Letter

Superconductivity-induced improper orders in nonsymmorphic systems

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(Received 20 November 2023; revised 23 October 2024; accepted 24 October 2024; published 18 November 2024)

In this work, we highlight an overlooked mechanism that couples superconducting order parameters to orders in the charge and spin sectors such that the latter emerge as improper orders. At the core of this mechanism are nonsymmorphic symmetries and new families of modulated order parameters with two components of opposite parity. While nonsymmorphic systems have been extensively discussed in the context of topological band theory, our work demonstrates the profound effects of such symmetries on the interplay of ordered phases of matter. As a working example, we focus on the space group P4/nmm and provide a real-space perspective on the classification of order parameters. Our findings can account for the unusual phenomenology of $CeRh_2As_2$, a recently discovered heavy fermion superconductor, and open the door for the exploration of nonsymmorphic symmetries in the broader context of improper orders with potential applications to functional topological materials.

DOI: 10.1103/PhysRevB.110.L180503

The Landau theory of phase transitions has been a guiding principle in the understanding of ordered phases of matter based on the notion of symmetry breaking order parameters. Landau free energies can effectively capture the nontrivial interplay between phases of matter, such as intertwined [1], vestigial [2], and composite orders [3] emerging within strongly correlated systems. In this context, the notion of pair density wave (PDW) superconductors [4] has attracted a lot of attention and emphasized the idea that superconducting states can induce secondary order parameters, such as charge density waves, in analogy to the notion of improper orders in multiferroics [5–8]. Most of these works, however, rely on a symmetry analysis that is either based on the point group symmetry or solely on translational symmetry. Nonsymmorphic systems, with symmetries that combine point group operations and fractional lattice translations, have remained untapped.

Nonsymmorphic symmetries have been extensively investigated in the context of topological band structure [9–13], while in the study of superconductors, efforts have largely been focused on their effects on topological classification [14–16] and identification of unusual nodal structures [17–19]. Much of the symmetry analysis in the context of superconductivity relies on point groups, the space group symmetries that remain once one factors out translations, a trivial procedure in symmorphic systems. Nonsymmorphic symmetries complicate the process of factoring out translations, making the group theoretical analysis and the classification of superconducting states more cumbersome, particularly if one works in a momentum space representation [20,21].

Here, we take a complementary view of nonsymmorphic symmetries in the context of ordered phases of matter and classify the order parameters in the superconducting, charge, and spin sectors based on their textures in real space [22], taking explicit account of the nonsymmorphic nature of the crystal [23]. From this analysis, we find that nonsymmorphic symmetries give rise to new types of order parameter families which have two degenerate components with opposite parity, allowing for novel types of coupling between superconducting order parameters and orders in the spin or charge sectors. Remarkably, we find that these can induce odd-parity improper orders by the development of a primary order in the superconducting channel in centrosymmetric systems.

Within the Landau formalism, the coexistence of orders implies a coupling between the corresponding order

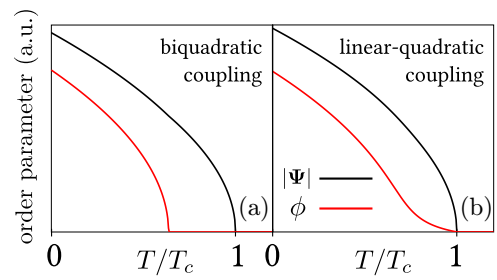


FIG. 1. Distinct couplings between a primary superconducting order parameter Ψ (potentially multicomponent), and a secondary order captured by ϕ. (a) Biquadratic coupling, $\sim\phi^2|\Psi|^2$, leading to two transition temperatures. (b) Linear-quadratic coupling, $\sim\phi(\Psi_1^*\Psi_2 \pm \Psi_1\Psi_2^*)$, leading to a single transition temperature.

