1 Supplementary Text

1.1 Intensity model for the continuum

The central message of our work is that one can experimentally distinguish the magnetic molecular orbital’s form factor from the ionic one (28). We first verify in Fig. S11 that the radial $Q$ dependence of the form factor measured on the continuum has an energy-independent momentum structure, namely, the intensity shows a distinct maximum at $Q_0 = 2.5 \text{ Å}^{-1}$. To describe the magnetic electron cloud that underlies this behavior, we aim to use a ferromagnetic “cluster” of ionic electron clouds (26), hence the following effective model, to calculate the scattering intensity as a function of momentum transfer,

$$I_M(Q) = A \times |f(Q)|^2 \times \sum_m \left| \sum_n e^{-i(R_n \cdot Q)} \times e^{-\frac{(R_n - R_m)^2}{2\sigma_1^2}} \right|^2 + B,$$  \hspace{1cm} (S1)

where $A$ is a global normalization factor, $B$ is a constant background, and $f(Q)$ is the (isotropic) atomic form factor of individual Mn ions. $R_m$ denotes the coordinate of the “correlation center” in the unit cell which we will explain later, where the summation over $m$ goes through all symmetry-related centers. The summation over $n$ in $R_n$ goes through all Mn atoms, in order to describe interference on a chosen ferromagnetic cluster centered at $R_m$. In practice, we only need to consider atoms within a few times of $\lambda = 2\sqrt{2 \ln 2\sigma_1}$ (size of the cluster) from $R_m$.

We model the ferromagnetic clusters using three representative choices of the correlation centers: (1) The center of the nearest-neighbor equilateral triangle; there are four equivalent points (the summation over $m$ in Eq. S1) in the unit cell. (2) The midpoint between two nearest Mn atoms; there are twelve equivalent points in the unit cell. (3) Mn ions; there are four equivalent points in the unit cell. By adjusting the effective correlation length, we can adjust the size of the magnetic clusters. For instance, when the correlation length is small, under choice (1) the cluster becomes the nearest-neighbor equilateral triangle; under choice (2) the cluster represents a “diatomic molecule”; under choice (3) the cluster is reduced to the ionic
limit. Outputs of the model under the three choices, upon varying the correlation length, are presented in Figs. S12–S14. We find that only choice (1) in the small correlation-length limit can reasonably fit our experiment results. It corresponds to the nearest-neighbor equilateral triangle model that we describe in the main text. In this limit, our model can be simplified as,

$$I_M(Q) = A \times |f(Q)|^2 \times \sum_{j=1}^{4} |F_j(Q)|^2 + B,$$

(S2)

where $F_j(Q) = \sum_{R \in T_j} e^{-i(Q \cdot R)}$ summed over Mn positions represents a triangle with four ($j$) possible orientations. The physical meaning of this model is that spins on the three Mn atoms within a triangle are fully coherent and aligned, whereas spins belonging to different triangles are uncorrelated.

In fact, Eq. S2 already offers a reasonably global description of intensity variations of the continuum, with respect to (1) the agreement of simulation and experimental data of the inter-BZ INS intensity at high energy (Fig. S15), (2) insensitive dependence on the choice of the nominal valence value which affects $f(Q)$ (Fig. S16), and (3) the ratio $\frac{I(M_1=(0, 0.5, 0.5))}{I(M_2=(1, 0.5, 0.5))}$ (Fig. S17) consistent with the calculated value of 2.56. But still, the model in Eq. S2 lacks description of the intra-BZ structures of the continuum. Here, we propose two nearly equally good intra-BZ models, which are to be multiplied with the nearest-neighbor equilateral triangle form factor to describe the INS intensities:

1. Lattice Lorentzian model: In Figs. S6 and S7, the continuum shows a set of broad peaks at $Q = G + q$, positioned periodically in the reciprocal lattice. When considering the inter-triangle correlation in real space and using the normalized lattice Lorentzian function for the continuum peak (26), we obtain

$$I_M(Q) = A \times |f(Q)|^2 \times \left( \sum_{j=1}^{4} |F_j(Q)|^2 \right) \times \text{LL}(Q) + B,$$

(S3)
\[ \text{LL}(Q) = \frac{1}{2} \left( \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(H - h_0))} + \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(H + h_0))} \right) \times \frac{1}{2} \left( \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(K - k_0))} + \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(K + k_0))} \right) \times \frac{1}{2} \left( \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(L - l_0))} + \frac{\sinh(\xi^{-1})}{\cosh(\xi^{-1}) - \cos(2\pi(L + l_0))} \right), \]

where \( \text{LL}(Q) \) is the normalized lattice Lorentzian function, \( \xi = \xi_a = \xi_b = \xi_c \) is the correlation length in real space, \( h_0 = k_0 = l_0 \) is the continuum peak position. The best-fit parameters are \( h_0 = k_0 = l_0 = 0.5 \) r.l.u. and \( \xi = 0.35 \) l.u.

(2) Spherical shell model: Since the continuum is located on a thick and hollow spherical shell within the BZ (Fig. 2C), by modifying Eq. S2 with a spherical shell function, we obtain

\[ I_M(Q) = A \times |f(Q)|^2 \times \left( \sum_{j=1}^{4} |F_j(Q)|^2 \right) \times \text{Shell}(Q) + B, \tag{S5} \]

\[ \text{Shell}(Q) = \int_{\Omega=\{|Q' - G|=R_0\}} e^{-\frac{(Q - Q')^2}{2\sigma^2}} dQ', \tag{S6} \]

where \( \text{Shell}(Q) \) is the spherical shell function, \( G \) is the nearest integer Bragg point from \( Q' \), and \( R_0 \) and \( \sigma_0 \) describe the radius and Gaussian thickness of spherical shells, respectively. The best-fit parameters are \( R_0 = 0.76 \) Å\(^{-1}\) and \( \sigma_0 = 0.39 \) Å\(^{-1}\).

