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Generalized Bessel Functions in Incommensurate Structure Analysis

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Dedicated to Professor Pieter Maarten de Wolff on the occasion of the 21st anniversary of quasicrystallography

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Abstract

The analysis of incommensurate structures is computationally more difficult than that of normal ones. This is mainly a result of the structure-factor expression, which involves numerical integrations or infinite series of Bessel functions. Both approaches have been implemented in existing computer programs. Compact analytical expressions are known for special cases only. Recently, a new theory of generalized Bessel functions has been developed. The number of theoretical results and applications is increasing rapidly. Numerical properties and algorithms are being studied. A possible application of the generalized Bessel functions for incommensurate structure analysis is proposed. These functions can be used to derive analytical expressions for structure factors and all partial derivatives for a wide class of incommensurate crystals. The existing programs can be improved by taking into account some interesting numerical and analytical properties of these new functions, like recurrence relations, analytical expressions for derivatives, generating functions and integral representations. A new class of special functions, suitable for dealing with incommensurate structures in a more analytical way, is emerging.

1. Introduction

We must notice, in that direction, that it is important for him who wants to discover not to confine himself to one chapter of science, but to keep in touch with various others.

(Jacques Hadamard, 1945)

Quasiperiodic structure analysis has become a reasonably well established branch of crystallography. Quasicrystallography has celebrated its 20th anniversary (see Janssen, 1992). About 20 years ago, during the 9th International Crystallography Conference in Kyoto, Japan, two contributions of prime importance were presented. In the first, de Wolff & van Aalst (1972) described the incommensurate (IC) phase of Na_2CO_3 using a higher-dimensional space group. In the same session, Janner (1972) presented the symmetry analysis of a vibrating crystal, using entirely the same formalism. This was the starting point for this new and rapidly developing field.

The superspace-group theory, developed by de Wolff, Janssen & Janner (1981) has been extended and is now most frequently used in the analysis of all types of quasiperiodic structures: modulated (both incommensurate and commensurate) phases, composite (or intergrowth) materials and quasicrystals. This approach is well suited for diffraction-pattern analysis and structure refinement and is almost exclusively used in the corresponding computing procedures.

The first working example of IC-structure refinement was reported by van Aalst, den Hollander, Peterse & de Wolff (1976). The crucial step in this direction was made earlier by de Wolff (1974). He derived the structure-factor (SF) formula for an IC structure with displacive and/or occupational modulation within the framework of superspace-group theory. This formula, with minor modifications, is the basis for the analysis of all other IC structures.

At this time, it became clear that IC-structure refinement was a computationally much more demanding task compared with ordinary structure refinement. The main reason was that, excluding special cases, the SF could not be evaluated analytically but only by numerical integration. It appears that this was common belief rather than a mathematical proof.

Nevertheless, many IC structures have been successfully refined using algorithms based on de Wolff's formula. Numerical difficulties were, at least partially, overcome and several program systems to refine IC structures are currently available. This field has developed to such an extent that standardization is inevitable.

In this paper, we once more reconsider de Wolff's formula and demonstrate that the crucial part of his expression is related to some open problems in the

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theory of special functions. It is shown that, on the basis of some recent advances in the generalization of Bessel functions (BFs), the SF for a one-dimensional IC structure can be evaluated analytically.

2. Generalized Bessel functions

As is well known, BFs are widely used in crystallographic computing. They represent an important analytical tool in crystallographic statistics and direct-methods theory (see *e.g.* Giacovazzo, 1980). In IC-structure analysis, BFs are used to derive SF formulas.

Here, a short overview of the so-called generalized Bessel functions (GBFs) is given. We follow the development of the theory formulated by Dattoli, Giannessi, Mezi & Torre (1990), and further developed by Dattoli, Torre, Lorenzutta, Maino & Chiccoli (1991), Dattoli, Chiccoli *et al.* (1991), Dattoli, Chiccoli *et al.* (1992) and Dattoli, Mari *et al.* (1992). Up to now, more than ten articles and preprints have been made available.

GBFs can be thought of as a rather large set of functions sharing the same basic properties like recurrences, addition and multiplication theorems, expressions for derivatives *etc.* as ordinary BFs. One of the first functions of this type was introduced by Reiss (1980) to solve analytically some relativistic scattering problems. He considered the following function:

$$J_n(z_1, z_2) = \sum_{l=-\infty}^{\infty} J_{n-2l}(z_1)J_l(z_2), \qquad (2.1)$$

where $J_n(z)$ is the ordinary cylinder BF of the first kind, and proposed that it be called a two-variable GBF. Both variables z_1 and z_2 are, in general, complex. Similar functions can be defined by replacing one or both functions in the products by $I_n(z)$, a modified cylinder BF of the first kind.

