Symmetry Specification of Bands in Solids

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Band representations of space groups are defined and they are used for the symmetry specification of bands in solids. While the symmetry of atomic orbitals is specified around a single center, the band symmetry of a solid is defined with respect to a whole lattice of centers.

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The concept of bands was first introduced by Bloch[1] and has since been widely used in solid-state physics. However, until quite recently the concept of a band as a whole entity was not utilized because most of the experiments were involved with electronic states at the Fermi level in metals and at the top and bottom of the valence and conduction bands correspondingly in semiconductors. In recent years with the application of powerful sources of radiation[2] it became possible to extract information about states ranging over hundreds of electron volts and in such experiments the data about a band as a whole should become accessible. It is therefore of interest to reconsider the band concept in a solid.

The usual approach in defining the concept of a band in a solid is by specifying the symmetry of the Bloch functions at each point $\vec{k}$ in the Brillouin zone.[3] In a series of papers by Des Cloizeaux[4] it was shown that a close connection exists between Bloch functions and symmetry-adapted localized orbitals. In this Letter a specification of bands in solids is given based entirely on space-group symmetry.

It is instructive to compare the symmetry of a crystal with that of an atom. The atomic levels are specified by the rotational symmetry around one fixed center. In a crystal there is, as a rule, more than one center of point-group symmetry. Thus, in Figs. 1 and 2, I show examples of two space groups, C_i^1 and D_4^1, respectively.[5] In these figures the symmetry centers are given in the plane x-y. In the group C_i^1, all the symmetry centers are of the same kind and they contain the inversion only. Two centers differing by a Bravais-lattice vector are equivalent. For the group D_4^1, two kinds of centers are given in Fig. 2: with symmetry D_4 and D_2. From the point of view of symmetry, crystals differ from atoms in two aspects. Crystals have a number of point-group centers while atoms have only one. This is not a qualitative difference. A difference which is of qualitative nature is that in a crystal there is always a lattice of symmetry centers of a given kind. Such a lattice is obtained by choosing one center of given point symmetry and by applying to it all the elements of the space group.[3] One can therefore visualize a space group as consisting of lattices of symmetry centers. Correspondingly, in crystals the symmetry specification of states should be defined with respect to an infinite number of symmetry centers simultaneously.

While each Bloch function defines a single energy, a Wannier function reproduces energies belonging to a whole band.[6] This same idea holds also for general localized orbitals and the restriction to Wannier functions is unnecessary.[7,8] One should therefore expect that, for the symmetry specification of a band as a whole entity, local-

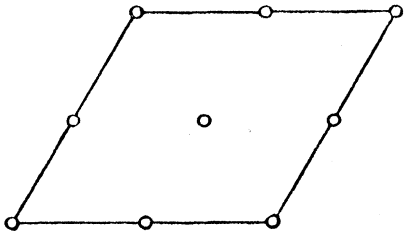

FIG. 1. Space group C_i^1. The circles denote inversion centers.

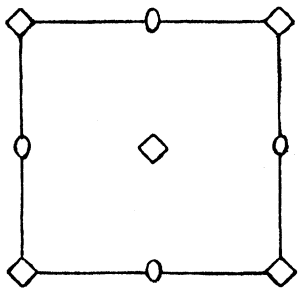

FIG. 2. Space group D_4^1. The squares denote centers with point symmetry D_4; the ovals, those with point symmetry D_2.

ized orbitals are more suitable than Bloch functions.

I shall define a band in a solid as a set of localized orbitals which are invariant under all the operations of the space group. Because of all the translations, such a set will form an infinite-dimensional representation of the space group. If an orbital $C(\vec{k},\vec{q})$ in the kq representation belongs to this set, then all the orbitals