To further demonstrate the necessity of the nearest-neighbor equilateral triangles, we modify Eq. S5 with a covalent factor \( p_{\text{cov}} \) (26, 65, 66) and remove the sense of inter-atomic interference \( (\sum_{j=1}^{4} |F_j(Q)|^2) \)

\[ I_M(Q) = A \times |f(p_{\text{cov}}Q)|^2 \times \text{Shell}(Q) + B, \tag{S7} \]

here, we use the isotropic magnetic form factor of Mn\(^{2+}\), but with an adjustable covalent compression \( p_{\text{cov}} \). This corresponds to the increased spatial extent of magnetization density near the Mn atoms. In order to have an intuitive understanding of the influence of \( p_{\text{cov}} \), Fig. S19 shows the intensity variation by changing \( p_{\text{cov}} \) from 1 to 2, under the same coefficient \( A \) and \( B \) in Eq. S7. With increased \( p_{\text{cov}} \), the intensity decreases more rapidly at the same \( Q \) position.
1.2 Spin-wave calculation and spectral weight of the continuum

To understand the observed (nearly) ferromagnetic spin waves, we fit the spin-wave spectra with the SpinW program (67). The magnetic Heisenberg Hamiltonian reads

\[ H = - \sum_{i<j} J_{ij} S_i \cdot S_j, \]  

(S8)

where \( J_{ij} \) is the magnetic exchange coupling of the spin \( S_i \) and \( S_j \). Assuming that the nearest-neighbor ferromagnetic exchange coupling \( J_1 (> 0) \) dominates, our best-fit values are \( J_1 = 21.8 \text{ meV} \) and \( 0.7 \pm 0.15 \mu_B/\text{Mn} \), with the Lande g-factor set equal to 2 and the magnetic form factor of Mn\(^{2+} \) ion, as shown in Fig. S20. Here, for the calculation of the “acoustic” spin-wave branch, it is still a good approximation to consider all the magnetic moments to reside on the Mn ions, because spin waves in this limit are nearly uniform motions of the magnetization density, and there is no difference from choosing the nearest-neighbor equilateral triangles as the fundamental units. In other words, if we imagine an observer looking at spin waves in real space in such a long-wavelength limit, the observer would not be able to tell whether MnSi is an ionic or a molecular-orbital magnet. The approximation gradually breaks down as the wavelength approaches the spatial extent of the triangles (see text).

Figure S21 shows the imaginary part of the dynamic magnetic susceptibility of the continuum (momentum-integrated in (2, 1, 0) BZ) (68), based on the absolute scattering cross sections and after accounting for the nearest-neighbor equilateral triangle form factor. The energy-integrated spectral weight from 45 meV to 260 meV in Fig. S20 is \( 1.1 \pm 0.2 \mu_B/\text{Mn} \). Due to the contamination of phonons below 45 meV, here we use a damped harmonic oscillator function (DHO) to fit \( \chi''(E) \) and extrapolate the data to zero and much higher energies (\( \sim 1 \text{ eV} \)) (26), which amounts to a total spectral weight \( 2.2 \pm 0.4 \mu_B/\text{Mn} \).
1.3 EBR-Restricted Maximally Localized Wannier Function Calculation

A suitable tight-binding basis is essential for properly describing low-energy physics such as magnetism in crystalline materials. While it is often taken for granted that atomic orbitals form such a basis in magnetic compounds, this assumption is problematic when orbital hybridization is significant. In such cases, obtaining a physically trackable and mathematically rigorous tight-binding model may be a nontrivial task. Rather than relying on intuition and inspection of DFT-calculated bands, which do provide valuable insights in the presence of certain characteristic features in the band structure such as an isolated flat band (21), here we adopt the concepts of band representation (BR) and elementary band representation (EBR), which have recently been developed in the context of topological quantum chemistry (9), to guide our determination of suitable tight-binding bases. We emphasize that this method of analysis respects all crystallographic symmetries. As a result, we expect previous understanding of MnSi based on symmetry arguments (such as Dzyaloshinskii-Moriya interactions and band topology) to be automatically compatible with our new molecular-orbital picture.

A BR is a collection of energy bands that are energetically isolated from the other bands. Generically, it may or may not be possible to reproduce a given BR using tight-binding models based on local orbitals that respect the crystallographic symmetries (and when this is not possible, the BR is topological (9, 10)). An EBR, in contrast, is defined by the formation of energy bands starting from a minimal set of local orbitals consistent with the symmetry – the orbitals must be an irrep of a maximal Wyckoff site’s point group (9, 10, 69). In other words, the simplest form of BR that can possibly be obtained with a tight-binding model is an EBR. More generally, BRs that can be described by tight-binding models must be decomposable into EBRs, whereas the process of EBR identification and BR decomposition (into EBR) can be facilitated by symmetry indicators (9, 10). An important example (in non-topological materials) is a non-degenerate and isolated (flat) band, which is always an EBR. Such band’s existence near the
Fermi level immediately calls for a “stand-alone” tight-binding description of the low-energy physics, yet this simple intuition is available only when there is at least one fixed point in the primitive cell that remains unchanged under all space-group operations.

Importantly, an EBR does not have to be, and is often not, a single band. Yet it remains to be a defining property of a minimal tight-binding model because of symmetry. In our present case, since the space group of MnSi is non-symmorphic, all EBRs (a total of four) contain either 4 or 8 bands. Our strategy here is hence to first identify bands near the Fermi energy as EBRs (or decomposable BRs), and then to find Wannier orbitals for each of the EBRs and BRs as a whole. To fix the gauge of the Wannier orbitals, we adopt the maximal localization criterion (4). We call this method “EBR-restricted MLWF calculation.” The strongest constraint is set by the identification of EBRs and BRs, which ensures that the obtained tight-binding model is a low-energy minimal model. Meanwhile, the maximal localization requirement not only satisfies the tight-binding philosophy, but also makes the computation of magnetic neutron scattering cross section (as a function of momentum) most conveniently separable into intra- and inter-BZ parts, the latter of which is our form factor, and the next Section provides a mathematical proof of it.

We have calculated the irreps of the 8 conduction bands at high-symmetry points of the BZ using the open-source program irvsp (70, 71). The result is listed in Table S1. By comparing to the EBR table for space group No. 198 on the Bilbao Crystallographic Server (https://www.cryst.ehu.es/cgi-bin/cryst/programs/bandrep.pl) (69), it is clear that these bands constitute the EBR labeled as $E \uparrow G$, where $E$ is a two-dimensional irrep of the site symmetry group $C_3$ of Wyckoff site $4a$, and $E \uparrow G$ indicates induced representation on space group $G$ (of MnSi). Similarly, we find that the next 12 bands deeper below $E_F$ are an $(A_1 + E) \uparrow G$ composite BR. These two EBR/BRs are entangled only slightly with each other, making it relatively straightforward to obtain high-quality MLWFs for each of them.

The minimal tight-binding model for low-energy physics is obtained by using the Bloch
states in the EBR $E \uparrow G$ as input. The model is expected to involve the Wyckoff $4a$ site, but because $4a$ is a “variable” site whose coordinate contains a continuous parameter (Fig. S1), the $4a$ label alone does not yet allow us to pin down the magnetization clouds (namely magnetic Wannier functions). The gauge freedom of Wannier functions is fixed by the maximally localized criterion. After minimizing the spreads of the Wannier functions, the Wannier centers of the EBR $E \uparrow G$ turn out to be very close to the centers of the nearest-neighbor equilateral triangles (Fig. 4B, Fig. S22C and Fig. S23, C1-C3), which deviate significantly from the Mn atomic sites and signal formation of molecular orbitals. It means that the $E$ in $E \uparrow G$ comes from the molecular sites $M_{i=1,2,3,4}$ (i.e. centers of the nearest-neighbor equilateral triangles, the corresponding local $z$ axes for $i = 1, 2, 3, 4$ are $[\bar{1}1\bar{1}], [1\bar{1}1], [\bar{1}1\bar{1}], [1\bar{1}1]$ and the local $x$ axes are respectively $[110], [\bar{1}0\bar{1}], [1\bar{1}0], [\bar{1}10]$) rather than the Mn (or Si) atomic sites, even though they all share the same Wyckoff label $4a$.

