Giant magneto-elastic effect in d² pyrochlores and the formation of a spin-lattice liquid

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We propose a giant magneto-elastic coupling effect in frustrated magnetic insulators consisting of a pyrochlore lattice of d² ions, such as Mo⁴⁺. The coupling between the spin and lattice significantly changes a subset of the superexchange interactions, and selects a low-temperature manifold of spin configurations that is unexpected from the uncoupled case. We propose a simple model Hamiltonian linking spin and lattice, and show that it supports a spin-lattice liquid state, and that it can be used to understand a number of the experimental features of Y₂Mo₂O₇.

The distinguishing feature of frustrated magnets, and the one that leads to most of their interesting features, is a massive degeneracy of low-energy states [1]. At low enough temperature this degeneracy is always lifted, and one way to do this is by magneto-elastic coupling to the lattice. In such a case the balance between the superexchange couplings can be altered by a structural distortion, and this relieves the frustration, resulting in, for example, a wealth of distortion-dependent ordered phases [2–6] or the formation of a valence-bond crystal [7, 8].

In contrast, we here describe a situation in which magneto-elastic coupling does not just act in a perturbative way on an already established manifold of low-energy spin configurations, but is a key ingredient in choosing the low-energy manifold, and for this reason we refer to the effect as “giant” magneto-elastic coupling. If local lattice distortions are themselves frustrated, we propose that the giant magneto-elastic coupling can select an extensive set of coupled spin and lattice configurations that are unexpected from the point of view of a pure spin model acting on the average, undistorted lattice structure, resulting in a spin-lattice liquid state.

The materials that we argue exemplify such physics are the insulating pyrochlore molybdates, R₂Mo₂O₇ (R=Y, Tb, Dy, Ho, Er, Yb, Lu [9, 10]), of which Y₂Mo₂O₇ is the best studied example [11–23]. The compounds are famous for being one of the first-discovered examples in which the magnetic (Mo⁴⁺) ions form a pyrochlore lattice of corner sharing tetrahedra [11] (Fig. 1a and 1b), which is generally associated with strong frustration, and remain somewhat unusual in having the magnetic ion on the B site of the A₂B₂O₇ structure. A spin glass forms at low temperature without apparent disorder [11, 15], and the origin of this unusual behaviour remains an open question [10].

Our proposition for Y₂Mo₂O₇ and related compounds, is that in the absence of magneto-elastic coupling, the low-temperature exchange Hamiltonian of the average Fd3m structure is that of spin ice, and favours a frustrated manifold of spin configurations in which on every tetrahedra two spins point in and two out (2-in-2-out). However, there is growing evidence that the lattice distorts away from the Fd3m structure, such that two Mo⁴⁺ ions move towards and two away from the tetrahedral centre [17–19, 21, 23]. We argue that the resultant (smaller than 10%) change of Mo-O-Mo bond angle alters the superexchange interaction by several times its original value, and even changes its sign. Taking this into account, the low-energy manifold of spin orientations and lattice positions consists of tetrahedra with three spins pointing in and one out or vice versa (3-1 configurations) coupled to 2-in-2-out displacements of the Mo ions. This manifold is extensive, and so a classical spin-lattice liquid may form. Freezing of the spin-lattice liquid could potentially give rise to the spin-glass phase found experimentally at low temperature.

Local electronic states: We start by considering the local electronic structure of a 4d² Mo⁴⁺ ion in the insulating R₂Mo₂O₇ materials. The largest energy scales are the onsite Coulomb repulsion, U, and the cubic crystal-field splitting, 10Dq. The latter forces the two electrons to reside in the t₂g manifold of yz, zx and xy d-orbitals. Hund’s coupling, J₄ ≈ 0.5eV [24], selects a 9-fold degenerate set of low-energy states, labelled by total spin S = 1 and total effective orbital angular momentum L eff = 1 [25]. This is further split by trigonal distortion of the O octahedra and spin-orbit coupling. The trigonal distortion is a feature of the materials at all accessible temperatures and consists of a compression of O octahedra along the local z'-axes, which point into/out of Mo tetrahedra and are shown in Fig. 1a. In Y₂Mo₂O₇ it is estimated from band structure calculations that Δ trig ≈ 160meV, where H trig = Δ trig [2/3 − (L eff) ²], and λ₂O ≈ 40meV [24], where H₂O = −λ₂O S · L eff [24]. This is in reasonable agreement with the λ₂O ≈ 58meV found experimentally for isolated Mo⁴⁺ ions [25].

The result of splitting the S = 1, L eff = 1 states is a low-energy doublet, labelled as J eff = ±2 and separated from the next lowest energy state by an energy ΔE = λ₂O [1 − λ₂O/Δ trig +... ] ≈ 30meV [26]. Since the splitting is approximately an order of magnitude larger than the low-temperature Curie-Weiss constant of θcw ≈ 4meV [22], we will just consider exchange between neighbouring
fig. 1. \(R_2\)Mo2O7 pyrochlores. (a) Mo ions (purple) are octahedrally coordinated by oxygen (grey) and form a pyrochlore lattice of corner sharing tetrahedra. \(J_{\text{eff}} = \pm 2\) states are represented by arrows pointing in/out of the Mo tetrahedron along the \(z'\) local axes. (b) 2-in-2-out lattice displacements (black arrows) create one long (blue), four medium (red) and one short (green) Mo-Mo bond on each tetrahedron. (c) \(\pi\)-type \(dpd\) hopping path, shown for idealised regular oxygen octahedra. The path shown is \(d_{\text{eff}}^{\uparrow\downarrow}-(p_1^y p_2^y)\)-\(d_{\text{eff}}^{\uparrow\downarrow}\), where Mo sites are labelled 1 and 2 and have associated local coordinates (x=red, y=green, z=blue). (d) \(\sigma\)-type hopping path allowed by trigonal distortion of the oxygen octahedra and exemplified by \(d_{\text{eff}}^{\uparrow\uparrow}-(p_1^y p_2^y)\)-\(d_{\text{eff}}^{\uparrow\uparrow}\). \(J_{\text{eff}}' = \pm 2\) doublets. This is different from the approach taken by a number of other theories, which assume an isotropic \(S = 1\) spin on every Mo site [27–29].

**Exchange interaction:** We next consider the oxygen mediated superexchange interactions between neighbouring Mo4+ ions. The geometry is simplest in the case of idealised undistorted oxygen octahedra, where local cubic axes can be aligned with the octahedra as shown in Fig. 1c. Supercorrelation occurs via a single intermediate oxygen with Mo-O-Mo bond angle \(\alpha = 2 \arctan 2\sqrt{2} \approx 141^\circ\). Within the cubic axes the dominant hopping channel is off-diagonal, bond-dependent and follows paths of the type \(d_{\text{eff}}^{\uparrow\downarrow}-(p_1^y p_2^y)\)-\(d_{\text{eff}}^{\uparrow\downarrow}\), where \(p_1^y\) and \(p_2^y\) denote orbitals on the same oxygen ion but in the local axes of the two different Mo ions (1 and 2 in Fig. 1c). In this case all the \(d-p\) bonds are \(\pi\)-type bonds.

