural change can be considered as reasonably small; e.g., the difference in $\varepsilon_V$ is less than $4 \times 10^{-4}$, as illustrated in Fig. 6d. Severe structural distortions occur at $x = 0.85$. All the absolute changes in the three strains at $x = 0.85$ are remarkably larger than those at $x = 0.65$: $\varepsilon_1$ changes relatively slightly ($-0.032 < \varepsilon_1 < -0.027$), whereas $\varepsilon_3$ and $\varepsilon_V$ vary by as much as 5% ($0.018 < \varepsilon_3 < 0.043$, $-0.047 < \varepsilon_V < -0.018$) (Fig. 6f,g and h, respectively). Videos attached in the supplementary information illustrate the specific evolution of the inverse concentration of Li and the volumetric strain.

In the meso-scale phase transformation phenomena, the structural distortions are heterogeneously generated in the nanodomain due to the blocking of diffusion in the $c$ direction and the rapid phase separation, which is
shown in the apparent red and blue regions of Fig. 6f,g and h. Therefore, the structural changes in NCM811 occur more severely in the third spinodal region, and, combined with the abrupt phase separation, limit the intrinsic specific capacity to less than 220 mAh g\(^{-1}\) for \(x = 0.81\). As shown in Fig. 7, the around 5% of anisotropic contraction and the ~3.9% of average contraction (Fig. 6h) in the nanodomain would cause the contraction of each primary particle, and then the gaps between the primary particles would result in the micro-crack generations in the secondary particles on the interfaces between the primary particles, which could be the origins and mechanism on the experimental observations of the micro-crack propagations\(^{25-29}\). Further, the heterogeneous distribution of the anisotropic strain changes causes the severe mechanical instability of the primary particles that could induce the generation of nano-cracks, which could be a crack opening of the micro-cracks.

In addition, Table 1 shows critical energy release rates of Li\(_{1-x}\)Ni\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) and Li\(_{0}\)Ni\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) calculated by DFT, which describe the critical energy for the crack generation and are related to the surface energy \(\gamma\) for brittle materials \((G_c = 2\gamma)\) based on Griffith’s theory. Though fully-lithiated NCM811 has low \(G_c\) (2.4308 J m\(^{-2}\)), the delithiated NCM811 has even lower \(G_c\) (~0.0064 J m\(^{-2}\)), which would result from the structural instability
between layers at lower Li concentrations. In other words, not only NCM811 is fragile to crack generation, but also it gets weakened at delithiated states, which means the 5% of anisotropic contraction could be enough to generate crack propagations.

Recently, Meng et al. reported that the severe crack generation in NCM811 particles induces a significant performance degradation [28]. According to the scanning electron microscopy (SEM) observation, particle fractures and fragmentation of NCM811 particles were evident after cycles. Due to this crack generation, the discharge capacity of NCM811 was remarkably decreased with increasing overpotentials during cycles. From our fundamental understanding, we suggest that the origin of crack generation is the contraction of primary particles with a mechanical instability caused by heterogeneous phase transformation and anisotropic strain changes. In addition, the lower $G_c$ at delithiated states contributes to a severe crack propagation. Finally, it is expected that these could be resolved by reducing the inhomogeneity and anisotropy of structural changes and increasing $G_c$.

### Conclusion

The intrinsic limitations of a Ni-rich NCM811 cathode material were investigated in terms of its phase transformations and structural distortions using multiscale approaches combining first-principles calculations and the CP phase-field model. The major redox mechanism of NCM811 was determined as a combination of the cationic redox reactions of Ni with the anionic redox reactions of O. The atomic-scale structural analysis showed that opposite lattice changes are generated until $x = 0.75$, followed thereafter by the gradual decrease all of the lattice parameters due to the collapse of the transition metal layers. The CP behaviours represent the three two-phase reaction regions, wherein the third exhibits a higher phase barrier and a sharp rise in the chemical potential. This causes rapid phase separation, forming an inactive and highly Li-deficient phase. In the meso-scale phase transformation, heterogeneous phase separations are observed, and severe phase transformation occurs near the third spinodal region at $x = 0.85$. Further, the ~3.9% of the average contraction and lower critical energy release rates including the heterogeneous distribution of the anisotropic strain changes observed by the meso-scale strain distributions could induce not only the nano-cracks in the nanodomain of the primary particles from the severe mechanical instability, but also the micro-crack generations on the interfaces between the contracted primary particles. Thus, the combination of the abrupt transformations to inactive phases with the heterogeneous collapse of the layered structure limits the intrinsic performance of NCM811. These findings may help to predict the maximum performance of Ni-rich NCM cathodes, and the mechanistic insights on the phase transformations and structural distortions could provide clues toward improving cathode materials for battery applications.

### Methodology

**First-principles calculations.** For the atomic-scale simulations, first-principles calculations were conducted using spin-polarized density functional theory (DFT) with the generalized gradient approximation (GGA) according to the Perdew-Wang 91 exchange-correlation functional [42]. The Vienna Ab Initio Simulation Package (VASP) was utilized to implement a plane-wave basis set and the projector-augmented wave (PAW) method [43,44]. To evaluate accurate electrochemical and $d$-orbital electronic properties, the Hubbard $U$ parameter was used [45]. The $U$ values for Ni, Co, and Mn (6.7, 4.91, and 4.64, respectively) were chosen from previous reports [37,46]. As computational parameters, a plane-wave cut-off energy of 500 eV and $k$-point meshes of $4 \times 4$ for Brillouin zone sampling were determined by a convergence test. The atomic model for NCM811 was developed by the 12 formula units ($f.u.$) of LiNi$_{0.833}$Co$_{0.083}$Mn$_{0.833}$O$_2$ using high-throughput calculations [31–35]. All the calculations were based on fully relaxed structures.

