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Magnetic quasicrystals: what can we expect to see in their neutron diffraction data?

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Abstract

The theory of magnetic symmetry in quasicrystals is used to characterize the nature of magnetic peaks expected in elastic neutron diffraction experiments. It has been established that there is no symmetry-based argument which forbids the existence of quasiperiodic long-range magnetic order. Suggestions are offered as to where one should look for the simplest kinds of antiferromagnetic quasicrystals.
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1. Introduction

In recent years, we have witnessed a careful experimental investigation on the question of long-range magnetic order in rare-earth based icosahedral quasicrystals [1–3]. Nevertheless, discussions of this matter have been somewhat unclear as to the actual nature of the magnetic order one would expect to see in antiferromagnetic (AF) quasicrystals, if they were to exist. A partial answer to this question can be obtained from a theory of the symmetry of magnetically ordered quasicrystals [4]. I intend to show here that such a theory not only provides a valuable tool for analyzing neutron diffraction data, but also helps to narrow down the possible magnetic ordering one would expect to see in the classes of quasicrystals that are known to exist today. I hope that this will help in guiding the continuing search for new quasicrystals with this unique physical property.

2. The spin density field and its symmetry

A magnetically-ordered crystal, whether periodic or aperiodic, is most directly described by its spin density field $\mathbf{S}(\mathbf{r})$. This field is a three-component real-valued function, transforming like an axial vector under O(3) and changing sign under time inversion. One may think of this function as defining a set of classical magnetic moments, or spins, on the atomic sites of the material. For quasiperiodic crystals, the spin density field may be expressed as a Fourier sum with a countable infinity of wave vectors

$$\mathbf{S}(\mathbf{r}) = \sum_{\mathbf{k}\in L} \mathbf{S}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{1}$$

The set L of all integral linear combinations of the wave vectors in Eq. (1) is called the *magnetic lattice*. Its *rank D* is the smallest number of wave vectors needed to generate it by integral linear combinations. For quasiperiodic crystals, by definition, the rank is finite. For the special case of periodic crystals the rank is equal to the dimension d of physical space.

In elastic neutron scattering experiments, every wave vector $\mathbf{k}$ in L is a candidate for a magnetic Bragg peak whose intensity is given by

$$I(\mathbf{k}) \propto |\mathbf{S}(\mathbf{k})|^2 - |\hat{\mathbf{k}}\cdot\mathbf{S}(\mathbf{k})|^2, \tag{2}$$

where $\mathbf{k}$ is the scattering wave vector and $\hat{\mathbf{k}}$ a unit vector in its direction. I have shown elsewhere [5] that under generic circumstances there can be only three reasons for not observing a magnetic Bragg peak at $\mathbf{k}$, even though $\mathbf{k}$ is in L: (a) the intensity $I(\mathbf{k})\neq 0$, but is too weak to be detected in the actual experiment; (b) the intensity $I(\mathbf{k})=0$ because $\mathbf{S}(\mathbf{k})$ is parallel to $\mathbf{k}$; and (c) the intensity $I(\mathbf{k})=0$ because magnetic symmetry requires the Fourier coefficient $\mathbf{S}(\mathbf{k})$ to vanish. I shall explain below exactly how this symmetry requirement, or 'selection rule', comes about.

The theory of magnetic symmetry in quasiperiodic crystals, which is described in more detail in Ref. [4], is a reformulation of Litvin and Opechowski's theory of spin space

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groups [6–8]. Their theory, which is applicable to periodic crystals, is extended to quasiperiodic crystals by following the ideas of Rokhsar, Wright, and Mermin's 'Fourier-space approach' to crystallography [9]. At the heart of this approach is a redefinition of the concept of point-group symmetry which enables one to treat quasicrystals directly in physical space [10]. The key to this redefinition is the observation that point-group rotations (proper or improper), when applied to a quasiperiodic crystal, do not leave the crystal invariant but rather take it into one that contains the same spatial distributions of bounded structures of arbitrary size.

