Quadrupolar ordering in half-integral spin systems

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Abstract

All possible couplings between a half-integral localised angular momentum in a cubic environment and lattice deformations are examined. When the cubic symmetry is broken the result can only be quadrupolar ordering. Application to $NdFe_4P_{12}$, $SmRu_4P_{12}$ and $GdRu_4P_{12}$ is discussed.

Key words: skutterudites; quadrupolar ordering

Several of the rare-earth filled skutterudites undergo metal-insulator (M-I) transitions, simultaneously accompanied by some kind of ordering. In $PrFe_4P_{12}$ anti-quadrupolar ordering has been observed directly [1], while in $TbRu_4P_{12}$ [2], $NdFe_4P_{12}$ [3], $SmRu_4P_{12}$ [4] and $GdRu_4P_{12}$ [2] magnetisation anomalies are observed at the M-I transition. An exception to this is $PrRu_4P_{12}$, which shows no sign of any kind of ordering at the M-I transition, but may also be anti-quadrupolar ordered at a lower temperature. The common feature of these materials is a Fermi surface instability, due to nesting of the Fermi surface at precisely one-half of the Brillouin zone (BZ). In $PrFe_4P_{12}$ and $PrRu_4P_{12}$, lattice distortions which double the unit cell and cut the BZ in half have been observed [5,6]. Band structure calculations [7] have shown that lattice distortions do in fact open a gap at the Fermi surface and group theory arguments explain both anti-quadrupolar ordering in $PrFe_4P_{12}$ and the absence of ordering in $PrRu_4P_{12}$ [8].

In this article, we summarise the results of a general analysis of lattice distortion modes which can lift angular momentum degeneracy within a cubic structure. We consider half-integral total angular momentum, which applies to the f-electron states in $NdFe_4P_{12}$ ($J = 9/2$), $SmRu_4P_{12}$ ($J = 5/2$) and $GdRu_4P_{12}$ ($J = 7/2$).

In general, the degeneracy in a half-integral angular momentum system is split by a cubic crystal field into states which transform according to the double representations Γ^6, Γ^7 and Γ^8 of the group O. Since the f-electrons appear in the Hamiltonian as pairs of creation and annihilation operators in the form $f^\dagger f$, we need to consider the products $\Gamma^6 \otimes \Gamma^6 = \Gamma^7 \otimes \Gamma^7 = \Gamma^1 \oplus \Gamma^4$ and $\Gamma^8 \otimes \Gamma^8 = \Gamma^1 \oplus \Gamma^2 \oplus \Gamma^3 \oplus 2\Gamma^4 \oplus 2\Gamma^5$. The coupling between the f-electrons and a lattice distortion can be written as $C^a A_i^a [f^\dagger f]_i^a$ where C^a are coupling constants, A_i^a are the distortion modes, a indexes the representation and i indexes the basis of the representation (when the representation dimension is greater than one). Time reversal symmetry excludes the Γ^2, both of the Γ^4, and one of the Γ^5 representations of $f^\dagger f$ from the coupling term. Lowest energy states are found for f, yielding angular momentum eigenfunctions which are expressed in terms of A_i. Symmetry breaking terms in the Hamiltonian for A are assumed, then specific forms of the distortion are found. These are used to find the actual f-electron angular momentum ground state wavefunctions, from which the various kinds of orderings can be determined. Table I summarises the properties of the ground state wavefunc-

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f	$f^\dagger f$	Degeneracy	Ordering	
Γ^6	Γ^1	2	none	
	Γ^4	-	does not couple	
Γ^7	Γ^1	2	none	
	Γ^4	-	does not couple	
Γ^8	Γ^1	4	none	
	Γ^2	-	does not couple	
	Γ^3	2	quadrupole	$J^2 - 3J_z^2$
	Γ_1^4	-	does not couple	
	Γ_2^4	-	does not couple	
	Γ_1^5	-	does not couple	
	Γ_2^5	2	quadrupole	$J_xJ_y - J_yJ_z - J_zJ_x$

Table 1
Kinds of ordering associated with the three types of half-integral angular momentum wavefunctions in a broken cubic symmetry environment. The first column labels the three cubic representations of the angular momentum ground state wave-function. The second column lists the representations of the product $f^\dagger f$, which must match the representation of the lattice distortion. The third column lists the degeneracy of the broken symmetry angular momentum ground state and the fourth column gives the resulting ordering.

tions found in this way.