Although the above function is defined as a sum of products of ordinary BFs, it shares with them many well known properties. For example, all the partial derivatives are expressed by functions of the same kind:

$$\frac{\partial J_n}{\partial z_k} = \tfrac{1}{2}(J_{n-k} - J_{n+k}), \quad k = 1, 2. \qquad (2.2)$$

Also, the following recurrence relation holds:

$$2nJ_n = \sum_{k=1}^{2} kz_k(J_{n-k} + J_{n+k}). \qquad (2.3)$$

The well known sum rules can be generalized. For example,

$$\sum_{n=-\infty}^{\infty} J_n = \sum_{n=-\infty}^{\infty} J_n^2 = 1. \qquad (2.4)$$

Finally, the integral representation is expressed thus:

$$J_n(z_1,z_2) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \mathrm{d}\varphi \times \exp[i(z_1\sin\varphi + z_2\sin 2\varphi - n\varphi)]. \qquad (2.5)$$

Many more interesting properties of this function and other GBFs have been derived so far. Only some selected results are presented here.

To follow the convention used in the original papers mentioned above, no new symbols are introduced for the new functions. Instead of a definition, variables and other relevant parameters will be indicated. This is because of the number of new GBFs, which is potentially unlimited.

To better understand why this function can be called a GBF, it is instructive to compare it with the Neumann addition theorem (see *e.g.* Watson, 1958) for ordinary BFs:

$$J_n(z_1 + z_2) = \sum_{l=-\infty}^{\infty} J_{n-l}(z_1)J_l(z_2). \qquad (2.6)$$

The new function can be considered as a first step beyond this addition formula. This is because of the charactistic 'jump' in the summation indices, which in turn comes from the anharmonicity apparent in the integral representation.

An important step towards a consistent theory of GBFs (see Dattoli, Giannessi, Mezi & Torre, 1990) was the introduction of the more general definition

$$J_n(z_1,z_2; t) = \sum_{l=-\infty}^{\infty} t^l J_{n-2l}(z_1)J_l(z_2). \qquad (2.7)$$

This function, called a two-variable one-parameter GBF, has properties similar to the previous one. Both the variables z_1 and z_2 and the parameter t are again complex in general. Expressions can be derived for all partial derivatives (including those with respect to t) as

$$\frac{\partial J_n}{\partial z_k} = (1/2)(t^{k-1}J_{n-k} - t^{1-k}J_{n+k}), \qquad (2.8)$$

$$\frac{\partial J_n}{\partial t} = (z_2/2)(J_{n-2} - J_{n+2}/t^2) \qquad (2.9)$$

and the following recurrence relation:

$$2nJ_n = \sum_{k=1}^{2} kz_k(t^{k-1}J_{n-k} + t^{1-k}J_{n+k}). \qquad (2.10)$$

The integral representation of this function is

$$J_n[z_1,z_2; \exp(i\theta)] = \frac{1}{2\pi}\int_{-\pi}^{\pi} \mathrm{d}\varphi \exp[i(z_1\sin\varphi + z_2\sin(\theta + 2\varphi) - n\varphi)]. \qquad (2.11)$$

Here, the second harmonic is shifted with respect to the first.

As before, this new function can be considered as a step beyond the second addition theorem, *i.e.* the

Graf formula:

$$s^n J_n(z) = \sum_{l=-\infty}^{\infty} t^l J_{n-l}(z_1) J_l(z_2), \tag{2.12}$$

where

$$z = [z_1^2 + z_2^2 + z_1 z_2 (t^2 + 1)/t]^{1/2},$$
$$s = [(z_1 + z_2 t)/(z_1 + z_2/t)]^{1/2}.$$

The new GBFs can be defined in many different ways. For example, one can modify the indices, thus adding much more flexibility. Some selected examples of GBFs studied in detail so far are:

$${}^{(s/q)}J_{n,m}(z_1,z_2) = \sum_{l=-\infty}^{\infty} J_{n-sl}(z_1) J_{m+ql}(z_2), \tag{2.13}$$

$${}^{(s/q)}J_{n,m}(z_1,z_2;t) = \sum_{l=-\infty}^{\infty} t^l J_{n-sl}(z_1) J_{m+ql}(z_2), \tag{2.14}$$

$${}^{(m)}J_n(z_1,z_2;t) = \sum_{l=-\infty}^{\infty} t^l J_{n-ml}(z_1) J_l(z_2). \tag{2.15}$$

Recently, Dattoli, Chiccoli *et al.* (1992) pointed out yet another mathematical origin of GBFs. They show that the well known Kelvin functions can be interpreted as a precursors of GBFs.

