Spin–lattice and electron–phonon coupling in 3d/5d hybrid Sr3NiIrO6

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While 3d-containing materials display strong electron correlations, narrow band widths, and robust magnetism, 5d systems are recognized for strong spin–orbit coupling, increased hybridization, and more diffuse orbitals. Combining these properties leads to novel behavior. Sr$_3$NiIrO$_6$, for example, displays complex magnetism and ultra-high coercive fields—up to an incredible 55 T. Here, we combine infrared and optical spectroscopies with high-field magnetization and first-principles calculations to explore the fundamental excitations of the lattice and related coupling processes including spin–lattice and electron–phonon mechanisms. Magneto-infrared spectroscopy reveals spin–lattice coupling of three phonons that modulate the Ir environment to reduce the energy required to modify the spin arrangement. While these modes primarily affect exchange within the chains, analysis also uncovers important inter-chain motion. This provides a mechanism by which inter-chain interactions can occur in the developing model for ultra-high coercivity. At the same time, analysis of the on-site Ir$^{4+}$ excitations reveals vibronic coupling and extremely large crystal field parameters that lead to a $t_2g$-derived low-spin state for Ir. These findings highlight the spin–charge–lattice entanglement in Sr$_3$NiIrO$_6$ and suggest that similar interactions may take place in other 3d/5d hybrids.

INTRODUCTION

Interest in 5d materials and 3d/5d hybrids has blossomed in response to recent scientific advances and applications in hard magnets, topological insulators, multiferroics, superconductors, and thermoelectrics. 1–6 5d materials are unique for several reasons. First, strong spin–orbit coupling competes with magnetic, crystal-field, many-body Coulomb, and other interactions to drive new physical behaviors,7 such as the $J_{\text{eff}} = 1/2$ state in certain iridates. 8,9 Second, the bonding interactions associated with the larger 5d orbitals promote inter-cation dimerization in pairwise, chain-like, and other complex orderings. 10,11 Third, the relativistic shifts in orbital energies, combined with spin–orbit and bandwidth effects, can drive band inversions leading to topological phases and enhanced Rashba splittings. 12–15 In contrast, 3d transition metal compounds typically display much narrower bandwidths, more robust magnetism, and stronger electron–electron interactions, and correlations. 16,17 When these two sets of properties are brought together, as in Sr$_3$NiIrO$_6$, new and potentially useful behaviors can emerge.

What makes Sr$_3$NiIrO$_6$ so remarkable is the extraordinary coercivity—up to 55 T depending on sample details. 18 By contrast, traditional hard magnets like Fe/Pt, Nd$_3$Fe$_4$B, Dy$_2$Fe$_{17}$Co$_6$B (x = 7 wt %), and LuFe$_2$O$_4$ have coercivities on the order of 1, 3, and 9 T, respectively. 19–21 The extraordinarily high coercive field is not due to ferromagnetic domains since the material is antiferromagnetic, though the exact mechanism remains to be understood. 18,22–24

