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k–q Functions and the Landau Theory of Second-Order Phase Transitions

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The use of k–q functions is introduced into the Landau theory of second order phase transitions. The expansion of an arbitrary density function in a crystal is given in terms of basis functions of irreducible representations of a space group which are linear combinations of k–q functions. This leads to a new condition on the irreducible representations which can be associated with second order phase transitions.

Nous introduisons les fonctions k–q dans la théorie de Landau de transitions de phase du second ordre. Le developpement d'une fonction quelquonque de densité dans un cristal s'exprime en fonctions de base des réprésentations irréductibles d'un groupe d'espace; ces fonctions de base étant des combinaisons linéaires de fonctions k–q. Ceci mène à une condition nouvelle sur les réprésentations irréductibles qui puissent être associées à une transition de phase du second ordre.

1. Introduction

In the Landau theory of second-order phase transitions in crystals [1], a density function $\varrho(\boldsymbol{r})$ which characterizes the crystal is expanded as

$$\varrho(\boldsymbol{r}) = \sum_{\boldsymbol{k}^*\alpha j} C_j^{\boldsymbol{k}^*\alpha} f_j^{\boldsymbol{k}^*\alpha}(\boldsymbol{r}). \tag{1}$$

The functions $f_j^{\boldsymbol{k}^*\alpha}(r)$, $j = 1, 2, \ldots, d$, for specific k^* and α, transform as a set of basis functions of the irreducible representation (irrep) $\Delta^{\boldsymbol{k}^*\alpha}$ of the symmetry space group F of the crystal before the phase transition. The sum in expansion (1) is over all irreps of the space group F and over a single set of basis functions of each irrep of F. The thermodynamic potential of the crystal is written as a function of pressure and temperature, and as a functional of $\varrho(\boldsymbol{r})$, and is expanded in a power series in terms of the coefficients $C_j^{\boldsymbol{k}^*\alpha}$. The values of the coefficients $C_j^{\boldsymbol{k}^*\alpha}$ which minimize the thermodynamic potential after the phase transition are determined, and then from (1) using these values of the coefficients one determines the symmetry of the crystal after the phase transition.

Implicit in expansion (1) is the existence for every space group F of a complete set of functions with the following two properties: 1. The complete set of functions can be partitioned into subsets, each subset of which consists of a set of functions which transform as a set of basis functions of an irrep of F. 2. There is one and only one subset of basis functions for each irrep of F. We will show in Section 2, by considering the so called k–q functions defined by Zak [2] that an expansion similar to (1) does exist. We show, however, that there exists in general more than a single subset of functions which transform as a set of basis functions of each irrep of F. Consequently, expansion (1) must be replaced

by an expansion of the form

$$\varrho(\boldsymbol{r}) = \sum_{\boldsymbol{k}^*\alpha jm} C_j^{\boldsymbol{k}^*\alpha m} f_j^{\boldsymbol{k}^*\alpha m}(\boldsymbol{r}) , \tag{2}$$

where there is an additional summation over an index m which indexes the subsets of functions which transform as sets of basis functions for a specific irrep $\Delta^{\boldsymbol{k}^*\alpha}$ of F.

In Section 3 we discuss the symmetry restrictions on the coefficients $C_j^{\boldsymbol{k}^*\alpha m}$ of expansion (2). We derive a new condition on these coefficients using properties of the $\boldsymbol{k}$–$\boldsymbol{q}$ functions and that the function $\varrho(\boldsymbol{r})$ is defined on a discrete set of points of the crystal. Lastly we discuss the relationship between this new condition and the condition on the coefficients derived by Kovalev [3].