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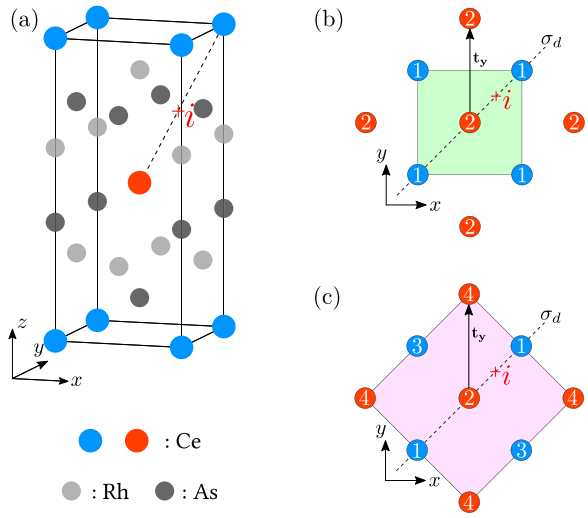


FIG. 2. (a) $CeRh_2As_2$ unit cell with two Ce sublattices (blue and red spheres). (b) Original unit cell (green) projected to the x-y plane containing two Ce atoms (1 and 2) and (c) enlarged unit cell (magenta) containing four Ce atoms (1–4). Dashed line represents the diagonal mirror plane, red cross is the global inversion center, coinciding with our chosen origin. Translation by one lattice constant, indicated by $\mathbf{t}_y$, is a trivial (nontrivial) operation in the original (enlarged) unit cell scenario.

parameters, consistent with all operative symmetries. The most straightforward gauge-invariant coupling between a primary superconducting order parameter Ψ and a secondary order parameter ϕ is quadratic in both sectors, e.g., $\sim\phi^2|\Psi|^2$, generally yielding two phase transitions, see Fig. 1(a). On the other hand, a linear-quadratic coupling acts as a temperature-dependent linear term for ϕ upon the development of the primary superconducting order, which results in the simultaneous onset of both orders, see Fig. 1(b). Crucially, if ϕ has symmetry properties associated with a nontrivial irreducible representation, these have to be compensated for by the superconducting order parameter bilinear in the coupling term. This generally requires a two-component superconducting order parameter $\mathbf{\Psi} = (\Psi_1, \Psi_2)$, which allows for a term $\sim\phi(\Psi_1\Psi_2^* \pm \Psi_1^*\Psi_2)$ in the free energy. A particularly challenging scenario is that of an odd-parity improper order in centrosymmetric systems. Due to the global inversion symmetry, order parameters classified from the perspective of point group symmetries are labeled as either even or odd parity. From this naive classification, superconducting bilinears are invariably even parity, making the required linear-quadratic coupling for an odd-parity improper order impossible. In this work we show that, in the absence of accidental degeneracies, modulated superconducting orders in nonsymmorphic systems can sustain multicomponent order parameters with components of opposite parity, allowing for the emergence of odd-parity improper orders triggered by a primary superconducting order.

A recently discovered heavy-fermion material, $CeRh_2As_2$, might be one example of such unusual phenomenology. This material, depicted in Fig. 2(a), realizes an exotic phase diagram with two superconducting phases as a function of a c-axis magnetic field [24]. While the pairing symmetry of the two phases is to date unclear, nuclear magnetic resonance (NMR) [25] and nuclear quadrupole resonance (NQR) [26] measurements reveal antiferromagnetic order coexisting with the low-, but not with the high-field superconducting phase. Most intriguingly, specific heat and thermal expansion measurements indicate a single phase transition [27,28], suggesting that the onset of superconductivity coincides with that of magnetism in the entire low-field phase, in a range of magnetic fields spanning 4 T, potentially characterizing the magnetic order as an improper order. Two candidate antiferromagnetic textures with moments localized at the Ce sites were identified: (i) layered antiferromagnet with moments along the z axis, M_z, depicted in Fig. 3(b); (ii) in-plane antiferromagnet, M_{plane}, depicted in Fig. 3(c). Note that both orders break inversion symmetry and that M_z is odd parity. For the improper onset of M_z, the required coupling term $\sim iM_z(\Psi_1\Psi_2^* - \Psi_1^*\Psi_2)$ therefore calls for a parity-mixed two-component superconducting order parameter.