Let us consider two relations:

$$\mathrm{ber}_n(\bar{z}) = \sum_{l=-\infty}^{\infty} (-1)^{n+l} J_{n+2l}(z) I_{2l}(z), \tag{2.16}$$

$$\mathrm{bei}_n(\bar{z}) = \sum_{l=-\infty}^{\infty} (-1)^{n+l} J_{n+2l+1}(z) I_{2l+1}(z), \tag{2.17}$$

where $\bar{z} = z2^{1/2}$. It is easy to see that both Kelvin functions are special cases of GBFs defined above:

$$\mathrm{ber}_n(\bar{z}) = (-1)^{n(-2/2)} J_{n,0}(z, iz), \tag{2.18}$$

$$\mathrm{bei}_n(\bar{z}) = i(-1)^{n+1(-2/2)} J_{n+1,1}(z, iz). \tag{2.19}$$

Furthermore, one can also define an important new class of GBFs by replacing one ordinary BF by a modified one:

$${}^{(m)}\tilde{J}_n(z_1,z_2;t) = \sum_{l=-\infty}^{\infty} t^l J_{n-ml}(z_1) I_l(z_2), \tag{2.20}$$

and establish that

$$\mathrm{ber}_n(\bar{z}) = (-1)^n \,\Re[{}^{(-1)}\tilde{J}_n(z,z;i)], \tag{2.21}$$

$$\mathrm{bei}_n(\bar{z}) = (-1)^n \,\Im[{}^{(-1)}\tilde{J}_n(z,z;i)], \tag{2.22}$$

where $\Re$ and $\Im$ mean the real and imaginary parts, respectively.

We would like to mention here that the GBF defined above appears also in the SF expression for IC structures (Paciorek & Kucharczyk, 1985) if the modulation-function amplitude and phase fluctuations are explicitly taken into account, a step beyond de Wolff's original formula.

It is possible to construct GBFs with more variables and parameters. For example, one can define the following three-variable two-parameter GBF starting from the previously defined two-variable one-parameter one:

$$J_n(z_1,z_2,z_3;t_1t_2) = \sum_{l=-\infty}^{\infty} t_2^l J_{n-3l}(z_1,z_2;t_1) J_l(z_3). \tag{2.23}$$

Further extensions are illustrated by the following two examples:

$$J_n(\{z\}_M) = \sum_{l=-\infty}^{\infty} J_l(z_M) J_{n-Ml}(\{z\}_{M-1}), \tag{2.24}$$

$$J_n(\{z\}_M;\{t\}_{M-1}) = \sum_{l=-\infty}^{\infty} [t_{M-1}^l J_l(z_M) \times J_{n-Ml}(\{z\}_{M-1};\{t\}_{M-2})], \tag{2.25}$$

where the following short notation was introduced:

$$\{z\}_M \equiv (z_1, \ldots, x_M),$$
$$\{t\}_M \equiv (t_1, \ldots, t_M).$$

With similar definitions for modified GBFs, the following generalized Jacobi–Anger expansions can be derived:

$$\sum_{n=-\infty}^{\infty} \exp(in\theta) J_n(\{z\}_M) = \exp\left(\sum_{k=1}^{M} iz_k \sin k\theta\right), \tag{2.26}$$

$$\sum_{n=-\infty}^{\infty} \exp(in\theta) I_n(\{z\}_M) = \exp\left(\sum_{k=1}^{M} z_k \cos k\theta\right), \tag{2.27}$$

It is now clear that these new functions are perfectly suited to deal with anharmonic IC structures, replacing the ordinary BFs used so far. It is the main purpose of this study to demonstrate this.

3. Generalized Jacobi–Anger expansion

The theory of GBFs has become a rapidly developing new field of mathematical analysis. Not only do they provide numerous new useful analytical expressions but, which seems to be equally important, this theory provides many new analytical techniques to tackle various computing problems. The development is strongly stimulated by physical applications. This means that some GBFs are studied in detail, whereas others are only briefly mentioned. For example, the function $J_n(z_1,z_2;i)$ is a solution of a Schrödinger-type equation and was studied more deeply than the others.