We work in the Mott insulator picture, and for two electrons in the \(t_{2g}\) manifold, the derivation of a spin-orbital Hamiltonian from a multi-orbital Hubbard model is a standard procedure [26, 30–32]. In order to arrive at an effective low-temperature model, it is required to project the full spin-orbital Hamiltonian for an \(S = 1\), \(L_{\text{eff}} = 1\) configuration onto the \(J_{\text{eff}}' = \pm 2\) doublet. Since no matrix elements connect \(J_{\text{eff}}' = 2\) to \(J_{\text{eff}}' = -2\), the Hamiltonian can be written as \(\mathcal{H}_{\text{eff}} = J_\text{eff} \sum_{\langle ij \rangle} \sigma_i \sigma_j\), where \(\sigma = \pm 1\) labels the doublet states, and can be thought of as an Ising “spin” pointing into or out of tetrahedra (see Fig. 1a). \(J_\text{eff} > 0\) favours antiferromagnetic alignment in the local trigonal axes, which corresponds to ferromagnet exchange in global axes, and low-energy states consist of the extensively-degenerate spin ice configurations with a 2-in-2-out arrangement. \(J_\text{eff} < 0\) favours ferromagnetic alignment in the local trigonal axes, corresponding to antiferromagnet exchange in global axes and therefore unfrustrated all in/out arrangements on tetrahedra. In the case of undistorted cubic octahedra we find that \(J_\text{eff} < 0\) for any value of \(J_\text{eff} / U\).

In reality the oxygen octahedra are trigonally distorted, and in \(Y_2\)Mo2O7 the Mo-O-Mo bond angle in the average \(F\bar{d}3m\) structure is \(\alpha = \alpha_{av} = 127^\circ\) [12, 20, 23]. The displacement of the O relative to the undistorted case opens up a \(\sigma\)-type hopping channel exemplified by the path \(d_{\text{eff}}^{\uparrow\uparrow}-(p_1^y p_2^y)\)-\(d_{\text{eff}}^{\uparrow\uparrow}\) and shown in Fig. 1d. The \(\sigma\) channel becomes comparable to the original \(\pi\)-bonding channel for a relatively small trigonal distortion, and as a result we find \(J_{\text{eff}} > 0\) for \(\alpha = 127^\circ\), favouring a 2-in-2-out set of low-energy configurations [26].

Due to the competition between the \(\pi\) and \(\sigma\) channels, the value of \(J_{\text{eff}}\) is extremely sensitive to the bond angle, as shown in Fig. 2a. This is reminiscent of the situation in quasi-1D cuprates [33–35]. Serendipitously, the bond angle at which the exchange interaction cancels is close to \(\alpha = 127^\circ\), both in our simple analytical calculations and also in more involved band structure calculations [24]. Deviations of the Mo-O-Mo bond angle from its average value thus lead to very large relative changes in \(J_{\text{eff}}\).

In addition to the trigonal distortion, there has been growing evidence in \(Y_2\)Mo2O7 of a distribution of Mo-Mo bond lengths at low temperature [17–19, 21, 23]. Recent pair distribution function (PDF) analysis is consistent with two Mo ions displacing in and two out of each tetrahedron without forming a superstructure, while Mo-O bond lengths remain approximately constant [23]. As a result there are three classes of bonds, with significantly
different PDF analysis with our calculations yields on each tetrahedron one short bond with $a < \alpha_{sv}$ and $J_{sl} > 0$, four medium bonds with $a \approx \alpha_{sv}$ and $J_{sm} > 0$ and one long bond with $a > \alpha_{sv}$ and $J_{sa} < 0$ [46]. This conclusion remains robust, even if the bond angle deviations are smaller than the $\sim 11^\circ$ reported in [23] and shown in Fig. 2b. The magnitude of $J_{sl}$ is significantly larger on the short and long bonds than the medium bonds, and we therefore find a very strong magneto-elastic coupling effect.

**Spin-lattice model**: Next we consider the minimal model that captures the essence of the microscopic analysis. Mo lattice sites are allowed to displace in a 2-in-2-out pattern (Fig. 1b), corresponding to the triplet normal mode of a tetrahedron \[2, 4, 8\]. The resultant bond angles are $\alpha = \alpha_{sv} + \delta \alpha$ on the long bond, $\alpha = \alpha_{sv}$ on the medium bonds and $\alpha = \alpha_{sv} - \delta \alpha$ on the short bond, with $\delta \alpha > 0$ (see Fig. 2b). For simplicity, we allow $\delta \alpha$ to vary globally but not locally. Spins are constrained to point into or out of tetrahedra and described by $\sigma = \pm 1$. The resultant spin-lattice Hamiltonian is,

\[
H_{sl} = \sum_{\langle ij \rangle} \left[ (J_{sl}(\alpha_{sv}) - g \delta \alpha_{ij}) \sigma_i \sigma_j + K \delta \alpha_{ij}^2 \right],
\]

where $J_{sl}(\alpha_{sv})$ is the superexchange interaction for undistorted bonds, $g = \partial J_{sl}/\partial \alpha|_{\alpha=\alpha_{sv}}$ describes at first order the angular dependence of the interaction, $\delta \alpha_{ij} \in \{-\delta \alpha, 0, \delta \alpha\}$ and $K$ is the elastic energy cost of distorting the lattice.

The ground state depends on the ratio \[g^2/(4KJ_{sl}(\alpha_{sv}))\]. For \[g^2/(4K) < J_{sl}(\alpha_{sv})\] it is energetically favourable to have $\delta \alpha(T = 0) = \delta \alpha_{gs} = 0$ combined with a 2-in-2-out spin configuration on each tetrahedra, and as a result a spin ice forms at low $T$. For \[g^2/(4K) > J_{sl}(\alpha_{sv})\] the lowest energy is reached with $\delta \alpha_{gs} = g/(2K)$, and writing $J_{sa}(\alpha) = J_{sa}(\alpha_{sv}) \pm \delta J_{sa}$, one finds $\delta J_{sa} > 2J_{sa}(\alpha_{sv})$ on long and short bonds. For a given lattice distortion a tetrahedron has four degenerate low-energy 3-1 spin configurations, as shown in the inset of Fig. 3 [47]. The combined manifold of spin and lattice configurations is extensive [26], and so a spin-lattice liquid may be realised at low $T$.