2. Expansion of $\varrho(\boldsymbol{r})$

Let $(R \mid \boldsymbol{\tau}(R) + \boldsymbol{t})$ denote an element of a space group F. R is a proper or improper rotation matrix, $\boldsymbol{\tau}(R)$ a column matrix representing the non-primitive translation associated with R, and $\boldsymbol{t}$ a primitive translation. The set of all primitive translations $\boldsymbol{t}$ constitutes the subgroup T of F. One can associate with the subgroup T of F a group K of translations such that $\boldsymbol{t} \cdot \boldsymbol{K} = 2\pi n$ for all translations $\boldsymbol{t}$ of T and $\boldsymbol{K}$ of K where n is an integer dependent on $\boldsymbol{t}$ and $\boldsymbol{K}$. It has been shown that for a given space group F the eigenfunctions of the quantum mechanical operators of translations $\boldsymbol{t}$ of T in "direct space" and $\boldsymbol{K}$ of K in "reciprocal space" form a complete set of orthonormal functions. These eigenfunctions, called $\boldsymbol{k}$–$\boldsymbol{q}$ functions, are denoted by $\psi_{\boldsymbol{kq}}(\boldsymbol{r})$ where the indices $\boldsymbol{k}$ and $\boldsymbol{q}$ are, respectively, vectors in the first Brillouin zone and the first symmetric unit cell. The $\boldsymbol{k}$–$\boldsymbol{q}$ functions are [2]

$$\psi_{\boldsymbol{kq}}(\boldsymbol{r}) = \left(\frac{\tau}{(2\pi)^3}\right)^{1/2} \sum_{\boldsymbol{t}} \delta(\boldsymbol{r} - \boldsymbol{q} - \boldsymbol{t})\, \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{t}} , \tag{3}$$

where τ is the volume of the first symmetric unit cell and the sum is over all primitive translations $\boldsymbol{t}$ of the subgroup T of F.

Using the $\boldsymbol{k}$–$\boldsymbol{q}$ functions corresponding to a given space group F one can expand an arbitrary scalar function $\varrho(\boldsymbol{r})$ as follows:

$$\varrho(\boldsymbol{r}) = \sum_{\boldsymbol{kq}} C_{\boldsymbol{kq}} \psi_{\boldsymbol{kq}}(\boldsymbol{r}) , \tag{4}$$

where the sum is over all vectors $\boldsymbol{k}$ in the first Brillouin zone and vectors $\boldsymbol{q}$ in the first symmetric unit cell of the space group F.

We will now show that the complete set of $\boldsymbol{k}$–$\boldsymbol{q}$ functions can be partitioned into subsets of $\boldsymbol{k}$–$\boldsymbol{q}$ functions or linear combinations of subsets of $\boldsymbol{k}$–$\boldsymbol{q}$ functions which transform under elements of the space group F as sets of basis functions of irreps of F. To show this we first determine the transformational properties of the $\boldsymbol{k}$–$\boldsymbol{q}$ functions under elements $(R \mid \boldsymbol{\tau}(R) + \boldsymbol{t})$ of F:

$$(R \mid \boldsymbol{\tau}(R) + \boldsymbol{t})\, \psi_{\boldsymbol{kq}}(\boldsymbol{r}) = \psi_{\boldsymbol{kq}}((R \mid \boldsymbol{\tau}(R) + \boldsymbol{t})^{-1}\, \boldsymbol{r}) =$$

$$= \left(\frac{\tau}{(2\pi)^3}\right)^{1/2} \sum_{\boldsymbol{t}'} \delta(R^{-1}\boldsymbol{r} - R^{-1}\boldsymbol{\tau}(R) - R^{-1}\boldsymbol{t} - \boldsymbol{q} - \boldsymbol{t}')\, \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{t}'} . \tag{5}$$

The δ-function can be rewritten as $\delta(\boldsymbol{r} - \boldsymbol{\tau}(R) - \boldsymbol{t} - R\boldsymbol{q} - R\boldsymbol{t}')$ and replacing the sum over $\boldsymbol{t}'$ with a sum over $\boldsymbol{t}'' = R\boldsymbol{t}' - \boldsymbol{t}$ the right-hand side of (5) becomes

$$e^{iR\boldsymbol{k}\cdot\boldsymbol{t}}\left(\frac{\tau}{(2\pi)^3}\right)^{1/2}\sum_{\boldsymbol{t}'}\delta(\boldsymbol{r} - R\boldsymbol{q} - \boldsymbol{\tau}(R) - \boldsymbol{t}'')\, e^{iR\boldsymbol{k}\cdot\boldsymbol{t}''}.$$