Within this theory, it is possible to construct a suitable GBF for a particular application, following a variety of examples published so far. Such an approach is adopted here to construct a GBF suitable to evaluate analytically the SF for an anharmonic IC structure.

Let us consider the following truncated trigonometric series with complex coefficients:

$$\chi_N = \sum_{k=1}^{N} (z_k \sin k\varphi z_k \cos k\varphi). \quad (3.1)$$

Our first objective is to construct the following series expansion:

$$\exp(i\chi_N) = \sum_{n=-\infty}^{\infty} \nearrow_n(\{Z,z\}_N) \exp(in\varphi), \quad (3.2)$$

where the following notation is introduced:

$$\{Z,z\}_N = (Z_1,z_1, \ldots, Z_N,z_N). \quad (3.3)$$

Anticipating an application of the Graf theorem (see Watson, 1958), let us define the following quantities:

$$\varpi_k = (Z_k^2 + z_k^2)^{1/2}, \quad (3.4)$$

$$\Theta_k = (Z_k + iz_k)/\varpi_k, \quad (3.5)$$

where $k = 1, \ldots, N$.

The common approach is to use the following infinite sum of products involving ordinary BFs:

$$\exp(i\chi_N) = \prod_{k=1}^{N} P_k(Z_k,z_k), \quad (3.6)$$

$$P_k(Z_k,z_k) = \sum_{n=-\infty}^{\infty} J_n(\varpi_k)\Theta_k^n \exp(ikn\varphi). \quad (3.7)$$

This approach to the analysis of anharmonic IC structures has been developed by Petriček, Coppens & Becker (1985). An elaborate algorithm to evaluate this expression numerically was proposed by Petriček, Malý & Císařová (1991) and an extension to a higher-dimensional IC structure was given by Petriček & Coppens (1988).

In the harmonic case ($N = 1$), the result is the familiar Jacobi–Anger expansion with the coefficients

$$\nearrow_n(Z_1,z_1) = J_n(\varpi_1)\Theta_1^n. \quad (3.8)$$

Because both even and odd terms are included in the trigonometric series, this coefficient is not just the BF, but the BF multiplied by a complex number to the power equal to its order. This is quite frequent in many other applications. Furthermore, in our case, it is more convenient to consider $\nearrow_n$ as a function of Z_1 and z_1 rather than as a function of ϖ_1 and Θ_1.

Let us consider the case where $N = 2$. Using the GBF defined by (2.7) in the previous section, the following expansion coefficients can be deduced:

$$\nearrow_n(\{Z,z\}_2) = J_n(\varpi_1,\varpi_2;\Theta_2/\Theta_1^2)\Theta_1^n. \quad (3.9)$$

The properties of this function have been studied in detail owing to its many physical applications.

The crucial observation is that this extension is a first step of the following recurrence relation:

$$\nearrow_n(\{Z,z\}_N) = \sum_{l=-\infty}^{\infty} [\nearrow_l(Z_N,z_N) \nearrow_{n-Nl}(\{Z,z\}_{N-1})]. \quad (3.10)$$

Thus, the suitable GBF can be constructed for an arbitrary finite value of N.

The partial derivatives can be derived and are expressed by the same type of functions as

$$\frac{\partial \nearrow_n}{\partial Z_k} = (1/2)(\nearrow_{n-k} - \nearrow_{n+k}), \quad (3.11)$$

$$\frac{\partial \nearrow_n}{\partial z_k} = (i/2)(\nearrow_{n-k} - \nearrow_{n+k}), \quad (3.12)$$

where $k = 1, \ldots, N$ and the following recurrence relation holds:

$$2n \nearrow_n = \sum_{k=1}^{N} k(Z_k^+ \nearrow_{n-k} + Z_k^- \nearrow_{n+k}), \quad (3.13)$$

$$Z_k^{\pm} = Z_k \pm iz_k. \quad (3.14)$$

For the derivation, the following identities were used:

$$\Theta_k^{-1} = \left\{\frac{Z_k - iz_k}{Z_k + iz_k}\right\}^{1/2} = \frac{Z_k - iz_k}{\varpi_k}, \quad (3.15)$$

$$\frac{\partial \varpi_k}{\partial Z_k} = \frac{Z_k}{\varpi_k}, \quad \frac{\partial \Theta_k}{\partial Z_k} = -iz_k\frac{\Theta_k}{\varpi_k^2}, \quad (3.16)$$

$$\frac{\partial \varpi_k}{\partial z_k} = \frac{z_k}{\varpi_k}, \quad \frac{\partial \Theta_k}{\partial z_k} = iZ_k\frac{\Theta_k}{\varpi_k^2}, \quad (3.17)$$

where $k = 1, \ldots, N$.