The crystal structure consists of chains of alternating face-sharing NiO$_6$ trigonal prisms and IrO$_6$ octahedra stacked along the c axis with Sr atoms separating the chains. These chains are arranged in a triangular configuration in the ab plane. 25 Because Ir has a 4+$\text{e}$ charge, it was originally thought to have a $J_{\text{eff}} = 1/2$ state. 26,27 A trigonal distortion, however, breaks the symmetry and creates a slight deviation from the pure $J_{\text{eff}} = 1/2$. 28 Sr$_3$NiIrO$_6$ is part of a chemical family of quasi-one-dimensional 3d/5d hybrids with formula $A_2BBr_6$. Notably, these materials display increasing coercive magnetic fields as the $B$ site ion evolves from a 3d to a 4d to a 5d magnetic ion. 18,25,29 This suggests that the unusual properties of Ir and similar 5d ions must play an important role in creating the high coercivity. Recent calculations indeed suggest that it is the strongly anisotropic exchange interaction characteristic of the Ir$^{4+}$ ion that plays a key role in the high coercive magnetic field. 24 The strongest magnetic exchange is antiferromagnetic between Ni and Ir ions within c axis chains, which creates one-dimensional order below ~200 K. 27 Elastic neutron diffraction measurements identified two potential magnetic ground states at zero field: a partially disordered antiferromagnet or a more complex, spatially modulated state. 26 In light of the large Ni–Ir intra-chain exchange interactions, 27 the partially...
disordered antiferromagnet model is most likely and has been suggested for several $A_iB_8O_{16}$ materials with high coercive field.\textsuperscript{30-32} In this model, $c$ axis chains act like giant spin units due to the difference between the Ni and Ir moments, with frustrated antiferromagnetic interactions between chains in the $ab$ plane. Consequently, the ground state consists of two oppositely aligned chains and one with random orientation. In this model, gradual flipping of the randomly oriented third chains accounts for the spin glass-like dynamics with magnetic hysteresis and coercivity that is seen below 15 K in Sr$_3$NiIrO$_6$ and for the initial evolution of the magnetization up to the coercive field. At the coercive field, the second chain flips, leading to a sudden jump and the high coercive field. The extraordinary coercivity must result from the barrier to flipping of the second chain due to its many-body nature and interactions with the lattice including the anisotropic exchange interaction of Ir. Thus, if we are to achieve a complete understanding of the extraordinary coercive magnetic field in Sr$_3$NiIrO$_6$, we need to quantify how the magnetic order and Ir electronic state interact with the lattice.

To this end, we measured the infrared and optical properties of Sr$_3$NiIrO$_6$ and compared the response to high-field magnetization, first-principles lattice dynamics calculations, and simulations of spin–phonon coupling. While the phonons are nearly rigid across the magnetic ordering and freezing transitions, magneto-infrared work reveals three modes that track the magnetic response. What distinguishes these modes is how they modulate superexchange pathways around the Ir centers. The O–Ir-O bending mode near 310 cm$^{-1}$ is the dominant feature with an exceptionally large spin–lattice coupling constant—on the order of 10 cm$^{-1}$. That very specific local lattice distortions are involved in the approach to the coercive field provides further confirmation that the high-field transition in Sr$_3$NiIrO$_6$ is more than a simple domain reorientation process.\textsuperscript{18} At the same time, we reached beyond spin–lattice interactions to explore electron–phonon coupling. Analysis of the Ir$^{4+}$-on site $d$-$t$-d excitations reveals that they are vibronically activated. An oscillator strength analysis uncovers electron–phonon coupling involving the 177 cm$^{-1}$ Ni in-plane mode, which modulates the Ni–O–Ir bond angles (and thus the local Ir$^{4+}$ environments). We discuss these findings in terms of inter- and intra-chain coupling as well as how the diffuse character of the Ir 5d orbitals enlarges the crystal field parameters to give a spin configuration that stems from the $t_{2g}$-derived energy levels.

**RESULTS AND DISCUSSION**

Strong spin–lattice coupling and intra-chain interactions in Sr$_3$NiIrO$_6$

Figure 1a displays the infrared spectrum of Sr$_3$NiIrO$_6$. A symmetry analysis of the $R3c$ space group yields 7 $A_{2u}$ and 12 $E_g$ infrared-active phonons—consistent with our spectra. Our mode assignments are based on lattice dynamics calculations, which also provide symmetries and displacement patterns. These assignments are summarized in Table S1 (Supplementary Information) and allow the microscopic interaction indicated by the spectra to be fully understood. Spin–lattice coupling across the 75 K magnetic ordering and 15 K freezing temperatures is extremely weak (Supplementary Information), likely because these energy scales do not correspond to collective transitions.\textsuperscript{18,25,26} The signature in other thermodynamic probes is not strong either. Magnetoelastic coupling in applied field, however, is robust.

In order to search for elastic contributions to the record high coercivity, we measured the magneto-infrared response of Sr$_3$NiIrO$_6$ (Fig. 1). Here, magnetic field was increased step-wise from 0 to 35 T, and spectra were acquired at each step to avoid complications from magnetic hysteresis. The measurements therefore follow the line from the origin in Fig. 1b, shown more closely in Fig. 1c. The absorption difference ($\Delta \alpha = \alpha(30T) – \alpha(0T)$) in the upper portion of Fig. 1a highlights spectral differences. Three phonons are sensitive to magnetic field. The $E_u$ symmetry mode at 310 cm$^{-1}$ displays the largest magneto-infrared response (Fig. 1f). The $A_{2g}$ symmetry modes at 133 and 534 cm$^{-1}$ are also sensitive to changes in the microscopic spin arrangement (Fig. 1d, h). Interestingly, the two lower frequency phonons harden with applied field, whereas the higher frequency mode softens.