This generalized notion of symmetry, termed 'indistinguishability', is captured by requiring that any symmetry operation of the magnetic crystal leave invariant all spatially-averaged autocorrelation functions of its spin density field $\mathbf{S}(\mathbf{r})$ for any order n and for any choice of components $\alpha_i \in \{x,y,z\}$,

$$C^{(n)}_{\alpha_1 \ldots \alpha_n}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \lim_{V\to\infty} \frac{1}{V} \int_V \mathrm{d}\mathbf{r}\, S_{\alpha_1}(\mathbf{r}_1 - \mathbf{r}) \cdots S_{\alpha_n}(\mathbf{r}_n - \mathbf{r}). \quad (3)$$

I have shown in the Appendix of Ref. [11] that an equivalent statement for the indistinguishability of any two quasiperiodic spin density fields, $\mathbf{S}(\mathbf{r})$ and $\mathbf{S}'(\mathbf{r})$, is that their Fourier coefficients are related as

$$\mathbf{S}'(\mathbf{k}) = \mathrm{e}^{2\pi i \chi(\mathbf{k})} \mathbf{S}(\mathbf{k}), \quad (4)$$

where χ, called a *gauge function*, is a real-valued scalar function which is linear (modulo integers) on L. Only in the case of periodic crystals can one replace $2\pi\chi(\mathbf{k})$ by $\mathbf{k}\cdot\mathbf{d}$, reducing indistinguishability to the requirement that the two crystals differ at most by a translation $\mathbf{d}$.

With this in mind, we define the *point group* G of the magnetic crystal to be the set of operations g from O(3) that leave it indistinguishable to within rotations γ in spin space, possibly combined with time inversion. Accordingly, for every pair (g,γ) there exists a gauge function, $\Phi^{\gamma}_{g}(\mathbf{k})$, called a *phase function*, which satisfies

$$\mathbf{S}(g\mathbf{k}) = \mathrm{e}^{2\pi i \Phi^{\gamma}_{g}(\mathbf{k})} \gamma \mathbf{S}(\mathbf{k}). \quad (5)$$

Since $\mathbf{S}([gh]\mathbf{k}) = \mathbf{S}(g[h\mathbf{k}])$, one can easily establish that the transformations γ in spin space form a group Γ and that the pairs (g,γ) satisfying the point-group condition (5) form a subgroup of $G\times\Gamma$ which we call the *spin point group* $G_{\mathbf{S}}$. The corresponding phase functions, one for each pair in $G_{\mathbf{S}}$, must satisfy the *group compatibility condition*,

$$\forall (g,\gamma), (h,\eta) \in G_{\mathbf{S}}: \quad \Phi^{\gamma\eta}_{gh}(\mathbf{k}) \equiv \Phi^{\gamma}_{g}(h\mathbf{k}) + \Phi^{\eta}_{h}(\mathbf{k}), \quad (6)$$

where '$\equiv$' denotes equality modulo integers. A *spin space group*, describing the symmetry of a magnetic crystal, whether periodic or aperiodic, is thus given by a magnetic lattice L, a spin point group $G_{\mathbf{S}}$, and a set of phase functions $\Phi^{\gamma}_{g}(\mathbf{k})$, satisfying the group compatibility condition (6).

3. The diffraction pattern: a thinned-out magnetic lattice or a shifted nuclear lattice?

I said earlier that every wave vector in the magnetic lattice is a candidate for a diffraction peak unless symmetry forbids it. We are now in a position to understand how this happens. Given a wave vector $\mathbf{k}\in L$, we examine all spin point-group operations (g,γ) for which $g\mathbf{k}=\mathbf{k}$. These elements form a subgroup of the spin point group, called the *little spin group* of $\mathbf{k}$, $G^{\mathbf{k}}_{\mathbf{S}}$. For elements (g,γ) of $G^{\mathbf{k}}_{\mathbf{S}}$, the point-group condition (5) can be rewritten as

$$\gamma \mathbf{S}(\mathbf{k}) = \mathrm{e}^{-2\pi i \Phi^{\gamma}_{g}(\mathbf{k})} \mathbf{S}(\mathbf{k}). \quad (7)$$