We define the vector $\boldsymbol{k}'$, a vector in the first Brillouin zone, such that $\boldsymbol{k}' = R\boldsymbol{k} + \boldsymbol{K}(R, \boldsymbol{k})$, where $\boldsymbol{K}(R, \boldsymbol{k})$ is a translation belonging to K. In a like manner we define the vector $\boldsymbol{q}'$, a vector in the first symmetric unit cell, such that $\boldsymbol{q}' = R\boldsymbol{q} + \boldsymbol{\tau}(R) + \boldsymbol{t}(R, \boldsymbol{q})$ where $\boldsymbol{t}(R, \boldsymbol{q})$ is a primitive translation belonging to T. Replacing the sum over $\boldsymbol{t}''$ with the sum over $\boldsymbol{t}' = \boldsymbol{t}'' + \boldsymbol{t}(R, \boldsymbol{q})$, the right-hand side of equation (5) becomes

$$e^{i\boldsymbol{k}'\cdot(\boldsymbol{t}-\boldsymbol{t}(R,\boldsymbol{q}))}\left(\frac{\tau}{(2\pi)^3}\right)^{1/2}\sum_{\boldsymbol{t}'}\delta(\boldsymbol{r} - \boldsymbol{q}' - \boldsymbol{t}')\, e^{i\boldsymbol{k}'\cdot\boldsymbol{t}'}$$

and therefore

$$(R \mid \boldsymbol{\tau}(R) + \boldsymbol{t})\,\psi_{k\boldsymbol{q}}(\boldsymbol{r}) = e^{i\boldsymbol{k}'\cdot(\boldsymbol{t}-\boldsymbol{t}(R,\boldsymbol{q}))}\,\psi_{\boldsymbol{k}'\boldsymbol{q}'}(\boldsymbol{r})\,, \tag{6}$$

where $\boldsymbol{k}' = R\boldsymbol{k} + \boldsymbol{K}(R, \boldsymbol{k})$ and $\boldsymbol{q}' = R\boldsymbol{q} + \boldsymbol{\tau}(R) + \boldsymbol{t}(R, \boldsymbol{q})$.

We now define the subset $S_{k\boldsymbol{q}}$ of $\boldsymbol{k}$–$\boldsymbol{q}$ functions consisting of the function $\psi_{k\boldsymbol{q}}(\boldsymbol{r})$ for the specific values $\boldsymbol{k}$ and $\boldsymbol{q}$, and all distinct $\boldsymbol{k}$–$\boldsymbol{q}$ functions $\psi_{\boldsymbol{k}'\boldsymbol{q}'}(\boldsymbol{r})$ obtained using (6) by applying all elements of F to $\psi_{k\boldsymbol{q}}(\boldsymbol{r})$. The complete set of $\boldsymbol{k}$–$\boldsymbol{q}$ functions can be partitioned into subsets $S_{k\boldsymbol{q}}$. It follows from their definition that each subset $S_{k\boldsymbol{q}}$ consists of a set of $\boldsymbol{k}$–$\boldsymbol{q}$ functions which constitute a set of basis functions for a representation, possibly reducible, of the space group F. The representation $\Delta^{k\boldsymbol{q}}$ of F associated with each subset $S_{k\boldsymbol{q}}$ can be reduced into a direct sum of irreps $\Delta^{\boldsymbol{k}^*\alpha}$ of F. Let U denote the unitary matrix which reduces the representation $\Delta^{k\boldsymbol{q}}$, and $f_j^{\boldsymbol{k}^*\alpha}(\boldsymbol{r})$ the j-th basis function of a set of basis functions of the $\boldsymbol{k}^*\alpha$-th irrep of F contained in the reduced form of the representation $\Delta^{k\boldsymbol{q}}$ of F. These basis functions are linear combinations of the $\boldsymbol{k}$–$\boldsymbol{q}$ functions in $S_{k\boldsymbol{q}}$:

$$f_j^{\boldsymbol{k}^*\alpha n}(\boldsymbol{r}) = \sum_{\boldsymbol{k}'\boldsymbol{q}'} U_{(\boldsymbol{k}^*\alpha nj)(\boldsymbol{k}'\boldsymbol{q}')}\psi_{\boldsymbol{k}'\boldsymbol{q}'}(\boldsymbol{r})\,, \tag{7}$$