We quantify the magnetic field dependence of the 133, 310, and 534 cm$^{-1}$ phonons by integrating the absolute value of the absorption difference over a narrow frequency window ($\int_{\omega_{\text{low}}}^{\omega_{\text{high}}} |\Delta \alpha| \, d\omega$) at each field. This quantity is proportional to the field-induced frequency shift, although error bars on $\Delta \omega$ are much smaller.\textsuperscript{33} Comparison with the bulk magnetization (Fig. 1c) reveals that these changes grow as magnetization squared.\textsuperscript{34} This implies that the field-driven transition is not just a spin reorientation process; it also involves specific local lattice distortions. The magnetic field drives the spin rearrangement, while cooperative lattice distortions reduce the exchange interactions and the energy required to modify the microscopic spin arrangement. Similar mechanisms are active in other materials.\textsuperscript{34-36}

While the 48 T spin reorientation field is beyond the current reach of resistive magnets, the observed spin–phonon coupling is quite strong. We can estimate the spin–phonon coupling constants in Sr$_3$NiIrO$_6$ as $\omega = \omega_0 + \lambda (S_i - S_j)$. Here, $\omega_0$ is the unperturbed (zero field) mode frequency, $\omega$ is the perturbed (high field) mode frequency, and $(S_i - S_j)$ is the spin–spin correlation function.\textsuperscript{37} Taking the limiting low temperature value of the spin–spin correlation function as $\langle S_i \cdot S_j \rangle = -1/3$ for $S = 2$, 10, and 5 cm$^{-1}$ for the 133, 310, and 534 cm$^{-1}$ modes, respectively. By comparison, the highest value of $\lambda$ in the 3d/4f hybrid Ni$_3$TeO$_6$ at the same applied magnetic field (i.e., across the spin–flop transition) is 4 cm$^{-1}$.\textsuperscript{38} This suggests that higher fields may drive even stronger spin–lattice interactions, especially across the coercive field.\textsuperscript{39,40}

Examination of the calculated displacement patterns uncovers important similarities in the spin–lattice coupled modes that provide mechanistic insight into the field-driven process. The $E_u$ symmetry O–Ir–O bending mode at 310 cm$^{-1}$ is the most sensitive to field (Fig. 1g). This displacement pattern—with its strong O component—unambiguously modulates the superexchange interactions between Ir and its neighbors by changing the Ir environment. This motion also reduces the symmetry of the crystal and (as discussed below) introduces new terms into the magnetic Hamiltonian. Local lattice distortions of this type are thus important to the development of various spin rearrangements—such as that across the coercive field. The other two magneto-infrared-active features modulate the exchange interactions around the Ir centers as well—although by less effective routes. For instance, the $A_{2g}$ symmetry mode at 133 cm$^{-1}$ consists of Sr out-of-plane displacement and in-phase Ni displacement along the c axis (Fig. 1e) that slightly varies the Ni–O–Ir angle as a second-order effect. The $A_{2g}$ symmetry mode at 534 cm$^{-1}$, on the other hand, consists mainly of O stretching around the Ir center (Fig. 1i), which also impacts the superexchange angles. The aforementioned displacement patterns primarily affect exchange within the chains. A view along the chains (see animations of the displacement patterns in Supplementary Information) reveals that these modes have inter-chain motion as well. This supports the role of inter-chain interactions in the developing magnetic model\textsuperscript{18,26} and provides a mechanism by which such effects can occur.