Inspired by the physics observed in $CeRh_2As_2$, we investigate the space group P4/nmm (No. 129), also associated with several Fe-based superconductors [29,30], and discuss how unusual irreducible representations (irreps) with components of opposite parity emerge once we enlarge the symmetry group by extending the unit cell to account for modulated order parameters. The 16 symmetry operations in P4/nmm are generated by $\bar{C}_{4z} = \{C_{4z}|\mathbf{t}_x/2\}$, a rotation by $\pi/2$ about the z axis followed by $\mathbf{t}_x/2$, half a PLV translation along the x axis; $\sigma_d = \{\sigma_d|\mathbf{0}\}$, a mirror reflection along the diagonal plane ($x = y$); and inversion $i = \{i|\mathbf{0}\}$ (for the complete list of group operations see [30]). Given the nonsymmorphic nature of the space group, these 16 symmetry operations, when composed, do not close into themselves. If we are interested in homogeneous phases, we can redefine the composition of these operations modulo integer lattice vector translations such that they form a group. This procedure corresponds to factoring out translations to determine the little group at the Γ point in momentum space [20], which is isomorphic to D_{4h}. For this group, the symmetry elements are organized in ten conjugacy classes, leading to ten irreps which are labeled as even or odd parity [30].

On the other hand, modulated orders are characterized by finite wave vectors. In particular, if the wave vector corresponds to a point at the edge of the BZ, we expect unusual degeneracies in nonsymmorphic systems, as is extensively discussed in the context of electronic band structures [13]. To highlight the origin of these degeneracies, here we take an approach which we believe is much clearer and more intuitive than the standard approach proposed by Herring based on notions of factor groups and induced representations [21,31]. Choosing the simplest scenario, here we double the unit cell and introduce the notion of an extended group by adding to the original group new symmetry operations, which take one primitive unit cell into another in the doubled unit cell [22], see Figs. 2(b) and 2(c). The extended symmetry group is formed by the original 16 operations plus the composition of these with a PLV translation, here chosen to be $E' = \{E|\mathbf{t}_y\}$, which is the extension of the identity operation $E = \{E|\mathbf{0}\}$ (extended symmetry operations are denoted with a prime). Extending the group of symmetries to 32 elements leads to novel irreps [30]. If the space group is symmorphic, the

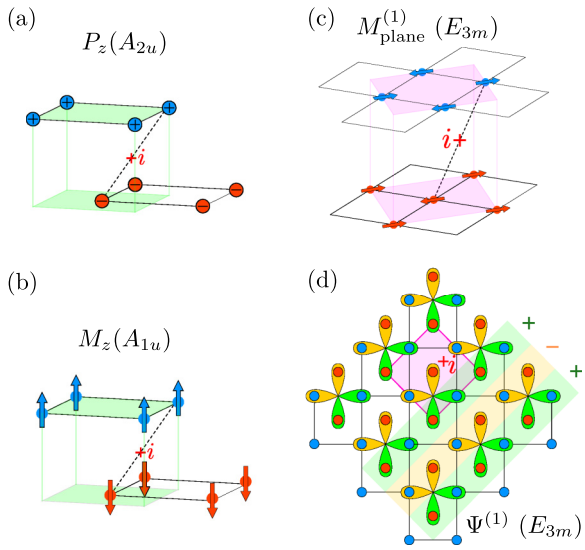


FIG. 3. Representative orders in the charge, spin, and superconducting sectors and their respective irreps. (a) Inversion-odd polar (P_z); (b) Layer antiferromagnet (M_z); (c) One component of in-plane antiferromagnet (M_{plane}); (d) One component of modulated superconducting order ($\Psi^{(1)}$). The pairing wave function is intrasublattice but antisymmetric between sites, resulting in a modulation in the projected x-y plane (+/−, marked by green and orange, respectively). In (c) and (d) the second components are obtained via 90° rotation, but one component is odd, while the other is even parity.

total number of irreps is simply doubled, and the new irreps behave as the original ones up to an extra minus sign under operations including a PLV translation. In contrast, if the group is nonsymmorphic, the irreps associated with the extended group can be fundamentally distinct from the original irreps.