$$\exp(-i\vec{k}\cdot\vec{R}_m)C(\vec{k},\vec{q}) \tag{1}$$

will also belong to it.[8] I shall therefore define a band in a solid by an infinite-dimensional representation of the space group on a basis of localized orbitals. I shall call it a band representation. Band representations can be reducible or irreducible depending on whether or not the basis can be split into invariant subbases. The irreducible band representations serve as elementary building bricks in the symmetry definition of bands in solids. The orbitals $C(\vec{k},\vec{q})$ used as bases for band representations can, in principle, be made orthogonal on different sites (Wannier functions). However, this is, in general, undesirable because orthogonality and localizability are mutually exclusive properties.[7] It is convenient to define the band representation and its basis in the kq representation. The reason for this is that in the latter the localized orbitals $C(\vec{k},\vec{q})$ are Bloch-like functions, e.g., they satisfy the same boundary conditions as Bloch functions do, and they can be given two meanings. When $\vec{k}$ and $\vec{q}$ are the variables of the kq representation, the function $C(\vec{k},\vec{q})$ is a localized orbital. However, the same function $C(\vec{k},\vec{q})$ for a fixed quasimomentum $\vec{k}$ is a Bloch-like function in the r representation[8] (the concept Bloch-like is used to point out that these functions have the same symmetry as the Bloch functions). This dual meaning of the orbitals in the kq representation is very useful in fully defining the symmetry of the Bloch functions at each point in the Brillouin zone from the knowledge of the corresponding band representation. It gives therefore the link between the band definition adopted in this Letter and the commonly used definition which is based on the symmetry specification of Bloch functions for each $\vec{k}$ vector separately.[3,4]

Since pure translations multiply the orbitals by phases [expression (1)] it is clear that the bases of band representations contain a limited number of orbitals

$$C_1(\vec{k},\vec{q}),\ C_2(\vec{k},\vec{q}),\ \ldots,\ C_f(\vec{k},\vec{q}). \tag{2}$$

When the space-group elements $(\alpha|\vec{t})$ (α a point-group element and $\vec{t}$ a translation[3]) are applied to them, we get

$$(\alpha|\vec{t})C_s(\vec{k},\vec{q})=\textstyle\sum_{s'}D_{s's}[(\alpha|\vec{t}),\vec{k}]C_{s'}(\vec{k},\vec{q}), \tag{3}$$

where $D[(\alpha|\vec{t}),\vec{k}]$ is a k-dependent matrix. The knowledge of the matrices in (3) for all $(\alpha|\vec{t})$ defines the symmetry properties of the orbitals $C_s(\vec{k},\vec{q})$. The operation of $(\alpha|\vec{t})$ on a wave function $C(\mathrm{k},\mathrm{q})$ is as follows:

$$(\alpha|\vec{t})C(\vec{k},\vec{q})=C(\alpha^{-1}\vec{k},\alpha^{-1}\vec{q}-\vec{t}). \tag{4}$$

Band representations can be constructed in the following way. Given a space group G, we find all the groups of the quasicoordinate $\vec{q}$, G_q, in the Wigner-Seitz cell.[3] To G_q belong all those elements $(\gamma|\vec{c})$ of the space group for which

$$(\gamma|\vec{c})\vec{q}=\vec{q}+\vec{R}_m, \tag{5}$$

where $\vec{R}_m$ is a vector of the Bravais lattice. A full list of the groups G_q is given in Ref. 5. Thus, G_q for all the points in Fig. 1 is the whole space group C_i^1. In Fig. 2 the q points labeled by the squares have as their symmetry the space group D_4^1, while those labeled by the ovals have a symmetry group D_2 (containing all the translations) which is a subgroup of D_4^1. The space group G can be decomposed with respect to G_q into cosets

$$G=G_q+(\alpha_2|\vec{a}_2)G_q+\cdots+(\alpha_f|\vec{a}_f)G_q, \tag{6}$$

where $(\alpha_2|\vec{a}_2),\ldots,(\alpha_f|\vec{a}_f)$ are elements that do not belong to G_q. Given the decomposition (6), we can generate the star for each vector $\vec{q}$, which contains the vectors $\vec{q}$, $(\alpha_2|a_2)\vec{q},\ldots,(\alpha_f|a_f)\vec{q}$. Thus the stars of all the $\vec{q}$ vectors in Fig. 1 contain only $\vec{q}$ itself. I proceed similarly for the $\vec{q}$ vectors labeled by the squares in Fig. 2. The stars generated at and assigned to each oval in Fig. 2 contain two vectors, $\vec{q}$ and $C_4^z\vec{q}$, where C_4^z is a rotation by $\pi/2$ around the axis z.

The band representations of G can be induced from the band representations of its subgroups G_q. An important rule can be established showing that not all G_q have to be considered for obtaining all the irreducible band representations of G. This rule says that if G_{q_1} is a subgroup of G_{q_2} and their common point-group elements as given in relation (5) are identical, then G_{q_1} can be excluded and is irrelevant in the construction of the band representations of G.

