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Theory of Crystal Anisotropy Based on a Non-Analytic Free Energy

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A non-analytic free energy alters many conclusions conscerning the crystal anisotropy. Especially most of the "forbidden effects" (for example, piezoelectricity in crystal of the point group 432) are liberated and regarded only as "improbable effects". Under a certain simple assumption, all such effects can be classified into several classes according to their "improbability indices".

1. Introduction

The traditional crystallography is based on the assumption that the free energy of crystal can be expanded into power series of such quantities as electric polarization or mechanical strain. This assumption imposes a rather severe restriction on the occurrence of crystal anisotropy[1]. Many "forbidden effects" result not from crystal symmetry but the analytic property of the free energy. The present paper intends to liberate such false "forbidden effects" and regard them as "improbable effects".

Consider a crystal whose point group is G_0 and expand its free energy by a set of parameters (c_1, c_2, $\cdots$, c_d) which are components of a d-dimensional irreducible representation Γ of G_0. We will use the notation

$$\eta^2 = \sum_i^d c_i^2, \qquad c_i = \eta \gamma_i,$$

(1)

where η takes only plus sign. The free energy F of the crystal is written in the traditional theory[2] as follows.

$$F = F_0 + \eta^2 A + \eta^3 \sum_\alpha B_\alpha f_\alpha^3 (\gamma_i) + \eta^4 \sum_\alpha C_\alpha f_\alpha^4 (\gamma_i) + \cdots,$$

(2)

where $f^{(3)}$, $f^{(4)}$, $\cdots$ are invariants of third, fourth, etc. order constructed from the γ_i. Many "forbidden effects" arise from the restriction that $f^{(n)}$ can not appear in the coefficient of η^m when n is larger than m.

Power series expansion, however, is not always possible in the vicinity of the critical point of phase transition[3]. Therefore the restriction stated above seems to lose its meaning. We should construct a more general theory by relaxing the restriction[1] as follows.

$$F = F_0 + \eta^2 \sum_{k=0}^{\infty} \sum_\alpha A_\alpha f_\alpha^{(2k)} (\gamma_i) + \eta^3 \sum_{k=1}^{\infty} \sum_\alpha B_\alpha f_\alpha^{(2k+1)}(\gamma_i) + \cdots,$$

(3)

Our new free energy has all the anisotropic terms which do not violate symmetry even in the coefficient of η^2. For example the initial dielectric constant of cubic

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crystal is no longer isotropic.

Such extraordinary anisotropy, however, has not been observed yet, so that it may be an improbable effect though not forbidden in principle. Let us consider how this improbability can be indicated.

2.   Improbability Index of Phase Transition

The concept of improbability of second-order phase transition is useful in the discussion below. The lower symmetry phase G induced by Γ is determined by the minimum of the coefficient of η^2. Our principle to estimate improbability is "the simpler, the more probable". A simple function is a more probable candidate of the coefficient of η^2 than a complex one. Then a transition determined by a simpler function is a more probable transition. What is a simple function?

As an example of transition parameter, let us take a T_{1u} representation of the point group m3m. In order to investigate the angular dependence of the coefficient of η^2, we should imagine a unit sphere in the representation space and draw contours of the coefficient of η^2 on the surface. Since the surface is divided into 48 equivalent areas as in Fig. 1., the pattern in one domain (for instance, the dotted area) is sufficient enough to determine those in others. Such a domain will be called a basic domain.[4]

The simplest function is constant everywhere in the domain. (If Γ is one-dimensional, this is the only case.)

The next simplest pattern may be expressed by a monotonic function which is approximately linear. A linear function has its minimum at one of the three corners of the triangle.

The third simplest function may have the minimum at an edge of the domain. A function which has its minimum in the interior of the triangle (at a general position) can be regarded as far more complex.

Let us assign improbability index 1, 2, and 3 to the transition determined by corners, edges, and general positions of the basic domain respectively. The transition determined by a constant function is possible only when Γ is one-dimensional and its improbability index is defined as 0.

The position in the domain corresponds to the degree of freedom of the transistion parameter in the lower phase. Therefore, if Γ is not one-dimensional, improbability index t is also defined as follows.[1]

$$t = \frac{1}{g_0} \sum_{a \in G_0} \theta_1^G(a) \, \overline{\theta_\Gamma(a)}, \tag{4}$$

where g_0 is the order of G_0, $\overline{\theta_\Gamma(a)}$ is the complex conjugate of the character of Γ, and

$$\theta_1^G(a) = \frac{1}{g} \sum_{x \in G_0} \theta_1(x \, a \, x^{-1}), \tag{5}$$

where g is the order of G, x and a are an element of G_0 and G respectively, and

$$\theta_1(x\,a\,x^{-1}) \begin{cases} = 1 \ (\textit{if } x\,a\,x^{-1} \textit{ is contained in } G). \\ = 0 \ (\text{if } x\,a\,x^{-1} \text{ is not contained in } G). \end{cases} \tag{6}$$
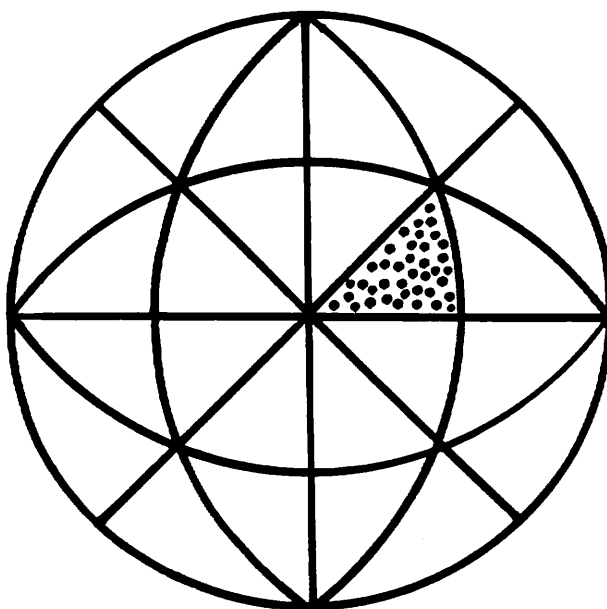

Fig. 1. Stereogram of unit sphere in representation space of T_{1u} of point group m3m. The surface of the sphere is divided into 48 equivalent "basic domains".

References

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