While surprising at first sight, these triangle-centered MLWFs are a robust result. To see it, we compare them to MLWFs calculated under Mn-site constraint. As both sets of MLWFs are constructed from the same EBR’s Bloch states, the resultant tight-binding models reproduce the band dispersion comparably well (Fig. S22A). However, the constrained MLWFs are more extended, seen from their 36% larger spread (15.4 Å$^2$, compared to 11.3 Å$^2$ of the triangle-centered MLWFs) and considerably wider contour surface enclosing half of the electron weight (Fig. S22, C and D). This difference is significant, because a Wannier orbital’s effectiveness in describing the INS cross section explicitly depends on its localization property (see the proof in next section). The constrained MLWFs are also dissimilar in shape to the atomic orbitals of Mn, which should not be the case if an ionic picture were effective. Meanwhile, the MLWFs are calculated to be the atomic orbitals of Mn ($e$ orbitals (38)) only when a much greater number of Bloch states – a total of 32 bands near $E_F$ – are taken as input. Despite being localized (Fig. S22E), the atomic orbitals fail to account for the low-energy physics (Fig. S22B): the tight-
binding model clearly deviates from the magnetic EBR when hybridizations with other atomic orbitals (primarily $p$ of Si) are neglected. The hybridizations push the atomic orbitals’ partial density of states (PDOS) into bands both above and far below $E_F$ (30), indicating covalency of the system. In Figs. S23 and S24, we further show that all electronic states within $\sim 6$ eV below $E_F$ are molecular orbitals, among which the PDOS near $E_F$ is exclusively contributed by these orbitals on the triangles. With all the supporting evidence, we conclude that the experimentally revealed magnetic molecular orbitals are fully consistent with our EBR-restricted MLWF calculation.

The MLWFs on a given molecular site form a two-dimensional irrep $E$ of the site symmetry group (72, 73) $G_{M_i}$ (isomorphic to $C_3,(111)$), and we label them as $W_{M_i,\mu=a,b}$ (Fig. S23, C1 and C2, the lattice-cell index $R$ is omitted for simplicity; note that for the convenience of plotting, we have chosen a real basis, such that each of the wave functions is off-center from $M_i$ and slightly less localized than the complex MLWFs). Band interpolation using these orbitals as the tight-binding basis is highly satisfactory (Fig. 4A, Fig. S22A, Fig. S23A and Fig. S24A). The intrinsic property of the MLWFs can be characterized by the $C_3$-invariant density function $n_{M_i} \equiv \frac{1}{2} \sum_{\mu=a,b} |W_{M_i,\mu}|^2$, which is visualised in Fig. S23, C1-C3.

The above molecular orbitals $W_{M_i,\mu}$ of the magnetic EBR (Fig. S23, C1 and C2) form a “stand-alone” subspace in the electronic structure. To see this, we need to show that an electron in these orbitals can hardly hop into orbitals (whether or not in the same lattice cell) outside the subspace. We use a two-orbital hopping toy model to set the stage: for a $2 \times 2$ matrix Hamiltonian, in which hopping $t$ is the off-diagonal elements, the energy-level difference measured from the average is given by $\sqrt{(\delta E/2)^2 + t^2}$, where $\delta E \equiv E_1 - E_2$ is the energy difference without the hopping. Using such a pairwise description for the Wannier orbitals, the significance of hopping can be quantified by a collection of dimensionless numbers $\eta_{ij}(R) = |E_i - E_j| / \sqrt{|E_i - E_j|^2 + 4t_{ij}(R)^2}$, where $t_{ij}(R) = \langle W_i(0)|H|W_j(R)\rangle$. 
is the hopping strength between the \( i \)-th and the \( j \)-th Wannier orbitals \( R \) cells apart, and 

\[ E_i = \langle W_i(0) | H | W_i(0) \rangle \]

is the on-site energy. By definition, \( \eta \) is between 0 and 1, and the two limits are hopping- and gap-dominated, respectively. If the molecular orbitals of the magnetic EBR indeed form a “stand-alone” subspace, an electron in any one of these orbitals should be able to hop into at least some other orbitals in the same EBR, giving rise to an \( \eta \) close to 0 (as the \( E_i \)’s are the same), but it cannot hop into any of the Wannier orbitals outside the EBR, so that those \( \eta \) should be close to 1. The last two columns of Table S2 show exactly this [for \( W_{Mn,\alpha} \), displayed in Fig. S23C1, chosen without loss of generality]. The result is nothing but an alternative way to see that the tight-binding bands formed by the molecular orbitals are well-separated from the other bands, as visualized in Fig. S23A.

Table S2 further enables us to show that our EBR-restricted Wannier orbital computation is mathematically more rigorous and trackable than a conventional method of using atomic orbitals to construct molecular orbitals, as has been done for Na\(_2\)IrO\(_3\) (21). To take the latter approach, one would need to first treat the symmetry properties of the atomic orbitals carefully (73), and then use physical intuition (such as with quantum chemistry) to construct molecular orbitals that can only “hop into themselves” by virtue of hopping cancellation between the constituent atomic orbitals. What we explain below and show in Table S2 is that, for MnSi, taking such an approach is a formidable (and, practically incomprehensible) task due to the system’s significant electron itinerancy.

To ensure that we start with an adequate mathematical description of the task, we have computed 32 atomically centered maximally localized Wannier functions [Mn \( 3d = a_{3z^2-r^2} + (e_{xy}, e_{x^2-y^2}) + (e_{xz}, e_{yz}) \) and Si \( 3p = a_z + (e_x, e_y) \) orbitals, \( z \) denotes the local \( C_3 \) axis; there are 4 atoms of each type in the primitive cell]. They respect the atomic-site symmetries and allow us to reproduce the full band structure ranging from \( \sim 6.5 \text{ eV} \) below to \( \sim 6.5 \text{ eV} \) above the Fermi level. The 8 atomic orbitals that have the largest contribution to the magnetic EBR are displayed
in Fig. 4 of main text. Limited by the $11 \times 11 \times 11$ k-grid used in our non-selfconsistent calculations, we are then able to place these atomic orbitals on an equal grid of the lattice-cell index $R$, forming a basis containing a total of 42592 atomic orbitals. A chosen molecular orbital from the magnetic EBR (1 out of 8) situated in the home cell can then be projected onto the atomic orbital basis, in order to reveal how the molecular orbital can be constructed from the atomic orbitals. We note that the numerical accuracy of our molecular orbitals is very high – the normalization of the 8 molecular orbitals in the home cell is $1 - \delta_N$ with the largest $|\delta_N| = 0.002$, and the orthogonality between them is $\delta_O$ with the largest $|\delta_O| = 6 \times 10^{-6}$. The atomic orbitals are similarly accurate.