For other applications, not excluding crystallographic ones, it may be more convenient to consider $\nearrow_n$ as a function of the ϖ_k and Θ_k variables. In that case, the partial derivatives are

$$\frac{\partial \nearrow_n}{\partial \varpi_k} = (\Theta_k/2)(\nearrow_{n-k} - \nearrow_{n+k}/\Theta_k^2), \quad (3.18)$$

$$\frac{\partial \nearrow_n}{\partial \Theta_k} = (\varpi_k/2)(\nearrow_{n-k} + \nearrow_{n+k}/\Theta_k^2), \quad (3.19)$$

where $k = 1, \ldots, N$ and the recurrence relation reads

$$2n \nearrow_n = \sum_{k=1}^{N} k\varpi_k(\Theta_k \nearrow_{n-k} + \nearrow_{n+k}/\Theta_k). \quad (3.20)$$

Finally, the following integral representation can be derived:

$$\nearrow_n(\{Z,z\}_N) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\varphi \exp(i\chi_N - in\varphi). \quad (3.21)$$

This type of integral appears in the general SF formula for any one-dimensional IC structure. It can thus be interpreted as an integral representation of a new special function, which can be called an N-variable N-parameter GBF.

In IC-structure refinement, this integral has to be evaluated numerically for an anharmonic structure. We are aware (Maino, 1993) that research is in progress on algorithms to evaluate GBFs. Their availability will eliminate the need for time-consuming numerical integration. Existing algo-

rithms can be improved by taking into account some analytical properties of these functions, especially the expressions for partial derivatives.

4. Modulation functions

The characteristic feature of any IC structure is the presence of periodic distortions, called modulation functions (MFs), which affect virtually every parameter used in the conventional structure description.

Let us consider a parameter p of the atom μ. In an unmodulated structure, the value of this parameter is $\bar{p}^\mu$. If this parameter is affected by a modulation, a real-valued periodic function is added to it:

$$p^\mu(\bar{x}_4) = \bar{p}^\mu + \tilde{p}^\mu(\bar{x}_4), \tag{4.1}$$

where $\bar{x}_4$ is the so-called internal coordinate. The period of this function is unity:

$$\tilde{p}^\mu(\bar{x}_4 + 1) = \tilde{p}^\mu(\bar{x}_4) \tag{4.2}$$

and, in most cases, following de Wolff's original assumption, their average value over the whole period vanishes:

$$\int_0^1 \mathrm{d}\bar{x}_4 \tilde{p}^\mu(\bar{x}_4) \equiv \langle \tilde{p}^\mu \rangle = 0. \tag{4.3}$$

A simplified notation for integration over the internal coordinate is also introduced.

MFs are represented by truncated Fourier or trigonometric series expansions. If the average parameter value is to be considered as a part of the MF, the expression is

$$p^\mu(\bar{x}_4) = \sum_{n=-N}^{N} p_n^\mu \omega^n, \tag{4.4}$$

where

$$\bar{p}^\mu \equiv p_0^\mu, \quad p_{-n}^\mu = p_n^{\mu *},$$

* means the complex conjugate term and

$$\omega = \exp(2\pi i \bar{x}_4). \tag{4.5}$$

Note that the zeroth-order term is equal to the average value.

Sometimes, it is more convenient to separate the average value and use a slightly modified expression for the intrinsic part of the MF:

$$\tilde{p}^\mu(\bar{x}_4) = \sum_{n=1}^{N} (p_n^\mu \omega^n + p_n^{\mu *} \omega^{n *}). \tag{4.6}$$

The most convenient form is the following one:

$$\tilde{p}^\mu(\bar{x}_4) = \sum_{n=1}^{N} (p_n^{\mu,s} s_n + p_n^{\mu,c} c_n), \tag{4.7}$$

where

$$s_n = \sin(2\pi n \bar{x}_4) \equiv \mathfrak{I}(\omega^n), \tag{4.8}$$

$$c_n = \cos(2\pi n \bar{x}_4) \equiv \mathfrak{R}(\omega^n). \tag{4.9}$$

This was also de Wolff's preferred choice.