To understand how nontrivial irreps are generated, we rely on two elementary results from group theory: (i) the number of irreps is equal to the number of conjugacy classes; (ii) the dimensions of irreps should follow the identity $\sum_i |d_i|^2 = |\mathbf{G}|$, where d_i is the dimension of the ith irreducible representation and $|\mathbf{G}|$ is the order of the group (the number of elements in the group). The order of the extended group in our example is twice the order of the original group. For symmorphic systems, the number of irreps of a given dimension is also doubled, trivially satisfying points (i) and (ii). For nonsymmorphic systems, the conjugacy classes in the extended group are not twice as many as in the original group. This happens because some of the original and extended operators necessarily coalesce into a single conjugacy class. This point can be understood by considering the conjugation of a generic spatial symmetry operation $O_B = \{R_B|\mathbf{t}_B\}$ by another generic operation $O_A = \{R_A|\mathbf{t}_A\}$ such that $O_A^{-1}.O_B.O_A = O_C$, with

$$O_C = \left\{R_A^{-1}R_BR_A|R_A^{-1}(R_B\mathbf{t}_A - \mathbf{t}_A + \mathbf{t}_B)\right\}, \tag{1}$$

where the dot denotes the composition of operations, and we used $O_A^{-1} = \{R_A^{-1}| - R_A^{-1}\mathbf{t}_A\}$. The presence of inversion operation in P4/nmm allows us to choose $O_A = \{i|\mathbf{0}\}$, such that the RHS of the equation above reads $\{R_B| - \mathbf{t}_B\}$. If O_B is nonsymmorphic with $\mathbf{t}_B$ corresponding to half a PLV translation, then $-\mathbf{t}_B = \mathbf{t}_B + PLV$. In the space group modulo integer PLV translations, associated with the original unit cell scenario, $\mathbf{t}_B + PLV \equiv \mathbf{t}_B$, see Fig. 2(b). As a consequence, $O_C = O_B$ and we do not get any information about conjugacy classes. On the other hand, in the extended symmetry group (the space group modulo two integer PLV translations) $\mathbf{t}_B + PLV \not\equiv \mathbf{t}_B$, see Fig. 2(c), such that $O_C = O'_B \neq O_B$. The relation $O_A^{-1}.O_B.O_A = O'_B$ indicates that O_B and O'_B belong to the same conjugacy class in the extended group. We conclude that all conjugacy classes containing nonsymmorphic operations in the original centrosymmetric symmetry group are enlarged in the extended symmetry group. This coalescence of conjugacy classes tells us that we have less than twice as many irreps in the extended group, and, consequently, the new irreps are generally not one-dimensional. The complete analysis is summarized in Table I and a more detailed discussion is provided in [30]. In this example, we find four new two-dimensional irreps in the extended group (labelled as E_{im}, $i = 1, \ldots, 4$, with m standing for mixed parity), with the unusual property of having zero character associated with inversion symmetry.

To better understand this last statement, we can conjugate inversion with a nonsymmorphic operation. Choosing $O_B = \{i|\mathbf{0}\}$, we find the RHS of Eq. (1) reads $\{i| - 2R_A^{-1}\mathbf{t}_A\}$. If O_A is nonsymmorphic and $\mathbf{t}_A$ is half a PLV, $-2R_A^{-1}\mathbf{t}_A$ is a PLV, and therefore nonsymmorphic group elements inevitably connect inversion $i = \{i|\mathbf{0}\}$ with $i' = \{i|\mathbf{t}_\mathbf{y}\}$, leading to the enlargement of the associated conjugacy class under the group extension. This result has strong implications. The fact that the counjugacy class associated with the inversion operation is enlarged tells us that the characters associated with inversion in the new irreps are zero [20]. As a consequence, the new two-dimensional irreps are associated with two-component basis functions with components of opposite parity. This fact is directly associated with known results in electronic band theory: our extended group is isomorphic to the abstract group G^2_{32}, the little group of P4/nmm at the M point [20]. This remarkable result challenges our intuition about inversion symmetry. Centrosymmetric systems with nonsymmorphic symmetries can be associated with mixed-parity irreps if the system is allowed to develop textures with wave vectors at the edge of the BZ.