The main conclusions following from the data summarized in Table S2 are two-fold: First, due to the spatial extent of the molecular orbitals which reflects electron itinerancy, the projection of a molecular orbital onto atomic orbitals up to a cut-off distance from the molecular orbital center only becomes “complete” when the cut-off distance is extremely large (12 Å, over twice the lattice constant, in order to lose no more than 1% of weight). Second, while the hopping into nearby molecular orbitals in the same EBR is always strong (“$\eta_{\text{min}}$ within EBR” in Table S2), hopping outside the EBR cannot be completely eliminated even up to such a large cut-off distance, although a converging trend is seen as the distance increases. Indeed, to obtain a decent atomic orbital weight and elimination of unwanted hopping, one would need to include as many as 147 atomic orbitals up to a distance of 4.6 Å, whereas including only 61 atomic orbitals up to a distance of 3.6 Å already makes the result considerably worse.

To provide some concrete numbers, the molecular orbital $W_{M_4,a}$ is a linear combination atomic orbitals “mainly” contributed by two nearby Mn atoms [see Fig. S23C1 for their relative locations]:

$$W_{M_4,a} = -0.41(Mn_1)x^2 - y^2 - 0.35(Mn_1)3z^2 - r^2 + 0.25(Mn_2)3z^2 - r^2 + 0.23(Mn_1)yz + 0.22(Mn_2)yz + 0.20(Mn_2)xy - 0.17(Mn_2)x^2 - y^2 + \cdots,$$

where each of the atoms has its own z axis defined by the local $C_3$ symmetry and different from the z axis of $M_4$. However, summing up the
above-listed (squared) weight of the atomic orbitals produces only 52% of the molecular orbital, the rest of which is contributed by many more atomic orbitals at further distances from the molecular orbital center. This clearly shows the difficulty of manually constructing molecular orbitals from atomic orbitals in the presence of strong electron itinerancy. Importantly, the multi-orbital superposition from the same Mn atoms indicates that the molecular orbitals are subject to strong Hund’s rule coupling, which promotes the ferromagnetism in the seemingly strongly dispersing magnetic EBR.

The wave function’s sign reversal between the two lead-contribution atoms [Fig. S23, C1 and C2] indicates that the molecular orbital is of anti-bonding nature: the electron density is small around the Mn-Mn bond center, and the nearest-neighbor equilateral triangle’s magnetization cloud has a “hollow” internal structure, which has been directly confirmed by our INS experiment. We have used the crystal orbital Hamiltonian population (COHP) method (74, 75) to verify the anti-bonding character near the Fermi energy (Fig. S24B). Since formation of covalent bonds is energetically motivated by the occupancy of bonding rather than anti-bonding states, for completeness, we have performed MLWF calculations for the aforementioned 12-band BR deeper below $E_F$. To our satisfaction, this BR is indeed formed by two bonding-typed molecular orbitals with high electron densities between nearby Mn and Si atoms (Fig. S23). We thus conclude that a thorough microscopic explanation for the formation of magnetic molecular orbitals has been obtained for MnSi.

1.4 Cross sections of Stoner excitations from a spin-polarized EBR

Here we derive the magnetic neutron scattering cross sections of Stoner excitations. It is concluded that a form-factor-like quantity associated with the maximally-localized Wannier functions of the magnetic bands provides a good approximation for the wide-range momentum dependence of the cross section, given that the relevant bands all belong to a common elemen-
tary band representation in the unpolarized state. As an EBR can be described by a minimal tight-binding model of essentially a single orbital (and its symmetry-related counterparts) on the crystal lattice, once the orbital is determined as the MLWFs, a spin-flip operator’s matrix elements between Bloch states can be conveniently computed from the MLWFs’ electron densities.

The spin operator $\hat{S}_\alpha$ ($\alpha = x, y, z$) can be written as

$$\hat{S}_\alpha = \hat{\Psi}_\alpha^\dagger(r) S^\alpha \hat{\Psi}(r) = \sum_{\sigma \sigma'} \hat{\psi}_\sigma^\dagger(r) S^\alpha_{\sigma \sigma'} \hat{\psi}_{\sigma'}(r),$$

where $S^\alpha$ are the Pauli matrices and $\hat{\Psi}_\alpha^\dagger(r) = \begin{bmatrix} \hat{\psi}_\alpha^\dagger(r) & \hat{\psi}_\alpha^\dagger(r) \end{bmatrix}$ is the creation operator of spinor wave functions. $\hat{\psi}_\sigma^\dagger(r)$ can be expressed (76) by the creation operator $\hat{C}_{n,k,\sigma}^\dagger$ of single-particle Bloch states $\psi_{n,k,\sigma}(r)$ ($n$: band index; $k$: wave vector; hereafter, all position and momentum variables are vectors)

$$\hat{\psi}_\sigma^\dagger(r) = \frac{1}{N} \sum_{nk} \psi_{n,k,\sigma}^*(r) \hat{C}_{n,k,\sigma}^\dagger,$$

where $N$ is the number of mesh points in the Brillouin zone and the normalization condition is $\langle \psi_{n,k} | \psi_{m,k'} \rangle = N \delta_{nm} \delta_{kk'}$. In the basis of $\psi_{n,k,\sigma}(r)$, the spin operator is given by

$$\hat{S}_\alpha = \frac{1}{N^2} \sum_{k,n,m,k',\sigma,\sigma'} \psi_{n,k,\sigma}^*(r) S^\alpha_{\sigma \sigma'} \psi_{m,k',\sigma'}(r) \hat{C}_{n,k,\sigma}^\dagger \hat{C}_{m,k',\sigma'},$$

and its Fourier transform is

$$\hat{S}_q = \int d^3r e^{-iqr} \hat{S}_\alpha = \int d^3r e^{-iqr} \frac{1}{N^2} \sum_{k,n,m,k',\sigma,\sigma'} \psi_{n,k,\sigma}^*(r) S^\alpha_{\sigma \sigma'} \psi_{m,k',\sigma'}(r) \hat{C}_{n,k,\sigma}^\dagger \hat{C}_{m,k',\sigma'}.$$ 

The transverse components, which produce spin flips, are

$$\hat{S}_q^- = \int d^3r e^{-iqr} \hat{S}^- = \frac{1}{N^2} \int d^3r e^{-iqr} \sum_{k,n,m} \psi_{n,k,\sigma}^*(r) \psi_{m,k+q,\sigma}^+(r) \hat{C}_{n,k,\sigma}^\dagger \hat{C}_{m,k+q,\sigma}^+.$$
\[ \hat{S}_q^+ = \int d^3r e^{-iqr} \hat{S}^+ = \frac{1}{N^2} \int d^3r e^{-iqr} \sum_{k,n,m} \psi_{n,k,\uparrow}^* (r) \psi_{m,k+q,\downarrow} (r) \hat{C}_{n,k,\uparrow}^\dagger \hat{C}_{m,k+q,\downarrow}, \]

where we use the matrix representation \( S^- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \) and \( S^+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \). \( \hat{S}_q^+ \) and \( \hat{S}_q^- \) are Hermitian conjugates.