The full $g^2/(4K) - T$ phase diagram can be explored using Monte Carlo simulation, and is shown in Fig. 3 (see supplemental material [26] for details of the simulations). We set $g/(2K) = 0.2$ since this corresponds approximately to the experimental findings at low $T$ ($\delta \alpha_{gs} = 0.2 \approx 11^\circ$) [23]. As expected, for $g^2/(4K) < J_{sl}(\alpha_{sv})$ there is no distortion at any temperature and below a specific heat peak at $T \approx 0.8J_{sl}$ the system shows the characteristic behaviour of spin ice [48].

For $g^2/(4K) > J_{sl}(\alpha_{sv})$ there are two transitions as temperature is reduced, and this can be seen in simulations of the heat capacity shown in Fig. 4a. At $T = T_1$ there is a first-order liquid-gas-like transition in which $\delta \alpha(T)$ jumps discontinuously from $\delta \alpha(T > T_1) = 0$ to $\delta \alpha(T = T_1) \approx J_{sl}(\alpha_{sv})/g$. Below this there are three classes of bonds, long and short bonds with coupling $J_{sa}(\alpha_{sv}) \pm g \delta \alpha(T)$ and medium bonds with coupling $J_{sm}(\alpha_{sv})$ (see inset to Fig. 3). For a fixed lattice configuration, the long and short bonds form non-intersecting loops that visit every lattice site and on which the sign of the coupling alternates. Strong spin correlations form on these loops at the transition temperature, favouring configurations of the type $\sigma = (1, 1, -1, 1, 1, -1, -1,...)$. The correlations increase on further decreasing $T$, and this is related to the increasing density of tetrahedra with a 3-1 spin configuration. The loops themselves are not static, but constantly rearranging themselves subject to the 2-in-2-out constraint on the lattice displacements. The distribution of loop lengths follows the same power-law scaling as is found in spin-ice [38], despite the interaction of lattice displacements via spin degrees of freedom (see supplemental material [26] for more details about loops).

At lower $T$ there is a second-order transition at $T = T_2$, in which the system excludes loops with length $l_{loop} = 4m + 2$ ($m = 1, 2, ...$) in favour of those with length $l_{loop} = 4m + 4$, which we call loop symmetry breaking. This occurs because loops with length $l_{loop} = 4m + 2$ cannot simultaneously minimise the energy of every bond, as they are constrained to have an odd number of unsatisfied bonds, while loops with length $l_{loop} = 4m + 4$ can satisfy all the bonds (or have an even number of unsatisfied bonds) [26]. Below $T = T_3$ essentially all tetrahedra adopt a 3-1 spin configuration (Fig. 4b) and the energy saturates, but the number of allowed configurations remains extensive.
Our model contains two distinct regions that can be described as classical spin-lattice liquids, with spin and lattice degrees of freedom intimately coupled and an extensive number of available configurations. One interesting direction would be to determine the relevant gauge theory to describe the long-wavelength behaviour associated with these manifolds of states.

**Relation to experiment:** Many experiments have been performed on Y$_2$Mo$_2$O$_7$, providing a test of our theory. The presence of a large magneto-elastic coupling is clear from combining the calculated value of $g/J_\alpha(\alpha_{av}) \sim 20$ with the experimentally determined $\delta_{\alpha_{ss}} = g/(2K) \approx 0.2$ [23], to find $g^2/(4KJ_\alpha(\alpha_{av})) \sim 2$, which places the material on the right of the phase diagram in Fig. 3.

One of the main experimental features is a spin-glass transition at low temperature, and this is not captured by H$_d$, since it is translationally invariant and does not include a source of disorder, such as site vacancies [49]. However, the non-local dynamics in the low-temperature spin-lattice liquid state is likely to make it very susceptible to even small amounts of disorder, arising from oxygen non-stoichiometry or self-generated due to small local changes in the bond-angle $\alpha$ that have giant effects on the exchange couplings. Encouragingly the specific heat peak associated with the transition at $T = T_2$ contains approximately the same amount of entropy as is measured experimentally close to the spin-glass transition [22] ($\Delta S \approx 0.24 \log 2$). This is the temperature at which Monte Carlo simulations become difficult to equilibrate, and we propose that spin-glass freezing occurs in the vicinity of $T = T_2$, driven by a weak disorder not included in our model [50].

Experiments on Y$_2$Mo$_2$O$_7$ show evidence for a significant magneto-elastic effect above the spin-glass freezing temperature ($T_i \approx 22K$ [11, 15, 22]). For example NMR 1/T$_2$ measurements show that in an intermediate temperature range ($T_i < T \lesssim 100K$) the lattice becomes more ordered with increasing magnetic field, which suggests that the lattice is not only strongly coupled to the spins, but that the lattice degrees of freedom are not quenched [21]. From extrapolation of NMR linewidth measurements it has been suggested that a distribution of Mo-Mo bond lengths survives up to $\sim 430K$ [18]. Furthermore $\mu$s measurements performed above $T_i$ have been interpreted as showing evidence for a temperature dependent lattice distortion [19]. We therefore propose that above $T_i$ the material can be compared to our theory in the temperature range $T_2 < T < T_1$. In this region the model shows a temperature-dependent distortion of the Mo-Mo bonds (i.e. $\delta \alpha > 0$) and a strong coupling between spin and lattice, resulting in a spin-lattice liquid. The validity of H$_d$ breaks down approaching $T \sim \Delta E \approx 300K$, since the local electronic configuration is no longer confined to the low-energy doublet. As such, it seems likely that the first-order transition seen in the model, is, in the material, smeared out by the availability of higher-energy local states, which open-up new hopping channels and alter the Hamiltonian.

A particular mystery in Y$_2$Mo$_2$O$_7$ is why susceptibility measurements show a negative (AFM) Curie-Weiss temperature of $\theta_{cw} \approx -200K$ in the high temperature range 500 – 800K [39], a different Curie-Weiss temperature of $\theta_{cw} \approx -41K$ in the intermediate range 50 – 300K [22] but ring-features surrounding the $\Gamma$ point in low-temperature neutron-scattering measurements that can only be explained by including FM coupling [22]. Our model provides a resolution by proposing a mechanism by which AFM and FM interactions can coexist. Simulations in the temperature range $T_2 < T < T_1$, which should be compared with experiments at intermediate temperatures, show an emergent Curie-Weiss behaviour with $\theta_{cw} < 0$ (see Fig. 4c), despite the presence of strong correlations. At the same time simulations of the magnetic structure factor, $S(q)$, within our model, exhibit a pattern that is completely different from the pure FM (spin ice) case or the pure AFM (all in/out) case. As can be seen in Figs. 4d, for $T > T_2$ there is only weak scattering at $q = 0$ but stronger scattering at some points on a ring surrounding $q = 0$. Potentially this could develop into a more uniform ring of scattering with the introduction of disorder or small further-neighbour interactions. At temperatures of 300K and higher, the local electronic state is no longer confined to the ground state doublet, and a change in the Curie-Weiss behaviour is unsurprising.