Going back to the discussion on $CeRh_2As_2$, considering the space group P4/nmm modulo PLV translations (the little group at the Γ point), we can classify the order parameters in the charge, spin, and superconducting sectors in terms of irreps, which are either even or odd under parity [30]. In contrast, if we classify the order parameters according to the space group modulo two PLV translations, we find orders associated with irreps labeled as E_{im} having two components that transform differently under inversion [30]. Curiously, the magnetic order with in-plane moments depicted in Fig. 3(c) belongs to the irrep E_{3m}, and it cannot couple to any superconducting order through the desired linear-quadratic term in the absence of accidental degeneracies. On the other hand, the layered antiferromagnet M_z [shown in Fig. 3(b)] is associated with the irrep A_{1u}, which is odd parity, and can couple linearly to quadratic terms in the superconducting order parameter if the latter is associated with irreps E_{3m} or E_{4m} [an example of an E_{3m} order parameter is given in Fig. 3(d)]. This

TABLE I. Character table for P4/nmm modulo two primitive lattice vector translations, isomorphic to the abstract group G^2_{32}. The first line shows the original ten conjugacy classes of P4/nmm modulo PLV translations (isomorphic to D_{4h} and the abstract group G^9_{16} [20]). After group extension, four conjugacy classes split (↙↘), while the others double (⇓). Group elements are labeled according to their associated point group operation. Bar (tilde) marks operations accompanied by a half PLV translation (two orthogonal half PLV translations). Operations marked with a prime are extended by a full PLV translation. The first ten irreps have well-defined parity, and their labels follow that of the D_{4h} point group. The last four irreps are new to the extended group and have mixed parity. Subscripts correspond to even (g), odd (u), or mixed (m) parity. In gray, we highlight the columns that are simply doubled for the initial ten irreps given the splitting of the conjugacy classes. In yellow, we highlight the columns with zero characters due to the coalescence of the original and extended operations in the same conjugacy class.

G^9_{16}	E		$\tilde{C}_{2z}$		$2\bar{C}_{4z}$	$2\bar{\sigma}_x$	$2\sigma_d$		i	$\tilde{\sigma}_h$	$2\bar{S}_4$	$2\bar{C}_{2x}$	$2C_{2\bar{d}}$	
	↙	↘	↙	↘	⇓	⇓	↙	↘	⇓	⇓	⇓	⇓	↙	↘
G^2_{32}	E	E'	$\tilde{C}_{2z}$	$\tilde{C}'_{2z}$	$4\bar{C}_{4z}$	$4\bar{\sigma}_x$	$2\sigma_d$	$2\sigma'_d$	$2i$	$2\sigma_h$	$4\bar{S}_4$	$4\bar{C}_{2x}$	$2C_{2\bar{d}}$	$2C'_{2\bar{d}}$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	1	−1	−1	−1	1	1	1	−1	−1	−1
B_{1g}	1	1	1	1	−1	1	−1	−1	1	1	−1	1	−1	−1
B_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	1	1
E_g	2	2	−2	−2	0	0	0	0	2	−2	0	0	0	0
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1
A_{2u}	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
B_{1u}	1	1	1	1	−1	−1	1	1	−1	−1	1	1	−1	−1
B_{2u}	1	1	1	1	−1	1	−1	−1	−1	−1	1	−1	1	1
E_u	2	2	−2	−2	0	0	0	0	−2	2	0	0	0	0
E_{1m}	2	−2	2	−2	0	0	2	−2	0	0	0	0	0	0
E_{2m}	2	−2	2	−2	0	0	−2	2	0	0	0	0	0	0
E_{3m}	2	−2	−2	2	0	0	0	0	0	0	0	0	2	−2
E_{4m}	2	−2	−2	2	0	0	0	0	0	0	0	0	−2	2