It is useful to transform from Bloch functions to Wannier functions \( W_{l_d,l_s,\sigma} (r-R) \equiv W_{l_d,\sigma} (r-l_s-R) \), where \( R \) is a lattice vector, \( l_s \) is a Wyckoff site (\( l_s = 1, \cdots, n_s \) with site multiplicity \( n_s \)) in the primitive cell, and \( l_d = 1, \cdots, d \) is the index within a \( d \)-dimensional irrep of the Wyckoff site. Together, the local orbitals induce the considered bands, and when the Wyckoff site is a maximal Wyckoff site, the induced bands form an EBR (9). In this case, we emphasize that although the number of bands \( (n_d d) \) can generally be greater than one, the bands cannot be further separated into smaller sets of bands because of band degeneracy and compatibility relationships enforced by symmetry. We denote \( l = (l_d, l_s) \) to simplify the notation. According to the transformation

\[ \psi_{n,k,\sigma} (r) = \sum_{l,R} e^{i k R} W_{l,\sigma} (r-R) U_{l,n,\sigma}^\dagger (k), \]

\[ \hat{C}_{n,k,\sigma}^\dagger = \sum_{l,R} e^{i k R} U_{l,n,\sigma}^\dagger (k) \hat{T}_{l,R,\sigma}, \]
where \( \hat{T}_{l,R,s}^\dagger \) is the creation operator of Wannier function \( |W_{l,R,s}\rangle \), we have

\[
\hat{S}_q^- = \frac{1}{N^2} \int d^3r e^{-iqr} \sum_{k,n,m} \psi_{n,k,+}^* (r) \psi_{m,k+q,+} (r) \hat{C}_{n,k,+} \hat{C}_{m,k+q,+} \\
= \frac{1}{N^2} \sum_{k,n,m,l,l',l',R} \sum_r e^{-ikR} W_{l1}^\dagger (r - R) U_{nl} (k) e^{-iqr} e^{i(k+q)R'} W_{l'l'}^\dagger (r - R') U_{l'm'} (k + q) d^3r \hat{C}_{n,k,+} \hat{C}_{m,k+q,+} \\
= \frac{1}{N^2} \sum_{k,n,m,l,l',l',R} \sum_r e^{-ik(R-R')} W_{l1}^\dagger (r - R) U_{nl} (k) e^{-iqr} e^{iqR'} W_{l'l'}^\dagger (r - R') U_{l'm'} (k + q) d^3r \hat{C}_{n,k,+} \hat{C}_{m,k+q,+} \\
= \frac{1}{N^2} \sum_{k,n,m,l,l',l',R} \sum_r e^{-ik(R-R')} U_{nl} (k) U_{l'm'}^\dagger (k + q) \int W_{l1}^* (r - (R - R')) e^{-iqr} W_{l'l'}^\dagger (r) d^3r \hat{C}_{n,k,+} \hat{C}_{m,k+q,+} \\
= \frac{1}{N} \sum_{k,n,m,l,l',R} \sum_{R} e^{-ikR} U_{nl} (k) U_{l'm'}^\dagger (k + q) \hat{\rho}_{W,R}^W (q) \hat{C}_{n,k,+} \hat{C}_{m,k+q,+} \\
= \frac{1}{N} \sum_{k,n,m,l,l',R} \sum_{R} e^{-ikR} U_{nl} (k) U_{l'm'}^\dagger (k + q) \hat{\rho}_{W,R}^W (q) \\
\times \sum_{l_1 l_2, R_1 R_2} e^{ikR_1 - i(k+q)R_2} U_{l_1 n}^\dagger (k) U_{ml_2} (k + q) \hat{T}_{l_1 R_1}^\dagger \hat{T}_{l_2 R_2}^\dagger \\
= \frac{1}{N} \sum_{k,l,l',R} \sum_{R} \hat{\rho}_{W,R}^W (q) \sum_{R_1 R_2} e^{ikR_1 - i(k+q)R_2} \hat{T}_{l R_1}^\dagger \hat{T}_{l' R_2}^\dagger \\
= \sum_{R_1 R_2} \sum_{l,l'} \hat{\rho}_{W,R_1 - R_2}^W (q) e^{-iqR_2} \hat{T}_{l R_1}^\dagger \hat{T}_{l' R_2}^\dagger,
\]

where \( \hat{\rho}_{W,R}^W (q) \equiv W_{l1}^\dagger (r - R) W_{l'1} (r) \) is the density matrix of the Wannier functions and its Fourier transform is

\[
\hat{\rho}_{W,R}^W (q) \equiv \int \rho_{W,R}^W (r) e^{-iqr} d^3r = \int W_{l1}^* (r - R) W_{l1} (r) e^{-iqr} d^3r.
\]

We further transform the operator basis to \( k \) space: \( \hat{T}_{l R_1}^\dagger = \frac{1}{N} \sum_k e^{-ikR_1} \hat{T}_{l,k,l}^\dagger \). The states created by \( \hat{T}_{l,k,\sigma}^\dagger \) are the so-called generalized Bloch states \( |\tilde{\psi}_{l,k,\sigma}\rangle \equiv \sum_n U_{nl} (k) |\psi_{n,k,\sigma}\rangle \), which are labeled by the local index \( l \) rather than the band index \( n \), and which are typically not eigenstates.
of the Hamiltonian any more (see Eq. (8) in (4)). The energy of \( |\tilde{\psi}_{l,k,\sigma}\rangle \) is give by

\[
E_{l,k,\sigma} = \left\langle 0 \left| \hat{T}_{l,k} + \hat{H}_{l,k} \right| 0 \right\rangle = \sum_{R_1 R_2} e^{i k (R_1 - R_2)} \left\langle W_{l,\sigma} (r - R_2) \left| \hat{H} \right| W_{l,\sigma} (r - R_1) \right\rangle
\]

\[
= \sum_{R} e^{i k R} \left\langle W_{l,\sigma} (r) \left| \hat{H} \right| W_{l,\sigma} (r - R) \right\rangle .
\]