FIG. 4: Physical characteristics of H$_d$ [Eq. 1] from Monte Carlo simulation for $g^2/(4K) = 2J_\alpha$. Error bars are smaller than the point sizes. (a) Lattice distortion, $\delta_{\alpha}$ and heat capacity $C/T$, showing two transitions. Results are shown for $L = 3$ (total number of spins $N = 16L^3$), for which equilibration is possible across the lower-T transition, and are consistent with simulations with larger L. (b) Fraction of tetrahedra displaying 2-in-2-out (red), 3-in (blue) or 4-in (green) spin configurations. (c) Inverse magnetic susceptibility. The fit to $1/\chi = 3(T - \theta_{cw})/\mu_{eff}^2$ gives $\theta_{cw} = -0.1J_\alpha$ and $\mu_{eff} = 1$. (d) Structure factor $S(q)$ in the spin-lattice liquid phase ($L = 12$), with a white circle showing the experimentally determined ring of scattering in Y$_2$Mo$_2$O$_7$ [22].
In conclusion, we have proposed the idea of giant magneto-elastic coupling, where the magneto-elastic effect is large enough to select an otherwise unexpected low-temperature manifold of spin configurations. We have argued that this is an important feature in $\text{Y}_2\text{Mn}_2\text{O}_7$ and related compounds, and have demonstrated that a simple model supports a spin-lattice liquid and can reproduce some experimental features.

One way to test our idea would be to use magnetic field to control the lattice or uniaxial pressure to control the magnetism. Large magnetic fields will suppress the 2-in-2-out lattice displacements by selecting spin configurations (either 2-in-2-out or 3-1) that are incompatible with the displacement. Intermediate fields will have a more subtle effect, splitting the low-energy spin-lattice configurations, and could be an interesting direction for further study.

Finally we note that our model provides a simple way to understand why some pyrochlore systems form spin ices, while others form a spin glass with a significant local lattice distortion; $f$-electron spin-ice compounds, such as $\text{Dy}_2\text{Ti}_2\text{O}_7$, sit on the left side of the phase diagram in Fig. 3 due to the primarily dipolar nature of the interaction resulting in a weak magneto-elastic coupling effect, while in $\text{Y}_2\text{Mn}_2\text{O}_7$ a strong magneto-elastic effect due to competition between superexchange hopping channels places them on the right side of the phase diagram.

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Changes in the Mo-O bond lengths produce a negligible change of the superexchange interaction compared to changes in the Mo-O-Mo bond angle

We note that the mechanism by which we arrive at the 3-1 ground state is quite different from previous work, where a partially ordered monopole crystal has been proposed [43–45]

Since we find $J_\alpha(\alpha_{av})$ is close to 0, we have checked that the phase diagram for $J_\alpha(\alpha_{av}) < 0$ is qualitatively similar to that for $J_\alpha(\alpha_{av}) > 0$. The main difference is that the value of $g^2/(4K)$ at which all-in-all-out order turns into a spin-lattice liquid is larger than the value at which a spin-ice becomes a spin-lattice liquid.

The lack of extrinsic disorder in $H_{sl}$ should not be confused with the prediction that arises from studying $H_{sl}$ of a low-temperature disordered lattice structure in which Mo ions fluctuate around their average position.

Using Monte Carlo to simulate the effect of disorder, and test whether it drives a spin-glass transition at temperatures close to $T_2$, is challenging, since it is very difficult to equilibrate the simulations due to the non-local nature of the dynamics and the strong correlation between spin and lattice degrees of freedom. We leave such a detailed investigation to future work.
Supplemental Materials: Giant magneto-elastic effect in d² pyrochlores and the formation of a spin-lattice liquid

LOCAL ELECTRONIC STATE OF d² IONS

Here we consider in more detail the local electronic state of a d² ion residing in a trigonally distorted oxygen octahedra and subject to spin-orbit coupling. The largest energy scale is the cubic crystal-field splitting of the 4d electron states, and as a result we consider only the t₂g levels. These are further split by a large Hund’s coupling, resulting in a low-energy manifold of states labelled by total spin S = 1 and total effective angular momentum L_eff = 1. The 9-fold degeneracy of these states is split by the combination of a trigonal flattening of the surrounding oxygen octahedra and spin orbit coupling, and we consider the local Hamiltonian,

$$H_{loc} = \Delta_{\text{trig}} \left[ \frac{2}{3} - \left( \frac{L'_{\text{eff}}}{2} \right)^2 \right] - \lambda_{SO} \mathbf{S} \cdot \mathbf{L}_{\text{eff}},$$

where S and L_eff are measured relative to the axis of the trigonal distortion, which points into/out-of Mo tetrahedra and defines the local z’ axis.

Diagonalisation of $H_{loc}$ gives the energy levels shown in Fig. S1. In general, the presence of a trigonal distortion means that the levels cannot be labelled by their total angular momentum, $J_{\text{eff}} = S + L_{\text{eff}}$. However, the lowest energy doublet is independently an eigenstate of both parts of $H_{loc}$ and can therefore be written in terms of the total angular momentum as $|J_{\text{eff}} = 2, J'_{\text{eff}} = \pm 2 \rangle = |S' = \pm 1, L'_{\text{eff}} = \pm 1 \rangle$.

In the main text we consider this lowest-energy doublet to be the only accessible state at low temperature, and this is valid as long as $T \ll \Delta E = \lambda_{SO} [1 - \lambda_{SO}/\Delta_{\text{trig}} + \ldots]$, where the energy difference between the levels has been expanded in terms of $\lambda_{SO}/\Delta_{\text{trig}}$.

SUPEREXCHANGE HAMILTONIAN ON THE PYROCHLORE LATTICE

Here we derive the superexchange Hamiltonian used in the main text. First we consider the idealised case of a pyrochlore lattice surrounded by regular oxygen octahedra. While this is never exactly the case in materials such as Y₂Mo₂O₇, due to a tension between the oxygen octahedra surrounding the Mo ions and the oxygen cubes surrounding the Y ions, it serves as a useful starting point. We then go on to consider the effect of trigonally disorting the oxygen octahedra, and show that the distortion can have a significant effect on the superexchange Hamiltonian.