Given a group G_q, its band representations can be found in an entirely elementary way. If $D(\gamma)$ is an irreducible representation of the point group of G_q, then the matrices $\exp(-i\vec{k}\cdot\vec{R}_m)D(\gamma)$ corre-

sponding to $(\gamma|\vec{R}_m)$ define an irreducible band representation of G_q. In this way one finds all the irreducible band representations of G_q from the irreducible representations of its point group.

Now let $\{C_1(\vec{k},\vec{q}), C_2(\vec{k},\vec{q}), \ldots, C_m(\vec{k},\vec{q})\}$ be a band representation of G_q. Then one can check that the functions

$$C_s(\vec{k},\vec{q}), (\alpha_2|\vec{a}_2)C_s(k,\vec{q}), \ldots, (\alpha_f|\vec{a}_f)C_s(k,\vec{q}), \quad (7)$$

with $s=1,\ldots,m$, form a basis for an irreducible band representation of the group G. By considering all the relevant G_q, one can find in this way all the irreducible band representations of G.

I shall demonstrate the construction of irreducible band representations on the groups C_i^1 and D_4^1 the symmetry centers of which are given in Figs. 1 and 2. The group C_i^1 has eight nonequivalent inversion centers (Ref. 5, page 78). It is possible to write the irreducible band representations for all these centers in one formula. All the centers in Fig. 1 have the symmetry $G_q=C_i^1$. Their stars contain therefore only one vector. Let I_r be the inversion around one of the centers $\vec{q}_r$. This inversion is connected with the inversion I around the origin of the crystal in the following way:

$$I_r=(\epsilon|\vec{q}_r)I(\epsilon|-\vec{q}_r)=(I|2\vec{q}_r). \quad (8)$$

It is clear that $2\vec{q}_r$ has to be a pure translation. Since I_r is represented by ± 1 $[I_rC^{(r)}(\vec{k},\vec{q})=\pm C^{(r)}(\vec{k},\vec{q})]$ all the band representations corresponding to different inversion centers q_r are given by the formula

$$IC^{(r)}(k,\vec{q})=\pm\exp(-i\vec{k}\cdot 2\vec{q}_r)C^{(r)}(k,\vec{q}). \quad (9)$$

The only other symmetry center for this group is $q=(x,y,z)$ which is invariant under translations only. Let us show that this center does not lead to additional band representations. The star for this center is $\{\vec{q},I\vec{q}\}$. This means that the orbitals $C(\vec{k},\vec{q})$ (an orbital without any symmetry) and $IC(\vec{k},\vec{q})$ will form together a basis for a band representation of C_i^1. This representation is, however, reducible. The reduction is achieved by forming two linear combinations $C(\vec{k},\vec{q})\pm IC(\vec{k},\vec{q})$. It is easy to check that they form bases for irreducible band representations of C_i^1 (even and odd, respectively) which have already been listed in Eq. (9). The latter gives therefore all the irreducible band representations of the group C_i^1.

Having in mind that the localized orbitals $C^{(r)}(\vec{k},\vec{q})$ in the kq representation are also the Bloch-like functions in the r representation we can claim that Eq. (9) gives all the symmetry types of bands for a solid with the symmetry C_i^1. Thus, the bands defined by $q_r=0$ are given by the relations $IC^{(0)}(\vec{k},\vec{q})=\pm C^{(0)}(\vec{k},\vec{q})$ or equivalently $C^{(0)}(-\vec{k},-\vec{q})=\pm C^{(0)}(\vec{k},\vec{q})$. Considering $C^{(0)}(\vec{k},\vec{q})$ as a Bloch-like function in the r representation, this relation defines its symmetry at all the symmetry points of the Brillouin zone for which $-\vec{k}=\vec{k}+\vec{K}_n$ ($\vec{K}_n$ a vector of the reciprocal lattice). But this is exactly what is needed for a symmetry specification of the band.[3] The same can be said about all the other inversion centers $\vec{q}_r$.