The Γ^3 and Γ^5 deformation modes may be represented by $(x^2+y^2-2z^2, x^2-y^2)$ and $A = (yz, zx, xy)$ respectively. Symmetry breaking picks out the component $x^2+y^2-2z^2$ of Γ^3 (used in Table I), and similar terms obtained by exchanging x, y and z. For Γ^5, the symmetry broken deformations are $A = (1,1,-1)$, $(1,-1,1)$, $(-1,1,1)$ or $(-1,-1,-1)$; $A = (1,1,-1)$ is used in Table I (note that all permutations of J_iJ_j should be included).

According to this scenario, there can be no ordering associated with either the Γ^6 or Γ^7 f-electron crystal electric field ground states. The Γ^8 state can couple to Γ^1, Γ^3 or Γ^5 distortions. Different types of quadrupolar ordering are found for the Γ^3 and Γ^5 distortions; in both cases the final ground state is doubly degenerate. A lattice distortion which does not lead to any kind of ordering (the Γ^1 mode) can couple to each of the three crystal field ground states.

The filled skutterudite have a point group symmetry of T_h, not O_h, due to the pnicogen (phosphorus, arsenic or antimony) ions. The lower symmetry introduces extra coupling constants in the $f^\dagger fA$ interaction term and in the symmetry breaking term which is cubic in A. The latter has the effect of rotating the quadrupole moments; in particular the $J^2 - 3J_z^2$ moment gets reduced in favour of a x^2-y^2 component.

In real systems, there may be more than one distortion mode for each representation, while others do not occur at all. For example, there is no Γ^2 distortion mode among the twenty-four degrees of freedom of the eight transition element ions which surround the rare earth ion in all of the filled skutterudite compounds, but the Γ^5 mode occurs twice.

In a cubic crystal field the total angular momenta $J = 5/2, 7/2$ and $9/2$ (corresponding to $SmRu_4P_{12}$, $GdRu_4P_{12}$ and $NdFe_4P_{12}$) split into levels which transform according to the representations $\Gamma^7 \oplus \Gamma^8$, $\Gamma^6 \oplus \Gamma^7 \oplus \Gamma^8$ and $\Gamma^6 \oplus 2\Gamma^8$ of O respectively. Which of these are the ground states is as of yet undetermined. Magnetic entropy on $NdFe_4P_{12}$ suggests that the degeneracy is lowered from four to two below the M-I transition [9], so that apparently one of the Γ^8 states is the ground state. In $SmRu_4P_{12}$ a second magnetic transition is observed just below the M-I transition; in this context it can only be explained by a Γ^8 ground state.

Lastly, we discuss how the lattice distortions are related to the M-I transition. In $PrFe_4P_{12}$ and $PrRu_4P_{12}$, it is known that the M-I transition occurs simultaneously with a doubling of the unit cell, which also changes the lattice structure from body-centred cubic to simple cubic. In order for this occur, the lattice deformation must alternate in sign between neighbouring rare earth sites, and the resulting ordering is anti-quadrupolar. Whether or not the various modes can actually open a gap at the Fermi surface remains to be shown. Band structure calculations on $PrFe_4P_{12}$ found that a Γ^3 type distortion of iron ions opens a gap everywhere except at a few points, while a Γ^1 type distortion involving the phosphorus ions is responsible for the full M-I transition in $PrRu_4P_{12}$ [7]. In fact, because the Pr f-electrons have a Γ^3 type crystal field ground state, the Γ^1 and Γ^3 deformation modes are the only ones which are allowed by symmetry to couple to the local angular momentum in $PrFe_4P_{12}$ and $PrRu_4P_{12}$. The presence of magnetisation anomalies at the M-I transition in $SmRu_4P_{12}$, $NdFe_4P_{12}$ and $GdRu_4P_{12}$ seems to rule out Γ^1 type distortions. The Γ^3 distortion mode is certainly a good candidate for these compounds, but at this point the possibility of a Γ^5 distortion mode cannot be excluded.

In summary, we have found all of the various types of ordering of localised half-integral angular momenta which can occur in a distortion of the cubic environment.

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