Superexchange in idealised case with regular octahedra

In the Y₂Mo₂O₇ structure, oxygen octahedra surrounding each of the 4 basis sites of the pyrochlore lattice have different orientations. As such it is useful to set-up a local cubic coordinate system for each site, as shown in Fig. S2.
Rotation matrices from local cubic to global cubic coordinates are given by,

\[ R^T_0 = \begin{pmatrix} -2/3 & 1/3 & -2/3 \\ 1/3 & -2/3 & -2/3 \\ -2/3 & -2/3 & 1/3 \end{pmatrix}, \quad R^T_1 = \begin{pmatrix} -2/3 & 1/3 & -2/3 \\ -1/3 & 2/3 & 2/3 \\ 2/3 & 2/3 & -1/3 \end{pmatrix}, \]
\[ R^T_2 = \begin{pmatrix} 2/3 & -1/3 & 2/3 \\ 1/3 & -2/3 & -2/3 \\ 2/3 & 2/3 & -1/3 \end{pmatrix}, \quad R^T_3 = \begin{pmatrix} 2/3 & -1/3 & 2/3 \\ -1/3 & 2/3 & 2/3 \\ -2/3 & -2/3 & 1/3 \end{pmatrix}. \] (S2)

We consider oxygen mediated \(d-p-d\) hopping between neighbouring sites. The \(d-p\) hopping matrices taking \((d_{yz}, d_{zx}, d_{xy})\) to \((p_x, p_y, p_z)\) are given by [36, 37] (see also Ref. [40]),

\[ P_x^\pm = \pm V_{pd\pi} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad P_y^\pm = \pm V_{pd\pi} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad P_z^\pm = \pm V_{pd\pi} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \] (S3)

where \(V_{pd\pi}\) parametrises the \(\pi\)-bond hopping, the \(\pm\) refers to a positive or negative oxygen coordinate and \(x, y, z\) labels the axis on which the oxygen lies. On “integrating out” the oxygen orbitals one finds the \(d-d\) hopping matrices,

\[ \Lambda_{ij} = t P_{ij} R_i R_j^T P_{ji} \] (S4)

where \(t = V_{pd\pi}^2 / \Delta_{pd}\), \(\Delta_{pd}\) gives the energy difference between the \(d\) and \(p\) orbitals and \(P_{ij}\) is chosen appropriately for the bond in question. For the regular octahedra shown in Fig. S2, this gives the bond-dependent hopping matrices,

\[ \Lambda_{13} = \Lambda_{20} = t \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \quad \Lambda_{10} = \Lambda_{32} = t \begin{pmatrix} -\frac{1}{2} & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} \end{pmatrix}, \quad \Lambda_{03} = \Lambda_{12} = t \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \] (S5)

and it can be seen that the dominant hopping process is off-diagonal in the local coordinates. The nearest-neighbour hopping Hamiltonian is given by,

\[ \mathcal{H}_{\text{hop}} = \sum_{\langle ij \rangle} \sum_{\alpha,\beta} a^\dagger_{is} \Lambda_{ij}^{\alpha\beta} \beta_{js} + \text{h.c.}, \] (S6)

with \(\alpha, \beta \in \{d^{xz}, d^{zx}, d^{yz}\}\) measured in the local cubic coordinates and \(s \in \uparrow, \downarrow\).

![Local cubic coordinate systems for a pyrochlore lattice surrounded by regular oxygen octahedra. The 4 basis sites of the pyrochlore lattice (purple) form a tetrahedra and are surrounded by corner-sharing oxygen octahedra (grey). Global coordinates follow the axes of the bounding cube, while local coordinates \(x\) (red), \(y\) (green) and \(z\) (axes) are site dependent. Black lines show the local anisotropy \(z'\) axes associated with a trigonal octahedral distortion.](image)

It is also necessary to specify the on-site Coulomb interaction, and in the local octahedral coordinates this is given
by [41],
\[
H_{\text{site}} = (U - J_H) \left[ \sum_{\alpha,\beta} n_{\alpha\uparrow}n_{\beta\downarrow} + \sum_{\alpha<\beta} (n_{\alpha\uparrow}n_{\beta\uparrow} + n_{\alpha\downarrow}n_{\beta\downarrow}) \right] - 2J_H \sum_{\alpha<\beta} (S_\alpha \cdot S_\beta + \frac{3}{4} n_\alpha n_\beta) \\
+ J_H \left[ \sum_{\alpha} n_{\alpha\uparrow}n_{\alpha\downarrow} + \sum_{\alpha<\beta} (\alpha_\uparrow^{\dagger}\beta_\downarrow^{\dagger}\beta_\uparrow^{\dagger}\alpha_\downarrow^{\dagger}) \right],
\]
where \(U\) is the on-site Coulomb repulsion between electrons in the same orbital, \(J_H\) is Hund’s coupling, \(n_{\alpha s} = \alpha_\downarrow^{\dagger}\alpha_\downarrow\), \(n_\alpha = n_{\alpha\uparrow} + n_{\alpha\downarrow}\) and \(S_\alpha = (\frac{1}{2}[\alpha_\uparrow^{\dagger}\alpha_\downarrow + \alpha_\downarrow^{\dagger}\alpha_\uparrow], \frac{1}{2}[\alpha_\uparrow^{\dagger}\alpha_\downarrow + \alpha_\downarrow^{\dagger}\alpha_\uparrow], \frac{1}{2}(\alpha_\uparrow^{\dagger}\alpha_\uparrow - \alpha_\downarrow^{\dagger}\alpha_\downarrow))\).