In this new basis, a spin-flip operator becomes

\[
\hat{S}_q^- = \sum_{R_1 R_2 l l'} \sum_{l l'} \tilde{\rho}_{l' R_1 - R_2}^W (q) e^{-i q R_2} \hat{T}_{l l'}^{\uparrow \uparrow} \hat{T}_{l' R_2}^{\uparrow \uparrow} = \sum_{R_1 R_2 l l'} \sum_{l l'} \int d^3 r e^{-i q r} W_{l l'}^* (r - R_1) W_{l' l}^\uparrow (r - R_2) \frac{1}{N^2} \sum_{k k'} e^{-i k R_1 + i k R_2} \hat{T}_{l k}^{\uparrow \downarrow} \hat{T}_{l' k}^{\uparrow \downarrow} \]

\[
= \frac{1}{N} \sum_{k} \sum_{R_1 R_2 l l'} \sum_{l l'} \int d^3 r e^{-i q r} W_{l l'}^* (r - R_1) W_{l' l}^\uparrow (r - R_2) e^{-i k R_1 + i (k + q) R_2} \hat{T}_{l k}^{\uparrow \downarrow} \hat{T}_{l' k + q}^{\uparrow \downarrow} \]

\[
= \frac{1}{N} \sum_{k} \sum_{l l'} \left( \sum_{R} \tilde{\rho}_{l' R_1 - R_2}^W (q) e^{-i k R} \right) \hat{T}_{l k}^{\uparrow \downarrow} \hat{T}_{l' k + q}^{\uparrow \downarrow} .
\]

Assuming that the MLWFs are sufficiently localized, the leading term is contributed by the \( R = 0 \) condition:

\[
\hat{S}_q^- \approx \sum_{k} \sum_{l l'} \int W_{l l'}^* (r) W_{l' l}^\uparrow (r) e^{-i q r} d^3 r \hat{T}_{l k}^{\uparrow \downarrow} \hat{T}_{l' k + q}^{\uparrow \downarrow} ,
\]

thus the matrix element is independent of the \( k \) summation. The continuum’s magnetic scattering cross section is

\[
\frac{d\sigma}{d\Omega dE} \propto \sum \left| \left\langle \tilde{\psi}_{l,k,\downarrow} \left| \hat{S}_q^- \right| \tilde{\psi}_{l',k+q,\uparrow} \right\rangle \right|^2 \delta (E + E_{l,k,\downarrow} - E_{l',k+q,\uparrow})
\]

\[
+ \left| \left\langle \tilde{\psi}_{l,k,\uparrow} \left| \hat{S}_q^+ \right| \tilde{\psi}_{l',k+q,\downarrow} \right\rangle \right|^2 \delta (E + E_{l,k,\uparrow} - E_{l',k+q,\downarrow})
\]

\[
= \sum_{l' l} \left| \int W_{l l'}^* (r) W_{l' l}^\uparrow (r) e^{-i q r} d^3 r \right|^2 \delta (E + E_{l,k,\downarrow} - E_{l',k+q,\uparrow})
\]

\[
+ \sum_{l' l} \left| \int W_{l l'}^* (r) W_{l' l}^\downarrow (r) e^{-i q r} d^3 r \right|^2 \delta (E + E_{l,k,\uparrow} - E_{l',k+q,\downarrow}) .
\]
We can integrate over energy $E$, since the relative intensity variations versus $q$ are nearly $E$-independent. It is understood that, upon doing so, the delta functions above (energy conservation) will be combined with the $k$ summation under the constraint that the excitations must promote electrons from occupied to unoccupied states, leading together to an intra-Brillouin-zone dependence of the cross section. The remaining inter-Brillouin-zone dependence becomes:

$$
\frac{d\sigma}{d\Omega} (q) \propto \sum_{ll'} \left| \int W_{ll'}^* (r) W_{l'l} (r) e^{-iqr} d^3r \right|^2 + \left| \int W_{ll'}^* (r) W_{l'l} (r) e^{-iqr} d^3r \right|^2.
$$

Recall that the Wannier functions are defined as $W_{ld,ls,\sigma} (r - R) \equiv W_{ld,\sigma} (r - l_s - R)$. Again, in the limit that the MLWFs are well-localized, the leading term is obtained by summation under the constraint $l = l'$:

$$
\frac{d\sigma}{d\Omega} (q) \propto \sum_{l} \left| \int W_{l}^* (r) W_{l} (r) e^{-iqr} d^3r \right|^2
$$

$$
\propto \frac{1}{n_s} \sum_{l_s=1}^{n_s} \left| \int \left( \frac{1}{d} \sum_{l_d=1}^{d} |W_{ld} (r - l_s)|^2 \right) e^{-iqr} d^3r \right|^2,
$$

where $\frac{1}{d} \sum_{l_d=1}^{d} |W_{ld} (r - l_s)|^2$ is the site-symmetric electron density of the Wannier functions. We have ignored the spin indices in this final result because the Wannier functions for the spin-majority and minority bands are the same if they belong to the same EBR (in the unpolarized state). This final result explains why we can use the triangle model to account for the inter-Brillouin-zone variations of the observed neutron scattering intensities, because: (1) the magnetic bands in MnSi form an EBR; (2) the MLWFs are centered on the entirety of the triangles; (3) the MLWFs are anti-bonding states, hence their electron density can be approximated by three (“coherently superposed”) Mn ionic moments on the vertices of individual triangle.
Fig. S1. Animation of MnSi’s crystal structure. The animation first presents MnSi’s structural derivation from rock salt. The body diagonal along which the atoms move (and its symmetry equivalent) represents the “variable” Wyckoff 4a site. Then, in the right panel, the Mn sub-lattice is viewed from a series of angles, demonstrating nearest-neighbor equilateral triangles as a structural motif.
Fig. S2. Sample preparation and characterization. (A) Left side: photograph of MnSi single crystals co-aligned on an aluminum sample holder. Right side: representative X-ray Laue pattern taken on a natural surface of a single crystal along $\langle 100 \rangle$ direction. (B and C) Q-scan profiles which indicate that the entire sample is nearly a single-domain, since the (0, 3, 4) reflection is over 40 times more intense than that at (0, 4, 3). (D) Neutron diffraction intensities of a selected Bragg reflection recorded upon rotating the sample. Solid line is Gaussian fit to the data, with full width at half maximum (FWHM) equal to 1.3 degrees. Data in (B)-(D) was obtained on 4SEASONS. (E and F) Uniform magnetization measured on a single crystal using a Quantum Design MPMS. The data indicates a helical magnetic order below 29.5 K and a saturated moment of 0.4 $\mu_B$ when the magnetic field is higher than 6000 Oe, consistent with previous results (77).
Fig. S3. Distinction between spin waves and acoustic phonons. Magenta solid lines indicate the spin waves, whereas black dashed lines indicate the acoustic phonon dispersions. The spin waves are most clearly seen in the (2, 1, 0) BZ. Data were obtained on 4SEASONS.