where the sum is over all pairs of indices $(\boldsymbol{k}'\boldsymbol{q}')$ of $\boldsymbol{k}$–$\boldsymbol{q}$ functions belonging to $S_{k\boldsymbol{q}}$, and the index $n = 1, 2, \ldots, d$ where d denotes the number of times the irrep $\Delta^{\boldsymbol{k}^*\alpha}$ is contained in the reduced form of $\Delta^{k\boldsymbol{q}}$. Since the $\boldsymbol{k}$–$\boldsymbol{q}$ functions are orthonormal and the matrix U unitary, the functions $f_j^{\boldsymbol{k}^*\alpha n}(\boldsymbol{r})$ are also orthonormal. One can also invert equation (7),

$$\psi_{\boldsymbol{k}'\boldsymbol{q}'}(\boldsymbol{r}) = \sum_{\boldsymbol{k}^*\alpha nj} U^{-1}_{(\boldsymbol{k}^*\alpha nj)(\boldsymbol{k}'\boldsymbol{q}')} f_j^{\boldsymbol{k}^*\alpha n}(\boldsymbol{r})\,, \tag{8}$$

where the sum is over all basis functions of all the irreps in the reduced form of the representation $\Delta_{k\boldsymbol{q}}$ of F.

The expansion of an arbitrary scalar function $\varrho(\boldsymbol{r})$ given in (4) can be rewritten then, using (8), as (2). Where the sum is, as we show below, over all irreps of the space group F and where there is an additional summation over an index m which indexes the linear independent sets of basis functions of each irrep of F.

To show that the sum in (2) is over all irreps of F we consider a set $S_{k\boldsymbol{q}}$ of $\boldsymbol{k}$–$\boldsymbol{q}$ functions where $\boldsymbol{q}$ is a general vector, i.e. no two vectors $\boldsymbol{q}' = R\boldsymbol{q} + \boldsymbol{\tau}(R) + \boldsymbol{t}(R, \boldsymbol{q})$ for all elements $(R \mid \boldsymbol{\tau}(R))$ of F are the same. This set of $\boldsymbol{k}$–$\boldsymbol{q}$ functions constitutes a set of basis functions for a reducible representation

of F, which when reduced is the direct sum of all irreps $\Delta^{k^*\alpha}$ of F, for this specific value of k, and where each irrep appears once. Considering a second set S_{kq_1} of k–q functions, where q_1 is also a general vector and such that $q_1 \neq q$, we conclude that each irrep of F appears more than once in the summation on the right-hand side of (2) and one necessarily must include an additional summation over an index which we have denoted by m.

We have therefore shown that there exists a complete set of orthonormal functions $f_j^{k^*\alpha m}(r)$ which are linear combinations of k–q functions (see equation (7)) such that subsets of functions $f_j^{k^*\alpha m}(r)$ for constant k, α, and m, constitute a set of basis functions for the $k^*\alpha$-th irrep of the space group F. An arbitrary scalar function can be expanded with respect to this set of functions and this expansion is given in (2).

3. Symmetry Conditions

In the Landau theory of second-order phase transitions symmetry conditions on the coefficients of expansion (2) following from the minimization of the thermodynamic potential have been derived and are as follows [1]:

1. Non-zero coefficients $C_j^{k^*\alpha m}$ are associated with a single irrep $\Delta^{k^*\alpha}$ of the space group F, and a single value of the index m, and this irreducible representation $\Delta^{k^*\alpha}$ is such that:

2. The symmetric cube $[\Delta^{k^*\alpha}]^3$ of the irrep $\Delta^{k^*\alpha}$ does not contain the identity irrep of F.

3. The anti-symmetric square $\{\Delta^{k^*\alpha}\}^2$ of the irrep $\Delta^{k^*\alpha}$ does not contain any irrep in common with the vector representation of F.

While conditions 1 and 2 are generally accepted, there has been extensive discussion in the literature on the validity of condition 3 [4 to 8].