A spin-orbital Hamiltonian can be derived by the standard method of treating \(t^2/U\) as a small parameter and considering virtual hopping processes of the type \(d^2d^2 \rightarrow d^2d^l \rightarrow d^2d^2\) [30–32]. This results in,
\[
H_{\text{SO}} = \frac{t^2}{U} \sum_\gamma \sum_{(ij)\|\gamma} \left[ (S_i \cdot S_j + 1) \hat{J}_{ij}^{(\gamma)} + \hat{K}_{ij}^{(\gamma)} \right],
\]
where \(\gamma\) refers to the three types of bonds (01, 23; 02, 13; 03, 12) shown in Fig. S2, \(S_i\) is a spin-1 operator on site \(i\) measured in the global coordinate system,
\[
\hat{J}_{ij}^{(\gamma)}(\eta) = (1 + 2\eta R)A_{ij}^{(\gamma)} - \eta R \hat{B}_{ij}^{(\gamma)} - \eta R \hat{C}_{ij}^{(\gamma)}, \quad \hat{K}_{ij}^{(\gamma)}(\eta) = 2\eta R A_{ij}^{(\gamma)} + 2\eta R \hat{B}_{ij}^{(\gamma)} - (1 + \eta R) \hat{C}_{ij}^{(\gamma)},
\]
\(\eta = J_H/U, \quad R = 1/(1 - 3\eta), \quad r = 1/(1 + 2\eta)\) and,
\[
A_{ij}^{(\gamma)} = \left[ \frac{14}{9} \tau_i^{\gamma} \tau_j^{\gamma} + \frac{64}{81} (\tau_i^{\gamma} \tau_j^{\gamma} + \tau_i^{\gamma} \tau_j^{\gamma}) + \frac{1}{81} (\tau_i^{\gamma} \tau_j^{\gamma} + \tau_i^{\gamma} \tau_j^{\gamma}) + \frac{65}{162} n_i n_j \right]^{(\gamma)} \\
- \frac{8}{81} (n_i (\tau_i^{\gamma} + \tau_j^{\gamma}) + (\tau_i^{\gamma} + \tau_j^{\gamma}) n_j)^{(\gamma)},
\]
\[
B_{ij}^{(\gamma)} = \left[ \frac{14}{9} \tau_i^{\gamma} \tau_j^{\gamma} + \frac{64}{81} (\tau_i^{\gamma} \tau_j^{\gamma} + \tau_i^{\gamma} \tau_j^{\gamma}) + \frac{1}{81} (\tau_i^{\gamma} \tau_j^{\gamma} + \tau_i^{\gamma} \tau_j^{\gamma}) + \frac{65}{162} n_i n_j \right]^{(\gamma)} \\
- \frac{8}{81} (n_i (\tau_i^{\gamma} + \tau_j^{\gamma}) + (\tau_i^{\gamma} + \tau_j^{\gamma}) n_j)^{(\gamma)},
\]
\[
C_{ij}^{(\gamma)} = \left[ \frac{65}{81} (n_i n_j) - \frac{16}{81} (\tau_i^{\gamma} + \tau_j^{\gamma} + \tau_i^{\gamma} + \tau_j^{\gamma}) \right]^{(\gamma)},
\]
where the orbital operators are bond dependent pseudospins and given by \(\tau^+ = \frac{1}{2}[(d^x)^\dagger d^z - (d^y)^\dagger d^y], \tau^- = (d^x)^\dagger d^y\) and \(n = (d^x)^\dagger d^x + (d^y)^\dagger d^y + (d^z)^\dagger d^z\) on 03 and 12 bonds and by related expressions on other bonds.

The effect of trigonal distortion and spin-orbit coupling

The effect of the trigonal distortion on the spin-orbital Hamiltonian is twofold, since it is necessary to take into account a modified hopping matrix, as well the way in which it combines with spin-orbital coupling to split the otherwise 9-fold degenerate local energy levels.

When considering trigonally distorted oxygen octahedra, we continue to use a local cubic coordinate system that is aligned with the idealised undistorted octahedra (see Fig. 1 in the main text). As a consequence, oxygen ions no longer sit on the axes of the local coordinates, and thus the \(d-p\) hopping matrices become more complicated. For example, using the tables given in Ref. [36, 37], the \(P^+_z\) matrix given in Eq. S3 should be replaced by,
\[
P^+_z = \left( \begin{array}{c}
\sqrt{3} nm^2 V_{pd\sigma} - (2lmn - 2lmn V_{pd\sigma}) \\
\sqrt{3} n^2 V_{pd\sigma} + n(1 - 2l^2) V_{pd\pi} \\
\sqrt{3} m^2 V_{pd\sigma} + m(1 - 2n^2) V_{pd\pi}
\end{array} \right) \left( \begin{array}{c}
\sqrt{3} lm^2 V_{pd\sigma} + m(1 - 2l^2) V_{pd\pi} \\
\sqrt{3} m^2 V_{pd\sigma} + m(1 - 2n^2) V_{pd\pi} \\
\sqrt{3} n^2 V_{pd\sigma} + n(1 - 2l^2) V_{pd\pi}
\end{array} \right),
\]
For trigonal distortions of the type found to exist in Y$_2$Mo$_2$O$_7$, the position of the oxygen ion on a 03 bond can be written as,

$$r_o = \left(\frac{1}{\sqrt{2}} \sin\left[\frac{\alpha_{\text{cub}} - \alpha}{2}\right], \frac{1}{\sqrt{2}} \sin\left[\frac{\alpha_{\text{cub}} - \alpha}{2}\right], -\cos\left[\frac{\alpha_{\text{cub}} - \alpha}{2}\right]\right), \quad (S12)$$

where $\alpha_{\text{cub}} = 2\arctan2\sqrt{2} \approx 141^\circ$ is the bond angle in the case of regular octahedra and $\alpha$ is the bond angle of the trigonally distorted structure, which for the average $Fd\bar{3}m$ structure of Y$_2$Mo$_2$O$_7$ is given by $\alpha \approx 127^\circ$. Inserting these values into Eq. S4 for the $d$-$d$ hopping matrix, one finds for the 03 bond and for $\alpha = 127^\circ$,

$$\Lambda_{03}(127^\circ) = t \begin{pmatrix} -0.63 & 0.36 & 0.0025 \\ 0.36 & -0.63 & 0.0025 \\ 0.0025 & 0.0025 & 0.0029 \end{pmatrix}. \quad (S13)$$

Comparison to Eq. S5 for the case of regular oxygen octahedra shows that the balance between diagonal and off-diagonal hopping of $d^{\pi}$ and $d^{\sigma}$ orbitals has changed significantly, while hopping to/from $d^{\rho}$ orbitals remains unimportant. For regular octahedra the off-diagonal $d^{\varphi} \leftrightarrow d^{\pi}$ hopping dominates, while for trigonally distorted octahedra the diagonal $d^{\varphi} \leftrightarrow d^{\varphi}$ and $d^{\pi} \leftrightarrow d^{\pi}$ hopping becomes more important. The reason for this is the appearance of a $\sigma$-bond hopping channel that competes with the original $\pi$-bond hopping channel as soon as the oxygen octahedra are not regular (see Fig. 1 in the main text). Due to the relative importance of the $\sigma$ channel ($V_{pd\varphi} = 4.8V_{pd\pi}$) even a relatively small change in the bond angle away from the case of regular octahedra can significantly alter the hopping matrix, and this is at the heart of the giant magnetoelectric effect proposed in the main text.

The combination of the trigonal distortion and the spin-orbit coupling split the 9-fold degenerate Hund’s-rule coupled $t_{2g}$ levels ($S = 1$, $L_{\text{eff}} = 1$), resulting in a ground state doublet labelled by $J_{\text{eff}}^z = \pm 2$, where the $z'$ axis points into or out of the tetrahedra and defines a trigonal coordinate system (see Fig. S2). If the energy gap between the doublet and the higher energy levels is considerably larger than the bandwidth, $t^2/U$, then the higher energy levels can be ignored. We assume this is the case and therefore project a modified version of $H_{\text{SO}}$ [Eq. S8] that takes the bond distortion into account into the manifold of local $J_{\text{eff}}^z = \pm 2$ states. Since none of the operators appearing in $H_{\text{SO}}$ [Eq. S8] connect $J_{\text{eff}}^z = 2$ and $J_{\text{eff}}^z = -2$, the Hamiltonian takes the simple form,

$$H_\alpha = J_\alpha(\alpha, \eta) \sum_{\langle ij \rangle} \sigma_i \sigma_j, \quad (S14)$$

where $\sigma = \pm 1$ represents the moment pointing into or out of tetrahedra along the local trigonal axis.