This implies that the Fourier coefficient $\mathbf{S}(\mathbf{k})$ is required to be a simultaneous eigenvector of all spin transformations γ in the little spin group of $\mathbf{k}$, with the eigenvalues given by the corresponding phase functions. If a non-trivial three-dimensional axial vector satisfying Eq. (7) does not exist then $\mathbf{S}(\mathbf{k})$ will necessarily vanish. If such an eigenvector does exist its form might still be constrained to lie in a particular subspace of spin space.

Of particular interest are spin transformations γ that leave the spin density field indistinguishable without requiring any rotation in physical space. These transformations are paired in the spin point group with the identity rotation e and form a normal and Abelian subgroup of Γ called the *lattice spin group* Γ_e. In the special case of periodic crystals, the elements of Γ_e are spin transformations that, when combined with translations, leave the magnetic crystal invariant.

The lattice spin group plays a key role in determining the outcome of elastic neutron scattering, for if a magnetic crystal has a non-trivial lattice spin group Γ_e then $\{e\}\times\Gamma_e \subseteq G^{\mathbf{k}}_{\mathbf{S}}$ for every $\mathbf{k}$ in the magnetic lattice, restricting the form of all the $\mathbf{S}(\mathbf{k})$'s. This may result in a substantial thinning-out of the magnetic lattice, whereby only a fraction of the wave vectors give rise to actual magnetic Bragg peaks. Because this thinning of the magnetic lattice is often quite extensive, it is common practice to describe the magnetic peaks not as a thinned-out magnetic lattice, but rather in terms of the nuclear lattice L_0 (the one observed above the magnetic ordering temperature) which is shifted by the so-called 'magnetic propagation vectors'. These two descriptions are in fact equivalent and with some care can be used interchangeably.

4. Where should we look?

In the past I have tabulated all the decagonal spin space groups [12], as well as all the lattice spin groups for icosahedral quasicrystals [4]. In the latter case I also listed explicitly, for every wave vector $\mathbf{k}$ in the magnetic lattice, whether through Eq. (7) symmetry requires $\mathbf{S}(\mathbf{k})$ to vanish or to take any special form. In a future publication I plan to provide complete tables of spin space groups and the

requirements which they impose on neutron scattering experiments for all the relevant quasiperiodic crystal systems (octagonal, decagonal, dodecagonal, and icosahedral).

Clearly, the theory of spin space groups provides a helpful tool for analyzing neutron diffraction experiments. It lists the patterns of magnetic Bragg peaks, compatible with each symmetry class, which can then be directly compared with experiment. But, on a more basic level, this theory answers one of the fundamental questions that have been debated in recent years, which is whether it is even possible to have long-range quasiperiodic magnetic order. It establishes that even though symmetry may impose constraints on the possible forms of magnetic order one can have in a given quasicrystal, it clearly does not forbid the existence of such order. *Thus, there is no symmetry-based argument which disallows long-range magnetic order in quasicrystals*.

Why is it then, that we have not yet observed unequivocal long-range magnetic order in a quasicrystal? It might be because *energetic* considerations lead to local frustration and spin-glass ordering; it might be due to some other *physical* argument; or — it might be simply because we have not found it yet. If this is the case, then a more practical question to ask of a theory of magnetic symmetry is whether it can offer any suggestions as to where to look for such order. Indeed, symmetry considerations may assist us in deciding in which quasicrystal systems to look first for the *simplest* kind of non-trivial magnetic ordering. Such ordering would be the quasiperiodic analog of a simple AF periodic crystal where half the spins are pointing 'up' and the other half are pointing 'down'. Symmetry arguments can guide us to those systems where such ordering is possible.