Another form is to introduce the amplitude and phase of MF explicitly and use one of the following expressions:

$$\tilde{p}^\mu(\bar{x}_4) = \sum_{n=1}^{N} p_n^\mu \sin[2\pi(n\bar{x}_4 + \varphi_n^\mu)], \tag{4.10}$$

$$\tilde{p}^\mu(\bar{x}_4) = \sum_{n=1}^{N} p_n^\mu \cos[2\pi(n\bar{x}_4 + \varphi_n^\mu)]. \tag{4.11}$$

This form is suitable for analysis of the influence of amplitude and phase fluctuations, leading to the new form of thermal displacement parameters in IC structures.

In the above expressions, all parameters labelled by the atom index μ and harmonic order n are adjustable parameters. They have all been used so far in practice.

In order to find the value of any parameter for an atom located in any cell (n_1, n_2, n_3) of the average structure, the internal coordinate must satisfy the relation

$$\bar{x}_4 = 2\pi \sum_{i=1}^{3} q_i(\bar{x}_i^\mu + n_i). \tag{4.12}$$

In all subsequent sections, this convention is adopted, which also leads to the simplest form of SF formula.

In some cases, it may be useful to adopt the convention proposed by Petříček *et al.* (1985) to handle rigid-molecule modulation. In these cases, the SF has to be changed accordingly.

5. de Wolff's structure factor

In this section, we reconsider the SF expression for an IC structure, restricting ourselves to one-dimensional modulation and (3 + 1)-dimensional superspace-group symmetry, as in de Wolff's original paper. However, we do not restrict ourselves to harmonic modulation but consider the case when atomic positions, occupation and thermal-displacement parameters are simultanously distorted by possibly anharmonic MFs.

Details concerning the superspace-group symmetry are not discussed here, only some notation is introduced (see Jannsen, Janner, Looijenga-Vos & de Wolff, 1992). An essential feature of this new kind of symmetry is the nontrivial symmetry transformation of a scalar MF (*e.g.* occupational and/or isotropic-thermal-displacement-parameter modulation). In ordinary structures, such a parameter is the same for all symmetry-equivalent atoms.

Let us consider the structure with superspace-group symmetry operations labelled g. Our objective is to evaluate the SF for a given reflection with indices $h_i, i = 1, \ldots, 4$.

The most convenient way to deal with symmetry is to apply the symmetry operations to reflection

indices whenever possible. This is similar to ordinary crystals (see Giacovazzo, 1992).

Let us introduce the following notation for the transformed reflection indices:

$$h_i^g = \sum_{j=1}^{4} R_{ji}^g h_j, \quad m(g) \equiv h_4^g, \tag{5.1}$$

and the real indices in the three-dimensional physical reciprocal space:

$$H_i^g = h_i^g + h_4^g q_i, \quad i = 1, \ldots, 3, \tag{5.2}$$

where q_i are the modulation vector components.

In some cases, an alternative notation is used for the symmetry-transformed satellite reflection (fourth) index, as introduced above.

The complex factor owing to a nonprimitive translation is denoted:

$$\Omega^g = \exp\left(2\pi i \sum_{i=1}^{4} h_i \tau_i^g\right). \tag{5.3}$$

As a next step, all quantities related to the displacive modulation are introduced. This kind of modulation deserves special attention, owing to the special role of atomic coordinates. In our approach, the average parameters are separated from MFs.

Thus, the geometrical part of the SF is separated into two factors. The first one is related to the average atomic position:

$$\exp\left(2\pi i \sum_{i=1}^{3} h_i^g \bar{x}_i^\mu\right) \equiv \exp\left(i\bar{\chi}^{\mu,g}\right). \tag{5.4}$$

The second one is explicitly dependent on the internal coordinate:

$$\exp\left(2\pi i \sum_{i=1}^{3} H_i^g \tilde{x}_i^\mu\right) \equiv \exp\left(i\tilde{\chi}^{\mu,g}\right). \tag{5.5}$$

The important difference is the use of h_i^g in the average coordinate expression, in contrast with H_i^g in the modulation part.