The value of $J_\alpha(\alpha, \eta)$ can be determined by comparing the different configurational energies of a pair of neighbouring moments, resulting in,

$$J_\alpha(\alpha, \eta) = -\frac{1 + r(\eta)}{6} \frac{t_{a_{1g}}(\alpha)^2}{U} + \left(\frac{7R(\eta)}{9} + \frac{r(\eta)}{6} - \frac{11}{18}\right) \frac{t_d(\alpha)^2}{U} - \left(\frac{5R(\eta)}{9} + \frac{r(\eta)}{3} - \frac{2}{9}\right) \frac{|t_{od}(\alpha)|^2}{U} - \left(\frac{2R(\eta)}{9} + \frac{r(\eta)}{3} + \frac{5}{9}\right) \frac{|t_{a_{1g}}(\alpha)|^2}{U}, \quad (S15)$$

where $t_{a_{1g}}(\alpha)$, $t_d(\alpha)$, $t_{od}(\alpha)$ and $t_{a_{1g}}(\alpha)$ are hopping parameters in the trigonal coordinate system, defined for 03 bonds according to,

$$\Lambda^{\text{trig}}_{ij}(\alpha) = \begin{pmatrix} t_{a_{1g}} & t_{a_{1g}} & t_{a_{1g}} \\ t_{a_{1g}} & t_{d} & t_{od} \\ t_{a_{1g}} & t_{a_{1g}} & t_{od} \end{pmatrix} = U \cdot \Lambda_{ij} \cdot U^\dagger, \quad U = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1/\omega & 1 \\ 1/\omega & \omega & 1/\omega \end{pmatrix}, \quad \omega = e^{2\pi i/3}, \quad (S16)$$

where the trigonal basis is $(a_{1g}, e_{g+}^1, e_{g-}^1)$. For other bonds the $U$ must be modified, but this does not affect the value of $J_\alpha(\alpha, \eta)$. Fig. 2 in the main text is plotted using the expression for $J_\alpha(\alpha, \eta)$ given in Eq. S15.

**PHYSICAL PROPERTIES OF $H_d$**

Here we describe in more detail the properties of the spin-lattice Hamiltonian $H_d$ [Eq. 1 in the main text].
Monte Carlo simulation details

We used Monte Carlo simulations to determine the properties of $H_{sl}$. Monte Carlo updates were performed consecutively for spin and lattice degrees of freedom. For the spin degrees of freedom a single spin-flip algorithm was employed. Updates of the lattice degrees of freedom (distortions into or out of a tetrahedra) were split into two steps. First a worm algorithm was used to move between lattice configurations in which each tetrahedra has a 2-in-2-out pattern [42]. The worm was formed taking into account the interaction of the lattice with the (fixed) spin degrees of freedom, and could therefore be made rejection free. Second, a global change to the magnitude of the lattice distortion, $\delta \alpha$, was proposed, and accepted or rejected according to the Metropolis criteria. Parallel tempering was employed to further improve equilibration.

Typically a Monte Carlo step involved $N$ attempts to make a single spin flip, one worm step and 100 attempts to change $\delta \alpha$, with parallel tempering after each 10 Monte Carlo steps. The number of spins was $N = 16 L^3$, where each unit cell has 16 sites, $L$ is the linear size of a cubic cluster and periodic boundary conditions were used. Simulations were performed for $L = 3, \ldots, 12$. Equilibration at the lower transition ($T = T_2$) proved difficult except for the smallest cluster sizes ($L = 3, 4$), due to the strong correlation between spin and lattice degrees of freedom. Overcoming this equilibration difficulty would almost certainly require a combined spin and lattice update. Typical acceptance ratios of the single spin-flip algorithm are shown in Fig. S3, and it can be seen that they become very small in the neighbourhood of $T = T_2$.

Thermodynamic properties

The Monte Carlo simulations were used to determine the thermodynamic properties of $H_{sl}$ and thus map out the phase diagram shown in Fig. 3 of the main text.

The first-order nature of the transition at $T = T_1$ can be ascertained from energy histogram analysis, as shown in Fig. S4. The double-peak structure is a sign of phase coexistence at the transition temperature. That the transition is of the liquid-gas type can be seen from the behaviour of the lattice displacement parameter, $\delta \alpha$, which plays the role of density, and jumps discontinuously at the transition (see Fig. S4). It can also be seen in Fig. S4 that the transition temperature is relatively insensitive to system size.

The nature of the lower transition is more difficult to determine, since our Monte Carlo simulations encounter equilibration problems in the vicinity of the transition for larger system sizes. Energy histogram analysis of small system sizes ($L = 3, 4$) appear to show a second-order transition. The cluster-size dependence of the transition temperature is hard to ascertain, due to the equilibration problems, and could be significant.

Loops

Here we explain in more detail the microscopic structure in the spin-lattice liquid phase (see Fig. 3 in the main text for the phase diagram).
FIG. S4: Characteristics of a first-order liquid-gas type transition at \( T = T_1 \), shown for \( g^2/(4J_{is}K) = 1.4 \). (a) Energy histogram analysis demonstrates a first-order transition, as can be seen from the double-peak structure. The \( L = 6 \) cluster has a transition at \( T = 1.57(2)J_{is} \). (b) The lattice displacement parameter, \( \delta \alpha(T) \), for varying system sizes, showing a jump at \( T = T_1 \). Error bars are smaller than the point size.

FIG. S5: A single tetrahedron showing lattice displacement and spin degrees of freedom. (a) A 2-in-2-out lattice displacement of the ions (individual displacements shown by black arrows) results in one long bond (blue), four medium bonds (red) and one short bond (green). Lattice displacements are fully specified by the bond colouring. (b) Spins point into (orange) or out of (light blue) the tetrahedron, and for a given lattice displacement there are four lowest energy configurations with a 3-1 configuration, one of which is shown (see also Fig. 3 in the main text). In the 3-1 spin configurations the bond energies of the medium bonds cancel, and only the long and short bonds contribute to the total energy.

The building blocks of the pyrochlore lattice are tetrahedra, and in the spin-lattice liquid phase these have two ions displaced towards and two away from their centres. Each tetrahedron thus has one long bond, four medium-length bonds and one short bond, and the long and short bonds are opposite one another (see Fig. S5). The effective spin model on a tetrahedron with a fixed lattice displacement consists, in the local Ising basis, of one ferromagnetic bond (long) four weakly antiferromagnetic bonds (medium) and one more strongly antiferromagnetic bond (short). As a result, an isolated tetrahedron with fixed lattice displacement has a fourfold-degenerate spin ground state, with three spins pointing in and one out or vice versa (see Fig. 3 in the main text). In these configurations, the four medium-length bonds host two satisfied interactions and two unsatisfied interactions, and therefore do not contribute to the energy.