I, therefore, close this essay with a short discussion of what this quasiperiodic AF order looks like, followed by the list of systems which are compatible with such order. It would then be up to the metallurgists and material scientists to find the right chemical systems which can sustain local magnetic moments and at the same time are likely to have stable phases in these crystal systems.

5. The quasiperiodic antiferromagnet

The simple AF crystal, whether periodic or aperiodic, has a lattice spin group Γ_e containing only two elements: the identity operation ϵ and time inversion τ. In the case of time inversion, the selection rule (7) becomes

$$\tau\mathbf{S}(\mathbf{k}) \equiv -\mathbf{S}(\mathbf{k}) = \mathrm{e}^{-2\pi i \Phi_e^\tau(\mathbf{k})}\mathbf{S}(\mathbf{k}), \tag{8}$$

which requires $\mathbf{S}(\mathbf{k})$ to vanish unless $\phi_e^\tau(\mathbf{k})\equiv 1/2$. On the other hand, application of the group compatibility condition (6) to $(e,\tau)^2=(e,\epsilon)$ gives two possible values for this phase,

$$\phi_e^\tau(\mathbf{k}) \equiv 0 \text{ or } \tfrac{1}{2}. \tag{9}$$

It is not too difficult to show that exactly half of the wave vectors in the magnetic lattice L have $\phi_e^\tau(\mathbf{k})\equiv 0$ and will, therefore, not appear in the neutron diffraction pattern. These wave vectors constitute a sublattice L_0 of index 2 in L. One can then describe the set of wave vectors appearing in the diffraction diagram either as the magnetic lattice L without all the wave vectors in L_0, or as L_0 shifted by $\mathbf{q}$, where $\mathbf{q}$, a 'magnetic propagation vector', is any vector in L which is not in the sublattice L_0. In the simplest scenario L_0 is also the nuclear lattice, but this is not necessarily the case.

Consider a one-dimensional spin chain with this lattice spin group. If the chain is periodic, then its (Fourier) magnetic lattice is given by all integral multiples of a single wave vector $\mathbf{b}^*$ (I will keep the superscript * as a reminder that we are in Fourier space). Because phase functions are linear, it suffices to specify the value of ϕ_e^τ on $\mathbf{b}^*$ and that will determine its value on any wave vector in the lattice. Of the two possible values (see Eq. (9)) the first, $\phi_e^\tau(\mathbf{b}^*)\equiv 0$ will result through the selection rule (8) in $\mathbf{S}(\mathbf{k})$ being zero every where and, therefore, $\mathbf{S}(\mathbf{r})=0$ as well. The only non-trivial assignment is therefore $\phi_e^\tau(\mathbf{b}^*)\equiv 1/2$ which through the selection rule (8) implies that all lattice wave vectors that are even multiples of $\mathbf{b}^*$ will be missing, or 'extinct', from the diffraction pattern.

If the spin chain is quasiperiodic, say having a rank of 2, then its magnetic lattice will be given by all integral linear combinations of two wave vectors, $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$, whose magnitudes are incommensurate. In this case the phase function ϕ_e^τ is fully determined by specifying its two independent values on $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$. At first glance, it would seem as if there are three distinct non-trivial assignments of values given by

$$(\phi_e^\tau(\mathbf{b}_1^*), \phi_e^\tau(\mathbf{b}_2^*)) \equiv (0, \tfrac{1}{2}) \text{ or } (\tfrac{1}{2}, 0) \text{ or } (\tfrac{1}{2}, \tfrac{1}{2}). \tag{10}$$