**Combined-phase (CP) phase transformation mechanics.** For the multiscale analyses from the atomic- to meso-scale, we adopted the CP transformation model [47,48] and the Cahn-Hilliard equation [49].

First, the DFT mixing enthalpy $H_{CP}(x)$ with respect to the normalized inverse Li content $x$ from 0.0 to 1.0 for battery electrodes can be defined as follows:

$$
H_{CP}(x) = E_{CP}^{DFT} - (1 - x)E_{L_1-xNi_{0.8}Co_{0.1}Mn_{0.1}O_2}^{DFT} - xE_{L_1-xNi_{0.8}Co_{0.1}Mn_{0.1}O_2}^{DFT},
$$

(1)

where $E_{L_1-xNi_{0.8}Co_{0.1}Mn_{0.1}O_2}$ represents the total energy of Li$_1$-Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ as calculated from DFT calculations. From the convex hull analysis of $H_{CP}(x)$, the CP free energy $f_{CP}(x)$ and the CP chemical potential $\mu_{CP}$ at finite temperature by considering the configurational entropy [50] can be determined based on the CP mixing enthalpy $H_{CP}(x)$ as follows:

$$
f_{CP}(x) = H_{CP}(x) + k_B T (x \ln x + (1 - x) \ln(1 - x)),
$$

(2)

$$
\mu_{CP} = -\frac{\partial f_{CP}}{\partial x},
$$

(3)

### Table 1. Critical energy release rates $G_c$ for a crack generation of Li$_{1-x}$Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ and Li$_{0.85}$Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ based on Griffith’s theory.

| Composition                  | Critical Energy Release Rate $G_c$ |
|------------------------------|-----------------------------------|
| Li$_{1-x}$Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ | 2.4388 m$^{-1}$                  |
| Li$_{0.85}$Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ | -0.8064 m$^{-1}$                  |
$$H_{CP}(x) = \sum \varepsilon_f(x - x_i)^2(x_f - x_i)^2, \quad x_i \leq x \leq x_f,$$

(4)

where, $k_B$ and $T$ represent the Boltzmann constant and absolute temperature, respectively. Furthermore, the enthalpy coefficient $\varepsilon_f$ in the reaction regions from $x_i$ to $x_f$ is obtained by parameterization from the CP mixing enthalpy $H_{CP}^f(x)$ as follows:

$$H_{CP}^f(x) = \frac{E_{Li_{1-x}Ni_xCo_{0.1}Mn_{0.9}O_2}^{DFT} - E_{Li_{1-x}Ni_xCo_{0.1}Mn_{0.9}O_2}^{DFT}}{x_f - x_i} - \frac{E_{Li_{1-x}Ni_xCo_{0.1}Mn_{0.9}O_2}^{DFT} - E_{Li_{1-x}Ni_xCo_{0.1}Mn_{0.9}O_2}^{DFT}}{x_f - x_i}.$$

(5)

The open-circuit voltage (OCV) $V_{DFT}$ was calculated using DFT at $0$ K as follows:

$$V_{DFT}^{f} = \sum (x, x_f) \left( E_{Li_{1-x}Ni_xCo_{0.1}Mn_{0.9}O_2}^{DFT} - (x_f - x_i) \mu_f \right).$$

(6)

To solve the meso-scale phase transformation phenomena, the CP Cahn-Hilliard energy function $G_{CP}$ was defined as follows:

$$G_{CP} = \int_V \rho V \left( f_f + \frac{\kappa_f^2}{2} |\nabla x_f| \right) dV,$$

(7)

where, $\rho$ represents the number of sites per volume $V$ and $\kappa^f$ is the gradient energy coefficient determined by the characteristic length $\lambda$ and enthalpy coefficient $\varepsilon_f$ as follows:

$$\kappa^f = \frac{2}{3} \lambda^2 \varepsilon_f.$$

(8)

We applied the semi-implicit Fourier-spectral method with a periodic boundary condition (PBC) to compute the Cahn-Hilliard equation. For non-dimensionalization, $k_B T$, $\lambda$, and $D/\lambda$ were used as the dimensionless energy, length, and time scales with the use of the diffusion coefficient $D$, respectively. Based on these dimensionless parameters, the Cahn-Hilliard equation can be written as follows:

$$\frac{\partial \nabla^2}{\partial t} = \nabla \left( \frac{\partial f_f}{\partial x} \right) + \kappa_f^2 \nabla^2 x = \nabla \left( h(x) + \kappa_f^4 \nabla^2 x \right).$$

(9)

Then, Eq. (9) can be re-written on the Fourier space with a wave vector $k$ as follows:

$$\frac{\partial \hat{k}}{\partial t} = -k^2 h_k - \kappa_f^4 k^4 x_k.$$

(10)

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**Author Contributions**
M.C. and J.M.L. conceived and designed this work. J.M.L., D.K. and T.H. performed the first-principles calculations. J.M.L. carried out the multiscale phase field simulations and calculated strain distributions with critical energy release rates. M.C., M.S.P, and K.C. supervised this study. M.C., K.C., M.S.P, and J.M.L. wrote the paper. All authors reviewed the manuscript.

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