On the pyrochlore lattice, the requirement that lattice displacements follow a 2-in-2-out rule, as in water ice, results in the formation of loops consisting of alternating long and short bonds. Each lattice site is visited by exactly one loop, and the loops are non-intersecting and are closed in the presence of periodic boundary conditions. The shortest possible loop has length \( l_{\text{loop}} = 6 \), and, due to the structure of the pyrochlore lattice, loops have to be even in length. Some example loops are shown in Fig. S6.

Configurations of the system are labelled by a combination of the loop structure (or equivalently the in/out lattice displacements) and the spin directions. There is an extensive set of degenerate ground-state configurations in which all tetrahedra have a 3-1 (three in and one out or vice versa) spin configuration of the type shown in Fig. S5 (see also Fig. 3 in the main text). These ground-state (gs) configurations consist of loops of length \( l_{\text{loop}} = 4 + 4m \) with \( m = 1, 2, 3, \ldots \) (i.e. loops of length \( l_{\text{loop}} = 2 + 4m \) are excluded) and Ising spin configurations on the loops of \( \sigma_{\text{loop,gs}} = (1, 1, -1, -1, 1, 1, -1, -1, \ldots) \). There are two types of local move that leave the system within the ground state manifold. One possibility is that the spins on a loop are all flipped simultaneously, taking \( \sigma_{\text{loop,gs}} \rightarrow -\sigma_{\text{loop,gs}} \) (see Fig. S7). A second possibility is that the bond displacements are exchanged around a closed set of medium-length bonds thus rearranging the loop structure of the lattice (see Fig. S8 for an example of a non-ground-state loop update).
FIG. S6: Loops of alternating long (blue, $J_\text{ls} < 0$) and short (green, $J_\text{ls} > 0$) bonds, shown both on the pyrochlore lattice and as 2D projections. (a) 6-site loops are frustrated in the sense that there must be at least one unsatisfied spin interaction on the loop (marked by a cross). (b) 8-site loops can satisfy all the spin interactions.

FIG. S7: Spin configurations on an 8-site loop. (a) A ground-state spin configuration of the loop. (b) Flipping all the spins on the loop gives the time-reversed ground-state configuration. (c) Flipping one spin creates a pair of kinks (black crosses) and these are associated with tetrahedral configurations outside the 3-1 ground-state. (d) Flipping a second spin moves the location of one of the kinks, and thus pairs of kinks can be separated.

Typically it is simultaneously necessary to flip some spins to ensure that the reconstructed loops retain the correct $\sigma_\text{loop,gs}$ structure.

FIG. S8: An example of a local loop and spin update that leaves the energy invariant. (a) Three 6-site loops in a kagomé plane of the pyrochlore lattice, with the planar projection of the lattice displacements shown as black arrows. Each loop has one kink associated with an unsatisfied spin interaction (marked by black crosses). (b) Reversing the lattice displacements on the central hexagon changes the loop structure from three 6-site loops to one 18-site loop. Since there is no simultaneous change of the spins, the number of kinks is not conserved, and in this example the 18-site loop has five kinks, two more than the three 6-site loops. (c) Flipping a spin removes two kinks and thus the energy (in the kagomé plane) of the new configuration is the same as that of the initial configuration.

One example of an excitation out of the ground state is the introduction of kinks into the otherwise periodic Ising configuration on a loop (see Fig. S7). For loops of length $l_\text{loop} = 4 + 4n$ the number of kinks has to be even, and each kink is associated with a 2-in-2-out (or potentially 4-0) spin configuration on the relevant tetrahedron. Excitations
can also involve the creation of loops with length $l_{\text{loop}} = 2 + 4m$, and the reason that these cost energy is that they have to contain at least one kink (see Fig. S6a). Further kinks can be created in pairs, and so the number of kinks is constrained to be odd.

Monte Carlo simulations show two phase transitions. At the high-temperature first-order phase transition ($T = T_1$) the lattice displacement parameter, $\delta\alpha$, acquires a finite value. For $T < T_1$ the bonds can therefore be divided into long, medium and short lengths with differing spin interactions, and it becomes meaningful to discuss the system in terms of loops of alternating long and short bonds. A non-local loop-spin order parameter can be constructed as the product of Ising spins around the loop projected onto its ground state value and given by,

$$O_{\text{loop}} = \sum_{\text{loops}} \sum_{i \in \text{loop}} \sigma_i \sigma_{i \text{gs}}^{l_{\text{loop}}, \text{gs}}, \quad (S17)$$

where $O_{\text{loop}} = 0$ for loops with uncorrelated spins and $O_{\text{loop}} = 1$ in the ground state. The behaviour of this order parameter in Monte Carlo simulations is shown in Fig. S9a, and it can be seen that it jumps from $O_{\text{loop}} \approx 0$ for $T > T_1$ to a finite value for $T < T_1$. Further reducing the temperature builds up spin correlations on the loops and therefore increases the value of $O_{\text{loop}}$.

The distribution of loop lengths can be measured by Monte Carlo simulations. In the bulk of the intermediate phase ($T_2 < T < T_1$) we find a power-law distribution of loop lengths, with no sign of a symmetry breaking between loops of length $l_{\text{loop}} = 4 + 4m$ and $l_{\text{loop}} = 2 + 4m$. This is shown in Fig. S10, where it can be seen that there is a crossover between different power laws at $l_{\text{loop}} = L^2$. This crossover is the effect of performing simulations on finite size
clusters, where loops can be divided into those that wind or don’t wind the system [38]. The power-law distribution we find matches well to that already determined for a 2-in-2-out manifold of states without further interactions [38]. As such, the fact that lattice displacements are effectively coupled via the spin degrees of freedom, doesn’t restrict their exploration of the full 2-in-2-out manifold in the bulk of the spin-lattice-liquid phase.

At lower temperature, Monte Carlo simulations show that there is a phase transition at $T = T_2$ at which the system begins to favour loops of length $l_{\text{loop}} = 4 + 4m$ over those with $l_{\text{loop}} = 2 + 4m$. This can be seen from studying the distribution of loop lengths, and a simple way of doing this is by considering,

$$O_{\text{mis}} = \frac{N_{4+4m} - N_{2+4m}}{N},$$

(S18)

where $N_{i+4m}$ is the number of sites belonging to loops of lengths $l_{\text{loop}} = i + 4m$. $O_{\text{mis}}$ measures the mismatch in the number of sites beween the two loop-length classes, and simulation results for its behaviour can be seen in Fig. S9b. It takes a relatively low value for $T > T_2$ before rapidly increasing at $T_2$ and saturating at $O_{\text{mis}} = 1$ approaching $T = 0$. 