The form of the spin–phonon Hamiltonian for Sr$_3$NiIrO$_6$ is very complicated—even when considering only intra-chain interactions—because various phonons break lattice symmetries and allow novel magnetic interaction terms (such as Dyzaloshinskii–Moriya) to emerge (see the Supplementary Information for details). This makes the first-principles calculation of every spin–phonon coupling parameter practically impossible. We
therefore developed a simplified approach to predict which phonon modes have a stronger effect on the magnetic structure (and vice versa). We began by considering the displacement pattern of the 310 cm$^{-1}$ mode and calculated the effect of this type of modulation on the ground-state spin arrangement. Similar calculations using the 177 cm$^{-1}$ mode pattern are included for comparison. As a reminder, the $E_g$ symmetry O-Ir-O bending mode at 310 cm$^{-1}$ engages in spin–lattice coupling, whereas (as we shall see below) the $E_u$ symmetry mode at 177 cm$^{-1}$ is the phonon that vibronically activates on-site $d$-to-$d$ excitations of Ir$^{4+}$. When the atoms are not displaced, the Ni and Ir moments are predicted to be collinear and parallel to the c axis (within error bars), consistent with the observed magnetism. Displacing atoms according to the pattern of the 310 cm$^{-1}$ mode leads to very significant tilting of the Ni spin moment as well as weaker tilting of the Ir spin (Fig. 1j).

As a result, the system becomes non-collinear. The 177 cm$^{-1}$ mode, on the other hand, leads to a much smaller effect on the magnetic structure, in line with a lack of field-induced changes of this mode. This reveals the complex nature of the spin–lattice coupling and suggests that the induced tilting may lower the magnetic switching barrier.

Electron–phonon coupling and strength of the crystal field interactions in Sr$_3$NiIrO$_6$

Equipped with a microscopic understanding of the elastic distortions in response to the magnetic field, we sought to determine whether similar phonons contribute to the electronic
Excitations of Ir$_4$ are slightly distorted from octahedral, creating a distortion away from phonon-assisted Sr$_3$Ir$_2$O$_7$, quantitative vibronic coupling analyses (such as we offer signif.

The temperature dependence of the oscillator strength is modeled as $f = f_0 + f_v \coth(h\nu/2kT)$, where $f_v$ is the frequency of the activating phonon, $f_v$ is the oscillator strength at base temperature, $v$ is the coupled phonon frequency. As a reminder, $f_0 = 5.68 \times 10^{-5}$, $v = 178 \text{ cm}^{-1}$.

**Figure 2b** displays the oscillator strength analysis of the Ir$^{4+}$ on-site excitations in Sr$_3$Ni$_2$O$_6$. There is a small deviation from the overall trend near 70 K that may be due to the spin ordering transition, but the size of our error bars precludes a detailed analysis. Examination reveals that the Ir-related $d$ to $d$ excitations are vibronically coupled with the 177 cm$^{-1}$ Fe phonon—which is present in the infrared spectrum (Fig. 2c). According to our calculations, this mode consists of Ni in-plane motion against Sr counter-motion that indirectly modulates the Ir environment (Fig. 2d). Thus, the vibronically coupled mode is separate and distinct from those involved in magnetoeelastic coupling. This separation offers the possibility of selective property control. We also carried out the same analysis for the more distorted Cu analog and unveiled coupling to a different displacement in which O motion more directly affects the Ir environment (Supplementary Information). This contrast likely emanates from the dissimilar chain configurations (linear for the Ni system and zigzag for the Cu analog), highlighting the importance of local symmetry in coupling processes.

**Table 1.** Vibronic coupling and crystal field parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>Element</th>
<th>Electronic state</th>
<th>$10Dq$ (eV)</th>
<th>$B$ (eV)</th>
<th>Coupled phonon frequency (cm$^{-1}$)</th>
<th>Displacement</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_3$Nil$_2$O$_6$</td>
<td>Ir</td>
<td>5d$^5$</td>
<td>3.24</td>
<td>1.18</td>
<td>177</td>
<td>Ni in-plane motion</td>
<td>This work</td>
</tr>
<tr>
<td>Sr$_3$Cu$_2$O$_6$</td>
<td>Ir</td>
<td>5d$^5$</td>
<td>2.33</td>
<td>0.86</td>
<td>273</td>
<td>O-$h$-O-bend</td>
<td>This work</td>
</tr>
<tr>
<td>Sr$_3$Ir$_2$O$_7$</td>
<td>Ir</td>
<td>5d$^5$</td>
<td>3.8</td>
<td>0.93</td>
<td>–</td>
<td>–</td>
<td>46,49</td>
</tr>
<tr>
<td>Li$_3$IrO$_3$</td>
<td>Ir</td>
<td>5d$^5$</td>
<td>2.7</td>
<td>0.95</td>
<td>–</td>
<td>–</td>
<td>45</td>
</tr>
<tr>
<td>Ni$_3$Te$_2$O$_6$</td>
<td>Ni</td>
<td>3d$^8$</td>
<td>1.10</td>
<td>0.11</td>
<td>–</td>
<td>–</td>
<td>51</td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>Fe</td>
<td>3d$^5$</td>
<td>1.59</td>
<td>0.09</td>
<td>525</td>
<td>In-plane, in-phase Fe-O stretch</td>
<td>52,53</td>
</tr>
</tbody>
</table>