coupling can be understood from the product decomposition of the superconducting bilinear $E_{3/4m} \otimes E_{3/4m} = A_{1g} \oplus A_{1u} \oplus B_{2u} \oplus B_{2g}$, and has strong implications for the phenomenology. Magnetism develops as an improper order, with a weaker temperature dependence $\propto T$ [see Fig. 1(b)], which might make its experimental observation more difficult. A slow onset for the improper magnetic order in $CeRh_2As_2$ is consistent with the apparent magnetic critical temperature being lower than the superconducting critical temperature, as reported by NMR [26] and NQR [25]. Recently, muon spin relaxation [32] and specific heat measurements [33] hinted at possible time-reversal symmetry breaking above T_c. Altogether, the onset temperature of magnetic order is still not settled, and our results should trigger a more in-depth experimental investigation in this direction. If magnetism onsets exactly at T_c, our analysis imposes stringent constraints on the nature of both magnetism and superconductivity. It necessarily indicates that the magnetic moments are aligned along the c axis and that superconductivity is of a very unusual type: a chiral pair-density wave (PDW) with two components of opposite parity. In this respect, our proposed order parameter is reminiscent of the "Bidirectional-II" PDW in Ref. [4], which supports induced magnetization-density wave order. However, in our scenario the multicomponent nature of the order parameter originates from its intricate sublattice structure and the nonsymmorphic symmetries. The chiral (time-reversal symmetry breaking) nature of the superconducting state is generally guaranteed based on an energetics analysis as this reduces the nodal structure from lines to points in real space. PDWs are known to induce other types of orders, however, previous treatments relied primarily on constraints imposed by translational symmetries [4], not capturing the full spectrum of possible improper phases.

In a broader context, we can also predict that a finite c-axis electric polarization [Fig. 3(a)], transforming under the A_{2u} irrep, can be induced as an improper order if the primary order parameter is in the E_{1m} or E_{2m} irreps, given the product decomposition $E_{1/2m} \otimes E_{1/2m} = A_{1g} \oplus A_{2u} \oplus B_{2g} \oplus B_{1u}$. Note that the validity of this statement goes beyond a superconducting primary order parameter and also applies to bilinears in the charge or spin sectors.

Going beyond the discussion on $CeRh_2As_2$, we note that the space group P4/nmm is the relevant symmetry group for a number of families of materials, including several Fe-based superconductors [29,30]. Moreover, our results can be easily generalized to other nonsymmorphic space groups. In the Supplemental Material [30], we compile a list of centrosymmetric nonsymmorphic materials with the corresponding space group and modulation wave vectors that sustain parity-mixed order parameters. In particular, the order parameters highlighted here might be key to understanding the unusual nature of time-reversal symmetry breaking (TRSB) at the onset of superconductivity in a number of nonsymmorphic materials [30,34,35]. For the case of elemental rhenium, TRSB has been directly associated with nonsymmorphic crystal symmetry in first-principles-based numerical calculations [36]. Furthermore, Weyl-Kondo semimetals, nonsymmorphic strongly correlated systems [37,38], are natural candidates to host unusual phenomenology similar to the one observed in $CeRh_2As_2$.

Concerning the experimental confirmation of our proposal, standard scanning tunneling experiments can directly indicate the development of modulated superconducting orders [4],

and nonreciprocal responses can indicate the breaking of both inversion and time-reversal symmetries. Unique signatures of the parity-mixed superconducting order parameter are also expected. Parity mixing allows for Lifshitz invariants of the form $\Psi_1^* D_i \Psi_2 + \Psi_2^* D_i^* \Psi_1 + \text{c.c.}$ (where D_i is the ith component of the covariant derivative). This term has been proposed to leave its signature on the optical conductivity due to the linear coupling between the Leggett mode and the U(1) vector potential [39,40].

In summary, our work highlights overlooked families of order parameters with unique symmetry properties and the unforeseen couplings between them. While there are multiple candidate mechanisms for stabilizing a pair-density wave order [4], modulated superconducting states with a staggered (commensurate) superconducting order parameter, also known as eta-pairing states [41], have remained elusive. Eta-pairing-like phases were shown to be stable in the Heisenberg-Kitaev model in the honeycomb lattice in the limit of strong spin-orbit coupling [42], and in an extended t-J model on the square lattice [43]. Furthermore, eta pairing has been shown to be a metastable phase in a photodoped strongly repulsive Hubbard model [44]. We relegate the examination of microscopic models in the context of $CeRh_2As_2$ for future work. We expect that our findings will open the door for more exotic vestigial and composite orders formed by order parameters with opposite parity. We also anticipate that these results will trigger new connections between the fields of strongly correlated systems and the emerging area of topological functional materials.

A.S. is grateful for financial support from the Swiss National Science Foundation (SNSF) through Division II (No. 184739). A.R. also acknowledges financial support from the SNSF through an Ambizione Grant No. 186043.

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