The above conditions were derived on the basis of considering the minimization of the thermodynamic potential. We shall now derive an additional condition by taking into account that the function $\varrho(r)$ is defined on a discrete set of points of the crystal. The density function $\varrho(r)$ which we consider can be written as

$$\varrho(r) = \sum_i \varrho(r_i)\, \delta(r - r_i)\,, \tag{9}$$

where the sum is over a discrete set of points r_i of the crystal. The symmetry space group of this set of points is F. The positions r_i can also be denoted by $r_i = q_i + t$ where q_i is a vector in the first symmetric unit cell and t a primitive translation belonging to the subgroup T of F. Equation (9) can then be rewritten as

$$\varrho(r) = \sum_{q_i t} \varrho(q_i + t)\, \delta(r - q_i - t)\,, \tag{10}$$

where the sum is over all positions q_i in the first symmetric unit cell and over all primitive translations t of T.

From (3) we see that the k–q function $\psi_{kq}(r)$ contains the δ-function $\delta(r - q - t)$. Comparing (4) and (10) we conclude that the expansion of $\varrho(r)$ in terms of k–q functions is of the form

$$\varrho(r) = \sum_{kq_i} C_{kq_i} \psi_{kq_i}(r)\,, \tag{11}$$

where the sum is over all vectors k and over only those vectors q corresponding to the positions q_i, the positions in the first symmetric unit cell at which the function $\varrho(r)$ is defined. Consequently, the expansion given in (2) is of the form:

$$\varrho(r) = \sum_{k^* jm}{}' C_j^{k^*\alpha m} f_j^{k^*\alpha m}(r) , \tag{12}$$

where $\sum'$ denotes that the sum is over only those basis functions $f_j^{k^*\alpha m}(r)$ which are linear combinations of the k–q functions $\psi_{kq_i}(r)$ appearing in (11). Consequently we have an additional condition placed on the irrep $\Delta^{k^*\alpha}$ which satisfies conditions (1) to (3):

4. A set of basis functions of the irrep $\Delta^{k^*\alpha}$ can be formed out of linear combinations of k–q functions $\psi_{kq_i}(r)$ where q_i are position vectors at which the function $\varrho(r)$ is defined.

For example, consider a function $\varrho(r)$ defined at the positions $r_i = t$. The space group F is in this case a symmorphic space group. Equation (11) becomes

$$\varrho(r) = \sum_{k} C_{k0}\psi_{k0}(r) .$$

A set of k–q functions S_{k0} consists of the functions $\psi_{k0}(r)$, $\psi_{k_2 0}(r)$, ... , $\psi_{k_n 0}(r)$ where the k-vectors k, k_2, ... k_n constitute the "star" k^* of the vector k. The set of functions S_{k0} constitutes a set of basis functions for the irrep Δ^{k^*1} of F, where $\alpha = 1$ denotes the identity irrep of the little group of the vector k. Consequently, expansion (12) is of the form

$$\varrho(r) = \sum_{k^* j} C_j^{k^*1} f_j^{k^*1}(r) ,$$

where the sum is over all irreps Δ^{k^*1} of F, each one once, and over no other irreps of F.

One can also determine from (12) in phase transitions associated with specific irreps of F that the function $\varrho(r)$ below the phase transition may necessarily vanish on a subset of points on which it is defined.

As an example of this consider the function $\varrho(r)$ defined on a set of points invariant under the space group $F = C_{2h}^1$ and where $q_1 = (0, 0, 0)$, $q_2 = (0, y, 0)$, and $q_3 = (0, -y, 0)$. For a specific vector k there are two sets of k–q functions S_{kq_1} and S_{kq_2} where the first set consists of k–q functions with $q = q_1$ and the second set with $q = q_2$ and q_3. The set of functions S_{kq_1} is a set of basis functions of the irrep Δ^{k^*1} of F, the set of functions S_{kq_2} of a representation of F which can be reduced to the direct sum of the irreps Δ^{k^*1} and Δ^{k^*4}, Δ^{k^*1} and Δ^{k^*2}, or Δ^{k^*1} if the little group of the vector k is, respectively, the point group C_{2h}, C_2, or C_s and C_1. The expansion of $\varrho(r)$ is therefore of the form