Fig. S4. Comparison between INS and DFT-calculated phonon spectra in the (2, 1, 0) BZ. Data were obtained on 4SEASONS.
Fig. S5. **Momentum (and energy) evolution of the spin excitations.** (A) Constant-$E$ cuts from 6 meV to 30 meV with $dE = \pm 0.7$ meV collected at $T = 4$ K and $E_i = 57$ meV on 4SEASONS, fitted with two symmetrically positioned Gaussian peaks on a constant background. (B-D) Fit parameters displayed as a function of the cut energy in (A). Error bars represent one standard deviation of the data. The spectrum undergoes an abrupt change at $q_{MO}$, which corresponds to an energy of $E_{MO}$ of about 20 meV, where the spin waves meet the nearly $E$-independent continuum.

Fig. S6. **Representative $E$-$Q$ slices along three high-symmetry directions.** (A-L) The continuum’s characteristic $Q$-dependence is nearly independent of energy. Data were obtained at $T = 4$ K and with $E_i = 162$ (4SEASONS), 300, 600 and 1000 meV (ARCS).
Fig. S7. Constant-$E$ cuts along three high-symmetry directions and comparison of INS intensity of the continuum between different temperatures. (A-C) Data are fit with Gaussian peaks with a constant background, offset for clarity. The measurements were performed at $T = 4$ K and with $E_i = 162$ (4SEASONS), 300, 600 and 1000 meV (ARCS). (D) Radial $Q$-dependent intensities measured with $E_i = 150$ meV (SEQUOIA). Error bars represent one standard deviation of the counting statistics.

Fig. S8. INS signal variation between 4 K and 40 K. The detailed balance factor has been divided from the data. It is seen that both the continuum and the spin waves (paramagnons) persist to above $T_N$. Measurements were performed on 4SEASONS.
Fig. S9. Comparison of intensity variations over the same set of Brillouin zones for the low- and high-energy parts of the continuum. Thin dashed lines indicate Brillouin-zone boundaries. Data were obtained on 4SEASONS.

Fig. S10. Relative variation of INS intensity of the spin waves and high-energy continuum in neighboring BZs. The intensity of the spin waves in the (1, 1, 0) BZ is much weaker than that in the (2, 1, 0) BZ, but the INS intensity of continuum above 45 meV in the (1, 1, 0) BZ is stronger than that in the (2, 1, 0) BZ. Data in (G)-(L) are fitted with single Gaussian peak with a constant background. All data in (A)-(L) were obtained on 4SEASONS.
Fig. S11. Radial momentum dependence of INS intensity of the continuum. (A) $E - Q$ dependence of the INS intensity. (B-G) Radial $Q$ dependence of signal extracted from constant-$E$ radial-$Q$ cuts that have avoided phonon scattering. The local maximum at $Q_0 = 2.5 \text{ Å}^{-1}$ is observed in all the data. The fitted non-magnetic background has been subtracted (see Eq. S2). Data were collected at $T = 4 \text{ K}$ with $E_i = 150 \text{ meV}$ (SEQUOIA), 300 meV, 600 meV and 1000 meV (ARCS).
Fig. S12. Simulation results with correlation center (see Eq. S1) located at the centers of nearest-neighbor equilateral triangles under different correlation length. (A-G) Best fit results using the least squares method with constant background. (H) The Mn sublattice with 4 types of nearest-neighbor equilateral triangles, on which the centers of triangles are denoted with red dots. When the correlation length exceeds the size of a triangle, the modeled cluster becomes more extensive than a single triangle and the agreement with the experimental data becomes much poorer. Data were collected with $E_i = 300$ meV (ARCS). Error bars represent one standard deviation of the counting statistics.
Fig. S13. Simulation results with correlation center (see Eq. S1) located at the midpoint of two nearest Mn ions under different correlation length. (A-G) Best fit results using the least squares method with constant background. (H) The Mn sublattice with 4 types of nearest-neighbor equilateral triangles, on which the midpoints of nearest Mn ions are denoted with orange dots. When the correlation length is smaller than half of the nearest Mn–Mn distance (1.4 Å), the cluster is essentially an Mn–Mn diatomic group. Data were collected with $E_i = 300\text{meV}$ (ARCS). Error bars represent one standard deviation of the counting statistics.
Fig. S14. Simulation results with correlation center (see Eq. S1) located at the Mn ions under different correlation length. (A-G) Best fit results using the least squares method with constant background. (H) The Mn sublattice. The distance of nearest Mn–Mn atoms is 2.8 Å. Data were collected with $E_i = 300\text{meV}$ (ARCS). Error bars represent one standard deviation of the counting statistics.
Fig. S15. Comparison between experimental data and simulation results described in Eq. S2. (A-D) INS intensity of the $KL$ plane for $H = 1, 1.5, 2, 3$, respectively. (E) INS intensity at a plane which is perpendicular to [111] direction. (F) INS intensities on the $Q_0$ shell. (G-L) The simulation results under the same conditions using Eq. S2, i.e., without considering intra-BZ models (shell or lattice-Lorentzian). All the experimental data were obtained at $T = 4$ K, $E = 75 \pm 10$ meV and with $E_i = 300$ meV (ARCS).

Fig. S16. Comparison between the experimental data and calculation results using Eq. S2 (or S3, S5, nearly no difference) with ionic form factor $f(Q)$ for different valence states of Mn. (A) The best agreement with INS data is obtained with Mn$^{2+}$. (B) Same as (A), but after subtracting the fit background and extrapolated to $Q = 0$. The red dashed and solid lines indicate the $Q$ lengths of $M_1 = (0, 0.5, 0.5)$ and $M_2 = (1, 0.5, 0.5)$ in Fig. S17, respectively. Error bars represent one standard deviation of the counting statistics.
Fig. S17. Relative variation of intensity of the continuum in its low-energy limit, measured at two different M points. The data (obtained on 4SEASONS) are fitted with a step-like function on a constant background, in order to extract the intensity of the continuum at its energy minimum. $I(M)$ corresponds to the height of the step function. Error bars represent one standard deviation of the counting statistics. The calculated nearest-neighbor equilateral triangle form factor ratio between $M_1$ and $M_2$ is 2.56, in agreement with the measurements.
Fig. S18. Comparison between experimental data and simulation results described in Eq. S3 and S5. (A-C) INS intensity of KL plane for $H = 1, 1.5, 2$, respectively. (D) INS intensity at a plane which is perpendicular to [111] direction. (E) INS intensities on the $Q_0$ shell. (F-J) Simulation results described in Eq. S3. (K) Isosurfaces of intra-BZ intensity described by the normalized lattice-Lorentzian function ($\text{LL}(Q)$). (L-P) Simulation results described in Eq. S5. (Q) Isosurfaces of intra-BZ intensity described by the spherical shell function ($\text{Shell}(Q)$). Experimental data were obtained at $T = 4$ K, $E = 75 \pm 10$ meV and with $E_i = 300$ meV (ARCS). Circles in (B), (G) and (M) indicate where the shell model describes the experiment slightly better than the lattice-Lorentzian model, but apart from that the two models are highly comparable.
Fig. S19. Relative variation of magnetic form factor calculated under different covalent factors, but with the same background and global normalization factor (see Eq. S7). The result for $p_{\text{cov}} = 1$ in (A) is the same as the “localized” curve in Fig. 3A (main text). INS data were collected with $E_i = 300 \text{ meV}$ (ARCS), and their error bars represent one standard deviation of the counting statistics.