In a similar way, the modulation of anisotropic thermal displacement parameters is introduced. The first part is the ordinary anisotropic temperature factor:

$$\exp\left(-\sum_{i,j=1}^{3} H_i^g \bar{B}_{ij}^\mu H_j^g\right) \equiv \exp\left(-\bar{\beta}^{\mu,g}\right). \tag{5.6}$$

The second one is the actual modulation:

$$\exp\left(-\sum_{i,j=1}^{3} H_i^g \tilde{\beta}_{ij}^\mu H_j^g\right) \equiv \exp\left(-\tilde{\beta}^{\mu,g}\right). \tag{5.7}$$

Note that H_i^g are now used in both expressions.

Using the notation introduced above, we can write down the SF expression, consequently separating parts depending explicitly on the internal coordinate. We also separate the occupational modulation, allowing the zeroth-order term to be part of the MF for this parameter. In addition, the factor resulting from nonprimitive translations is used separately.

The contribution from an atom μ transformed by symmetry operation g is proportional to the product of two parts. The first one is

$$\bar{F}^{\mu,g} = \exp\left(i\bar{\chi}^{\mu,g} - \bar{\beta}^{\mu,g}\right). \tag{5.8}$$

The second one results from modulations of coordinates and thermal displacement parameters:

$$\tilde{F}^{\mu,g} = \exp\left(i\tilde{\chi}^{\mu,g} - \tilde{\beta}^{\mu,g}\right). \tag{5.9}$$

The modification for isotropic temperature factors is straightforward and is not discussed here.

To include the occupational modulation, it is convenient to introduce the following quantity:

$$W^{\mu,g} = \sum_{n=-M}^{M} P_n^\mu \langle \tilde{F}^{\mu,g} \omega^{m(g)+n} \rangle, \tag{5.10}$$

where M covers the range of occupational-modulation harmonics.

This is the crucial part of the SF expression. With the assumption that the occupational MF has the form of the standard Fourier expansion (4.4) of a real function, the SF is the following finite sum of integrals over the internal coordinate.

$$F(\mathbf{h}) = \sum_{\mu,g} M^\mu f^\mu \Omega^s F^{\mu,g} W^{\mu,g}, \tag{5.11}$$

where the sum covers all symmetry-independent atoms μ and symmetry operations g, M^μ and f^μ are the multiplicity and the complex scattering factor of atom μ, respectively, and all quantities are evaluated for the reflection with four indices h_i, $i = 1, \ldots, 4$.

The following conclusions can be drawn from the expression above. First, that the SF can be evaluated analytically, if only an occupational modulation described by the standard Fourier expansion is present. Thus, all the difficulties come from the remaining modulations. Furthermore, if an analytical solution exists for displacive and/or thermal displacement modulation, it will also exist if an occupational modulation is added.

We can also recognize that

$$\langle \tilde{F}^{\mu,g} \omega^m \rangle \equiv [\mathcal{F}(\tilde{F}^{\mu,g})]_m, \tag{5.12}$$

where $\mathcal{F}$ means the Fourier transform. This relation has been used to derive a new algorithm to evaluate this expression. Instead of standard numerical integration procedures (*e.g.* Gaussian integration), other very efficient and accurate algorithms for Fourier-coefficient evaluation can be used (see Paciorek & Chapuis, 1992). The goal here is to demonstrate the existence of an analytical solution.

As a first step, let us formulate the general condition for which such a solution can be derived. One observes that the periodicity of MFs leads also to the periodicity of the subexpression above. This means

that

$$\tilde{F}^{\mu,g} = \sum_{m=-\infty}^{\infty} F_m^{\mu,g}\omega^m. \tag{5.13}$$

If such an expansion can be evaluated analytically, then

$$\langle \tilde{F}^{\mu,g}\omega^m \rangle = F_{-m}^{\mu,g}. \tag{5.14}$$

In such a case, the SF can be also evaluated analytically and reads

$$W^{\mu,g} = \sum_{n=-M}^{M} P_n^{\mu} F_{-m(g)-n}^{\mu,g}. \tag{5.15}$$

The existence of this solution depends only on the properties of the MFs used to describe displacive and/or thermal-displacement-parameter modulation.

Towards the end of this section, the notation is simplified by dropping all irrelevant indices from the SF subexpressions. We establish a relationship between these two types of modulation.