$$\varrho(r) = \sum_{m=1}^{2} \sum_{k^* j} C_j^{k^*1m} h_j^{k^*1m}(r) + \sum_{k^* j}^{C_{2h}} C_j^{k^*4} g_j^{k^*4}(r) + \sum_{k^* j}^{C_s} C_j^{k^*2} g_j^{k^*2}(r) ,$$

where

$$h_j^{k^*1m}(r) = B_{m1} f_j^{k^*1}(r) + B_{m2} g_j^{k^*1}(r)$$

and B is an arbitrary two-dimensional unitary matrix. $f_j^{k^*\alpha}(r)$ and $g_j^{k^*\alpha}(r)$ are linear combinations of k–q functions belonging to the sets S_{kq_1} and S_{kq_2}, respectively, and $\sum_{k^*}^{A}$ denotes a sum over all stars k^* of a vector k, where the little group of the vector k is the point group A.

If the irrep associated with the phase transition is Δ^{k^*2} or Δ^{k^*4}, or the appropriate value of k, then since the functions $g_j^{k^*2}(r)$ and $g_j^{k^*4}(r)$ are linear com-

binations of $\boldsymbol{kq}$ functions only of the set $S_{\boldsymbol{kq}_1}$, one concludes that below the phase transition $\varrho(\boldsymbol{r}) = 0$ for $\boldsymbol{r} = \boldsymbol{q}_1 + \boldsymbol{t}$, and that the non-zero values of $\varrho(\boldsymbol{r})$ are only at positions $\boldsymbol{r} = \boldsymbol{q}_2 + \boldsymbol{t}$ and $\boldsymbol{r} = \boldsymbol{q}_3 + \boldsymbol{t}$.

If the irrep associated with the phase transition is Δ^{k^*1} then the function $\varrho(\boldsymbol{r})$ is expanded in terms of the functions $h_j^{k^*1m}(\boldsymbol{r})$ for specific m. The functions $h_j^{k^*1m}(\boldsymbol{r})$ are linear combinations of functions $f_j^{k^*1}(\boldsymbol{r})$ and $g_j^{k^*1}(\boldsymbol{r})$. The exact form of the linear combinations is not unique but dependent on the arbitrary unitary matrix B. Because of this arbitrariness, below the phase transition, the function $\varrho(\boldsymbol{r})$ may be 1. non-zero only at $\boldsymbol{r} = \boldsymbol{q}_1 + \boldsymbol{t}$, 2. non-zero only at $\boldsymbol{r} = \boldsymbol{q}_2 + \boldsymbol{t}$ and $\boldsymbol{r} = \boldsymbol{q}_3 + \boldsymbol{t}$, or 3. non-zero at all positions $\boldsymbol{q}_i + \boldsymbol{t}$.

The fourth condition on the irreps $\Delta^{k^*\alpha}$ derived above is related to a condition on the irreps derived by Kovalev [3]. Consider the function $\varrho(\boldsymbol{r})$ defined on the discrete set of points $\boldsymbol{q}_i + \boldsymbol{t}$ which is invariant under the symmetry space group F. Define the group of the vector $\boldsymbol{q}_i + \boldsymbol{t}$, $\mathrm{F}_{\boldsymbol{q}_i+\boldsymbol{t}}$, as the subgroup of all elements of F such that

$$F(\boldsymbol{q}_i + \boldsymbol{t}) = \boldsymbol{q}_i + \boldsymbol{t} .$$

Applying an element g of $\mathrm{F}_{\boldsymbol{q}_i+\boldsymbol{t}}$ to $\varrho(\boldsymbol{r})$, summing over all elements of $\mathrm{F}_{\boldsymbol{q}_i+\boldsymbol{t}}$, and taking $\boldsymbol{r} = \boldsymbol{q}_i + \boldsymbol{t}$ one has

$$\varrho(\boldsymbol{q}_i + \boldsymbol{t}) = \sum_{jl} C_j^{k^*\alpha m} f_l^{k^*\alpha m}(\boldsymbol{q}_i + \boldsymbol{t}) \frac{1}{N} \sum_{g \in F_{\boldsymbol{q}_i+\boldsymbol{t}}} \Delta^{k^*\alpha}(g)_{lj} ,$$