Summary of $10Dq$ and Racah parameters for the 3d/5d materials in this study compared to the crystal field parameters of other Ir-containing compounds along with information about the vibronically coupled phonons. No vibronic coupling analysis was found for Sr$_2$IrO$_4$ or Li$_2$IrO$_3$ and the Ni$^2+$ excitations in Ni$_3$Te$_2$O$_6$ are not vibronically activated, so no phonons are implicated.

Inter-band excitations, like those in Sr$_3$Nil$_2$O$_6$, are responsible for the colors of transition metal-containing materials and have been extensively studied. Vibronic coupling, in which an odd-parity phonon mixes with a $d$ to $d$ excitation, is a common activation mechanism. Here, both spin and parity selection rules are broken due to coupling with a phonon. In this scenario, the temperature dependence of the oscillator strength is modeled as $f = f_0 + f_v \coth(h\nu/2kT)$, where $v$ is the frequency of the activating phonon, $f_0$ is the oscillator strength at base temperature, $f_v$ represents oscillator strength from other mixing processes; and $h$, $k_B$, and $T$ have their usual meanings. This model can be used to determine which phonon activates the electronic transition. While phonon-assisted $d$ to $d$ excitations have been reported in Sr$_3$Ir$_2$O$_7$, quantitative vibronic coupling analyses (such as we do here) are rare in 4d and 5d systems, and particularly so in 3d/5d hybrids.
increase spin–orbit coupling and Racah parameters in free ions.\textsuperscript{56} Importantly, the large 10Dq values separate the $t_{2g}$ and $e_{g}$ levels such that the $e_{g}$-derived bands in Sr$_3$NiIrO$_6$ play no role in determining the Ir spin configuration.

In summary, we combined infrared and optical spectroscopy with high-field magnetization and first-principles calculations to explore coupling processes involving the fundamental excitations of the lattice in Sr$_3$NiIrO$_6$—a material with significant spin–orbit interactions. These include both spin–lattice and electron–phonon processes. Magneto-infrared spectroscopy reveals that three phonons—all of which modulate the magnetic pathways around and the symmetry of the Ir centers—display strong spin–lattice interactions, demonstrating that the approach to the coercive field takes place with very specific local lattice distortions—different from expectations for simple domain reorientation in a ferromagnet. Examination of the mode displacement patterns also provides a specific mechanism for inter-chain interactions, a finding that is crucial to the development of the working magnetic model in Sr$_3$NiIrO$_6$ and related materials. At the same time, analysis of the on-site $t^{4+}_1$ excitations unveils vibronic coupling and extremely large crystal field parameters. For instance, 10Dq is a factor of two larger than that in traditional transition metal oxides, and the Racah parameter $B$ is a factor of 10 higher. Moreover, the phonon that activates the vibronic coupling has a completely different displacement pattern than those that are sensitive to magnetic field. We therefore find that certain phonons in Sr$_3$NiIrO$_6$ are strongly entangled with the spin and charge channels. In addition, the diffuse character of the Ir 5d orbitals determines the ground-state spin structure of Sr$_3$NiIrO$_6$, whereas spin–lattice interactions reduce the energy required to modify microscopic spin arrangements. Returning to the developing magnetic model of Sr$_3$NiIrO$_6$, we qualitatively expect that the ultra-high coercive field results from the high barrier to flipping a chain of strongly coupled Ni$^{3+}$ and Ir$^{4+}$ magnetic moments, which is effectively a many-body magnetic system. This barrier to flipping results from the interaction of the magnetic order with the lattice. This interaction has two parts: the interaction of the magnetic exchange interactions with lattice distortions and the mixing of the local spin–orbit coupled state of the Ir$^{4+}$ ion with the lattice. We quantified both in this work, thereby providing necessary insight to develop a complete model.