Fig. S20. Comparison between INS and SpinW-calculated acoustic spin-wave spectra in the $(2, 1, 0)$ BZ. Experimental data were obtained on SEQUOIA.
Fig. S21. Dynamic magnetic susceptibility determined from experiment as a function of energy. Solid line is fit to the $\chi''(E)$ of a damped harmonic oscillator. Squares and triangles are fit intensities based on spherical shell model and lattice Lorentzian model, and all data are integrated over the (2, 1, 0) BZ. Data were obtained at $E_i = 150$ meV (SEQUOIA), 300 meV, 600 meV and 1000 meV (ARCS). Error bar represent the joint uncertainty associated with the counting statistics, vanadium calibration and neutron-absorption calculation.
Fig. S22. *Ab initio* calculation of magnetic orbitals. (A) and (B) DFT-calculated bands near $E_F$ in comparison to tight-binding models. All legends are displayed in (B). For clarity, only spin-majority bands are shown (minority bands in Fig. S24). Three types of orbitals are compared for their effectiveness to describe the magnetic EBR at $E_F$ (see text): (1) MLWFs calculated from the EBR without site constraint, resulting in molecular orbitals (MOs) on nearest-neighbor equilateral triangles (NNETs). (2) MLWFs calculated from the EBR under Mn-site constraint. (3) MLWFs calculated from a total of 32 bands near $E_F$, resulting in approximate atomic orbitals (AOs), among which the displayed $e_{x^2-y^2}$ and $e_{xy}$ orbitals of Mn ($z \equiv$ the local $C_3$ axis) provide the closest description of the EBR, but deviation is significant and the PDOS enters bands outside the EBR. (C-E) Isosurface of the corresponding electron density that encloses 50% of the electron weight, shown on a structural motif. The spreads of electron density $\langle r^2 \rangle - \langle r \rangle^2$ are 11.3, 15.4, and 1.0 Å$^2$, respectively.
Fig. S23. A molecular-orbital description of occupied electronic states. (A) DFT-calculated spin-majority bands near $E_F$, along with tight-binding-model interpolated bands according to MLWF calculations. Two sets of bands (8 + 12) are seen within $\sim 6$ eV below $E_F$. The 8 bands closer to $E_F$ are the magnetic EBR discussed in the main text. The remaining 12 bands form a BR (not an EBR) which is jointly induced by an $E$ and an $A_1$ irrep of the Wyckoff 4$a$ site. MLWF calculation using this BR’s Bloch states as input results in a satisfactory tight-binding model, the local orbitals of which has the corresponding symmetries. These orbitals are molecular orbitals (MOs) as well, because their spatial extent is much greater than atomic orbitals. All of the EBR- (and BR-) restricted MLWFs (total of 20), MO(1), MO(2) and MO(3), are mutually orthogonal, and they are centered on the nearest-neighbor equilateral triangle, Mn, and Si sites (all Wyckoff 4$a$), respectively. These MOs form because of the covalent bonding nature between Mn and Si, together with the fact that every Mn is surrounded by a total of seven Si (Fig. S1) at similar distances (ranging from 2.3 to 2.5 Å) in the crystal structure. (B) Partial density of states of the MOs. It is seen that while MO(1) is exclusively responsible for the 8-band EBR near $E_F$, MO(2) and MO(3) jointly form the 12-band BR, as expected. (C1-C3) Wave functions and symmetrised electron density isosurfaces of MO(1) (isovalue corresponds to 15% of the maximal density), displayed in the “trillium flower” structural motif. (D1-D3) Same as (C1)-(C3), but for MO(2). (E1-E3) Same as (C1)-(C3), but for MO(3), which is a one-dimensional irrep (hence, only one wave function). With the understanding that all Mn atoms and nearest-neighbor equilateral triangles are symmetry-related, MO(1), MO(2) and MO(3) can be named after the shapes of their electron clouds as (trillium) “root”, “flower” and “stem” MOs, respectively.
Fig. S24. Electronic structure with both spin-majority and minority bands. (A) DFT-calculated bands and MLWF interpolation of the 8-band EBR running through $E_F$. (B) Spin-polarised crystal orbital Hamiltonian population (COPH) between nearest-neighbor Mn atoms.
## Table S1. Symmetry indicators at high-symmetry \( k \) points for the 8 conduction bands.

Numbers in parenthesis indicate degeneracy, and the energies are sorted (from left to right) in ascending order. Spin-majority and -minority bands give the same result.

| high-symmetry \( k \) point | symmetry indicators |
|-----------------------------|---------------------|
| GM | GM4 (3); GM4 (3); GM2 + GM3 (2) |
| X | X1 (2); X1 (2); X1 (2); X1 (2) |
| M | M3 +M4 (2); M1 + M2 (2); M3 + M4 (2); M1 + M2 (2) |
| R | R2 + R2 (4); R1 + R3 (4) |

## Table S2. Atomic orbital (AO)-projection and hopping analysis for the molecular orbitals (MOs).

Rows correspond to different cut-off distance for the MO-AO projection. The origin (denoted by a small dot in the figure) is taken as the Wannier center of the MO \( W_{M_a}^{M_a} \) in the EBR \( E \uparrow G \), and the first three chosen cut-off distances are displayed as transparent spheres centered at the origin, with their enclosed Mn atoms displayed as color-coded small spheres. Only Mn atoms are shown, despite some of the MO weight is contributed by Si AOs. The displayed “AO weight” is the sum of AO coefficient squared within the cut-off distance. A full list of \( \eta \) (between \( W_{M_a}^{M_a} \) and a total of 42592 MOs, after the AO projection and truncation) is computed for each cut-off distance, and only \( \eta_{\min} \) connecting \( W_{M_a}^{M_a} \) to MOs within and outside the magnetic EBR are displayed. \( \eta_{\min} \) is used as a figure of merit for accessing the quality of the construction of the MO from AOs, see description in text.

| distance \( \text{Å} \) | AO number | AO weight | \( \eta_{\min} \) within EBR | \( \eta_{\min} \) outside EBR |
|----------------------|-----------|------------|-----------------------------|-----------------------------|
| 1.78 | 10 | 0.542 | \( 1 \times 10^{-6} \) | 0.71 |
| 3.6 | 61 | 0.735 | \( 3 \times 10^{-8} \) | 0.78 |
| 4.6 | 147 | 0.866 | \( 4 \times 10^{-8} \) | 0.92 |
| 12 | 1614 | 0.991 | \( 1 \times 10^{-7} \) | 0.97 |
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