where N is the order of the group $\mathrm{F}_{\boldsymbol{q}_i+\boldsymbol{t}}$. Kovalev's condition, a necessary condition that the function $\varrho(\boldsymbol{r})$ which is defined at positions $\boldsymbol{q}_i + \boldsymbol{t}$ is not identically zero, follows immediately ($\chi^{k^*\alpha}(g)$ denotes the character of $\Delta^{k^*\alpha}(g)$): The irrep $\Delta^{k^*\alpha}$ is such that

$$\sum_{g \in F_{\boldsymbol{q}_i+\boldsymbol{t}}} \chi^{k^*\alpha}(g) \neq 0 \tag{13}$$

for at least one position vector $\boldsymbol{q}_i + \boldsymbol{t}$. If (13) equals zero for all vectors $\boldsymbol{q}_i + \boldsymbol{t}$, then the function $\varrho(\boldsymbol{r})$, defined at the positions $\boldsymbol{q}_i + \boldsymbol{t}$, is identically zero for all values of the coefficients $C_j^{k^*\alpha m}$. Consequently, there will be no phase transition associated with the irrep $\Delta^{k^*\alpha}$.

Condition (4) derived above replaces any need for the Kovalev condition. As we will now show, the function $\varrho(\boldsymbol{r})$ given in (12), for a given irrep, is identically zero if and only if the coefficients $C_j^{k^*m}$ are identically zero. Using (7) we have

$$\sum_{\boldsymbol{q}_i \boldsymbol{t}} |\varrho(\boldsymbol{q}_i + \boldsymbol{t})|^2 = \sum_{js} C_j^{k^*\alpha m} C_s^{k^*\alpha m^*} \times$$

$$\times \sum_{\substack{(\boldsymbol{k}_m \boldsymbol{q}_m) \\ (\boldsymbol{k}_p \boldsymbol{q}_p)}} U_{(\boldsymbol{k}^*\alpha m j)(\boldsymbol{k}_m \boldsymbol{q}_m)} U^*_{(\boldsymbol{k}^*\alpha m s)(\boldsymbol{k}_p \boldsymbol{q}_p)} \sum_{\boldsymbol{q}_i \boldsymbol{t}} \psi_{\boldsymbol{k}_m \boldsymbol{q}_m}(\boldsymbol{q}_i + \boldsymbol{t}) \psi^*_{\boldsymbol{k}_p \boldsymbol{q}_p}(\boldsymbol{q}_i + \boldsymbol{t}) .$$

The last summation can be replaced by the integral

$$\int \psi_{\boldsymbol{k}_m \boldsymbol{q}_m}(\boldsymbol{r}) \psi^*_{\boldsymbol{k}_p \boldsymbol{q}_p}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

since the functions $f_j^{k^*\alpha m}(\boldsymbol{r})$ are linear combinations of $\boldsymbol{k}$–$\boldsymbol{q}$ functions $\psi_{\boldsymbol{k}\boldsymbol{q}}(\boldsymbol{r})$ where $\boldsymbol{q}$ is some value $\boldsymbol{q}_i$. From the orthonormality of $\boldsymbol{k}$–$\boldsymbol{q}$ functions, and of rows of the matrix U it follows that

$$\sum_{\boldsymbol{q}_i \boldsymbol{t}} |\varrho(\boldsymbol{q}_i + \boldsymbol{t})|^2 = \sum_j |C_j^{k^*m}|^2$$

and that the function $\varrho(\boldsymbol{r})$ defined on the points $\boldsymbol{q}_i + \boldsymbol{t}$ is identically zero if and only if all coefficients vanish.

Condition (4) places a condition on the irreps of F which can be associated with a second-order phase transition which gives rise to a non-identically zero density function at positions $\boldsymbol{q}_i + \boldsymbol{t}$ of a crystal. Moreso, one can directly determine from equations (11) and (2), using the transformational properties (equation (6)) of the $\boldsymbol{k}$–$\boldsymbol{q}$ functions $\psi_{\boldsymbol{kq}}(\boldsymbol{r})$ where $\boldsymbol{q} = \boldsymbol{q}_i$, which of the irreps of F satisfy this condition.

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