**Methods**

High-quality single crystals were grown as described previously\textsuperscript{16,57} and either polished or combined with a transparent matrix to control optical density due to strong phonon absorption. Absorption was calculated as $\text{a} = \frac{2\hbar^2}{\pi}\langle T(\alpha) \rangle$, where $\hbar$ is concentration, $\alpha$ is thickness, and $T(\alpha)$ is the measured transmittance. Magneto-infrared and magnetization measurements were carried out at the National High Magnetic Field Laboratory using the 3T resistive and 65 T short-pulse magnets, respectively. Absorption was obtained at zero field, and magneto-infrared measurements tracked changes. Absorption differences were calculated as $\Delta \alpha = \alpha(0) - \alpha(T)$, where we integrated $[\alpha]_T$ over small energy windows (127–150, 290–335, and 530–545 cm$^{-1}$) to quantify changes and renormalize to the 35 T magnetization squared to match energy scales and provide a proper comparison.

First-principles calculations were performed using projector-augmented waves as implemented in VASP.\textsuperscript{18,55} The PBEsol functional was used to approximate the exchange correlation energy\textsuperscript{60,61} and density functional theory+U\textsuperscript{62} was utilized for the transition metals. For calculations of Sr$_3$NiIrO$_6$, $U = 5$ eV for Ni and $U = 1$ eV for Ir were used. For the Cu analog, $U = 5$ eV for Cu and $U = 1.5$ for Ir were used. Changing the values of $U$ and $J$ changes the obtained phonon frequencies but does not affect the physical picture. Phonons were calculated using both the direct method and density-functional perturbation theory, and the results were identical within numerical noise. An 8 × 8 × 8 Monkhorst–Pack grid\textsuperscript{63} and a plane wave energy cutoff of 500 eV gave good convergence. The crystal structure used in the phonon calculations was obtained by relaxing the experimentally reported structure in the magnetically ordered phase.

The complexity of the crystal and magnetic structure of Sr$_3$NiIrO$_6$ makes it impractical to perform a detailed first-principles calculation of the spin–phonon or spin–lattice coupling in this material. In order to gain insight about the spin–lattice coupling strength, we therefore performed noncollinear magnetic calculations in a series of crystal structures that were obtained by displacing the atoms according to the displacement pattern of particular phonon modes. (Results are presented in Fig. 1.) We considered displacements up to 0.5 Å in total for the 22 atom unit cell, which corresponds to an average of ~0.1 Å per atom. The magnetic ground state does not change and is still predominantly ferrimagnetic along the c axis for all of these structures. However, unlike the collinear ferrimagnetic state observed in the experiment and reproduced by first-principles calculations, the magnetic ground state for these displaced structures are tilted ferrimagnetic. The 310 cm$^{-1}$ displacement gives rise to large tilting of Ni moments—as much as ±10° for the larger displacements we considered. For reference, we also present the results of the same calculation for the 177 cm$^{-1}$ mode of same symmetry and find a much smaller tilting. This observation is not surprising, because the character of this mode does not change the exchange pathways significantly. (It is of 49% Sr, 13% Ni, 8% Ir, and only 29% O character.) This finding is also in line with the experimental result that this mode is not engaged in spin–lattice coupling.

**Data availability**

Data are available from the corresponding author upon reasonable request.

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**Author contributions**

J.L.M., T.B. and S.-W.C. devised the project. X.L. and S.-W.C. grew the samples. K.R.O., A.A.W., K.D.H., A.L.B., M.O. and J.L.M. carried out the spectroscopic measurements. V.S.Z., C.V.T. and J.S. measured the magnetic properties. A.P. and T.B. performed the theoretical calculations. K.R.O., J.L.M., V.S.Z. and T.B. wrote the manuscript, and all authors contributed to it.

**Additional information**

Supplementary Information accompanies the paper on the *npj Quantum Materials* website (https://doi.org/10.1038/s41535-019-0184-x).

**Competing interests:** The authors declare no competing interests.

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