It turns out that these three assignments are equivalent, leading to the same spin space group, due to the fact that for a quasiperiodic chain one has the added freedom of changing the basis of the magnetic lattice. A basis transformation from $(\mathbf{b}_1^*, \mathbf{b}_2^*)$ to $(\mathbf{b}_1^*+\mathbf{b}_2^*, \mathbf{b}_2^*)$ or to $(\mathbf{b}_1^*, \mathbf{b}_1^*+\mathbf{b}_2^*)$ takes one, respectively, from the first or second assignment in Eq. (10) to the third. Thus, the diffraction pattern of a quasiperiodic AF spin chain can always be described as a magnetic lattice given by wave vectors of the form $\mathbf{k}=n_1\mathbf{b}_1^*+n_2\mathbf{b}_2^*$ where all the vectors with n_1+n_2 are extinct. Equivalently, it may be described as a lattice L_0, generated by the wave vectors $\mathbf{b}_1^*+\mathbf{b}_2^*$ and $\mathbf{b}_1^*-\mathbf{b}_2^*$, and shifted by the vector $\mathbf{b}_1^*$.

Knowing the different possibilities in Fourier space allows us to immediately construct simple direct-space examples of AF spin chains having these symmetries. Fig. 1a and b show two periodic AF spin chains in which the 'magnetic unit cell' is twice or four-times as large as the 'nuclear unit cell'. Both of these chains will exhibit the same magnetic diffraction peaks, the only way to distinguish them being a direct comparison with the nuclear diffraction pattern, which can be obtained above the magnetic ordering temperature. Fig. 1c–e show three AF Fibonacci chains, obtained by setting the ratio b_1^*/b_2^* to the golden mean $(1+\sqrt{5})/2$, and using the three different assignments of the phase function values given in Eq. (10). Again, as discussed above, all three are

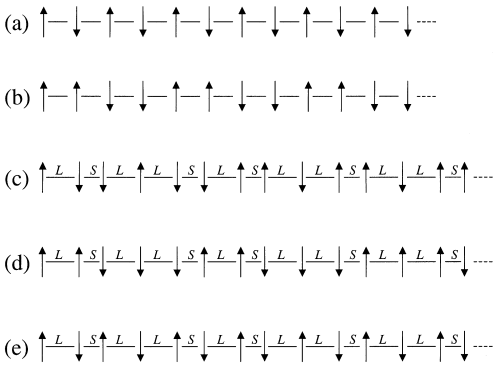

Fig. 1. Examples of antiferromagnetic spin chains: (a) and (b) are periodic with different magnetic unit cells; (c)–(e) the AF Fibonacci chains, obtained as described in the text by using a modified grid method. In (c) spins separated by a long (*L*) segment are anti-parallel and those separated by a short (*S*) segment are parallel; in (d) the opposite occurs; and in (e) all nearest-neighbor pairs are anti-parallel.

expected to have the same magnetic diffraction peaks and the only way to distinguish them is a comparison with the nuclear diffraction pattern.

Which of the actual quasicrystal systems that are known to exist today allow a simple AF order? Axial quasicrystals admit two kinds of simple AF order. Since they are all quasiperiodic in the plane normal to the *n*-fold axis and periodic along this axis, it is always possible to have periodic AF order along the *n*-fold axis. This would give an AF quasicrystal, but not in the true sense that we are interested in. Only when *n* is a power of 2 is it possible to have true quasiperiodic AF order in the plane normal to the *n*-fold axis [11]. *Thus, among the known axial quasicrystals one should concentrate the search for simple AF order in the octagonal crystal system*.

Only two of the three Bravais classes in the icosahedral system admit simple AF order [4]. Such order is possible if the nuclear lattice is either simple (giving a magnetic lattice which is body-centered in Fourier space) or if the nuclear lattice is face-centered in Fourier space (giving a simple icosahedral magnetic lattice). Unfortunately, most of the known icosahedral quasicrystals, including the rare-earth based ones, are face-centered in direct space and, therefore, do not allow simple AF order. Furthermore, icosahedral quasicrystals which are body-centered in direct space are not yet known to exist. *Thus, in the icosahedral system, one should look for simple AF order in crystals that have a simple icosahedral nuclear lattice*.

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