The group D_4^1 has a variety of symmetry centers. For the points with symmetry $G_q=D_4^1$ (denoted by a square in Fig. 2) there is only one vector in the star and it is very simple to find the band representations for all these points (there are four such inequivalent points; see Ref. 5, page 179). Formula (8) for the elements of D_4 becomes

$$\alpha_r=(\epsilon|\vec{q}_r)\alpha(\epsilon|-\vec{q}_r)=(\alpha|\vec{q}_r-\alpha\vec{q}_r). \quad (10)$$

Let the localized orbitals $C_1^{(r,l)}(\vec{k},\vec{q}),\ldots,C_m^{(r,l)}(\vec{k},\vec{q})$ form a basis for an irreducible representation l of D_4 with respect to the center q_r. Then from relations (10) it follows

$$\alpha C_s^{(r,l)}(\vec{k},\vec{q})=\exp[-i\vec{q}_r\cdot(\vec{k}-\alpha^{-1}\vec{k})]\times\sum_{s'=1}^{m}D_{s's}^{(r,l)}(\alpha)C_{s'}^{(r,l)}(k,\vec{q}). \quad (11)$$

This relation is of the same kind as (9) with the only difference that it can also contain a multidimensional representation $D^{(r,l)}$. For each $\vec{q}_r$ and l relation (11) defines an irreducible band representation of D_4^1 and, correspondingly, all symmetry types of bands for the D_4 centers. As an example let us consider the band symmetry defined by $\vec{q}_r=(\frac{1}{2}a,\frac{1}{2}a,0)$ (see Fig. 2) and the two-dimensional representation[3] of the point group D_4. Denote by β an element of the group of $\vec{k}$: $G_k=\{\vec{k}|\vec{k}=\vec{k}+\vec{K}_n\}$. In particular, for $\vec{k}=(\pi/a,\pi/a,\pi/c)$, $G_k=D_4^1$. When β is a rotation by π around the x axis, the exponential in (11) will be equal to -1. Similarly, one obtains the symmetry of the Bloch-like functions at each point $\vec{k}$ of the Brillouin zone. In this way formula (11) defines the type of band symmetry for any D_4 center and the representation of the point group D_4.

For the centers with D_2 symmetry the star contains two vectors. Thus, the vectors $q_1=(\frac{1}{2}a,0,0)$ and $q_2=(0,\frac{1}{2}a,0)$ form such a star (Fig. 2). With respect to the group G_q, the space group D_4^1 can be decomposed as follows:

$$D_4^1=D_2+C_4^zD_2. \quad (12)$$

The group G_q equals D_2 (containing all the translations). The band representations of D_2 are given by formula (11), where $D^{(r,l)}$ are now the representations of the point group D_2. According to Ref. 5, there are two inequivalent points (points f and e on page 179 of Ref. 5) with the symmetry D_2. The corresponding band representations of D_4^1 can be constructed according to the rule given in (7). It can be checked that by starting with the D_4- and D_2-symmetry points we obtain all the irreducible band representations of D_4^1.

In summary, this Letter gives for the first time a symmetry specification of bands in solids based entirely on band representations of space groups. These are new representations of groups which correspond to a band of energies rather than to a single energy as in the case of usual representations. While the symmetry of an energy level in an atom is specified with respect to a single center, the symmetry of a band in a solid is specified with respect to an infinite lattice of centers. This is in full correspondence with the concept of a band in a solid as derived from atomic levels of atoms placed on a lattice. The lattice of the symmetry centers is an invariant property of the band and if the full information about a band becomes accessible it should be possible to determine experimentally the position and the type of the lattice for each band in a solid.

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Magnetic Phase Transition near a Lifshitz Point: A Neutron Study of UAs

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Peculiar rodlike diffuse critical scattering above the type-I antiferromagnetic (AF/I) phase transition has been observed in the actinide compound UAs and demonstrates that the transition is in the vicinity of a Lifshitz point. A mean-field theory is proposed based on an anisotropic Hamiltonian and provides a reasonable description of the results.

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Recently there has been considerable interest in phase transitions associated with a so-called Lifshitz point, i.e., a multicritical point separating a uniformly ordered phase, a modulated phase, and a disordered phase.[1] In this Letter we present evidence to show that this criterion is almost satisfied for UAs near its antiferromagnetic ordering temperature. The critical scattering in UAs is anisotropic, exhibits a maximum at an incommensurate point in reciprocal space, and disappears when a superlattice peak appears at the commensurate wave vector. We analyze the critical behavior by developing a mean-field treatment of a Hamiltonian that includes strong cubic anisotropy.

The uranium monopnictides (all with the NaCl crystal structure) provide examples of a family of compounds with strong cubic anisotropy in the