Let us assume the existence of the following expansion for displacive modulation:

$$\exp(i\chi) = \sum_{m=-\infty}^{\infty} G_m(\chi)\omega^m, \tag{5.16}$$

and of the similar one for the thermal displacement modulation:

$$\exp(-\beta) = \sum_{m=-\infty}^{\infty} T_m(-\beta)\omega^m. \tag{5.17}$$

Allowing the complex arguments in the expansion coefficient functions, the common expansion of the form

$$\exp(i\chi - \beta) = \sum_{m=-\infty}^{\infty} F_m(\chi + i\beta)\omega^m, \tag{5.18}$$

will necessarily fulfil the following sum rule:

$$F_m(\chi + i\beta) = \sum_{l=-\infty}^{\infty} G_l(\chi)T_{m-l}(i\beta). \tag{5.19}$$

Furthermore, if only one type of modulation is present, the following relations should be satisfied:

$$G_m(\chi) = F_m(\chi), \tag{5.20}$$

$$T_m(-\beta) = F_m(i\beta). \tag{5.21}$$

In the above equations, one can easily recognize the familiar properties of BFs, *e.g.* addition theorems, imaginary argument transformations, relating ordinary and modified BFs and generating functions. However, the previous sections have shown the existence of a much wider class of functions with the same properties.

6. Analytical solution

To obtain an analytical solution, it is convenient to consider the SF as an implicit function of the refined parameters and introduce some intermediate complex quantities. In this section, only the contribution of the atom generated by the symmetry operation g from the independent atom μ is considered.

Let us illustrate this approach on the part of the SF depending only on the average structure parameters and define

$$\overline{\chi}^{\mu,g} + i\overline{\beta}^{\mu,g} = \overline{z}^{\mu,g}. \tag{6.1}$$

It is easy to recognize that

$$\Re\overline{z}^{\mu,g} = 2\pi \sum_{i=1}^{3} h_i^g \overline{x}_i^{\mu}, \tag{6.2}$$

$$\Im\overline{z}^{\mu,g} = \sum_{i,j=1}^{3} H_i^g H_j^g \overline{B}_{ij}^{\mu}. \tag{6.3}$$

For the subsequent calculations, the following partial derivatives are required:

$$\frac{\partial\overline{z}^{\mu,g}}{\partial\overline{x}_i^{\mu}} = 2\pi h_i^g, \tag{6.4}$$

$$\frac{\partial\overline{z}^{\mu,g}}{\partial\overline{B}_{ij}^{\mu}} = iH_i^g H_j^g. \tag{6.5}$$

One can easily see that this part of the SF is an explicit function of the intermediate complex argument and has the simple form

$$\overline{F}^{\mu,g} = \exp(i\overline{z}^{\mu,g}), \tag{6.6}$$

with trivial first derivative

$$\frac{\partial\overline{F}^{\mu,g}}{\partial\overline{z}^{\mu,g}} = i\overline{F}^{\mu,g}. \tag{6.7}$$

This rather formal approach becomes crucial if the modulation-dependent part of the SF is considered.

If the analytical form of both MFs is the same, both types of modulation can be combined into one MF expression with complex coefficients. The real part will be related to the displacive modulation and the imaginary part to the modulation of the thermal displacement parameters.

Furthermore, even and odd terms can be combined separately if (4.7) is the chosen form of both MFs, as is assumed here:

$$\tilde{p}^{\mu} = \sum_{k=1}^{N} (p_n^{\mu,s}s_n + p_n^{\mu,c}c_n), \tag{6.8}$$

where N is the highest harmonic order and zero padding is assumed if the range of harmonics in the displacive modulation is different from the thermal-displacement-parameter modulation.

Let us define the set of harmonic-order-dependent complex quantities:

$$\tilde{\chi}^{\mu,g} + i\tilde{\beta}^{\mu,g} = \sum_{k=1}^{N} (Z_k^{\mu,g}s_k + z_k^{\mu,g}c_k), \tag{6.9}$$

where (see § 5)

$$\Re Z_k^{\mu,g} = 2\pi \sum_{i=1}^{3} H_i^g x_{i,k}^{\mu,s}, \tag{6.10}$$

$$\Im Z_k^{\mu,g} = \sum_{i,j=1}^{3} H_i^g H_j^g B_{ij,k}^{\mu,s}, \tag{6.11}$$

$$\Re z_k^{\mu,g} = 2\pi \sum_{i=1}^{3} H_i^g x_{i,k}^{\mu,c}, \tag{6.12}$$

$$\Im z_k^{\mu,g} = \sum_{i,j=1}^{3} H_i^g H_j^g B_{ij,k}^{\mu,c} \tag{6.13}$$

and the partial derivatives with respect to the MF

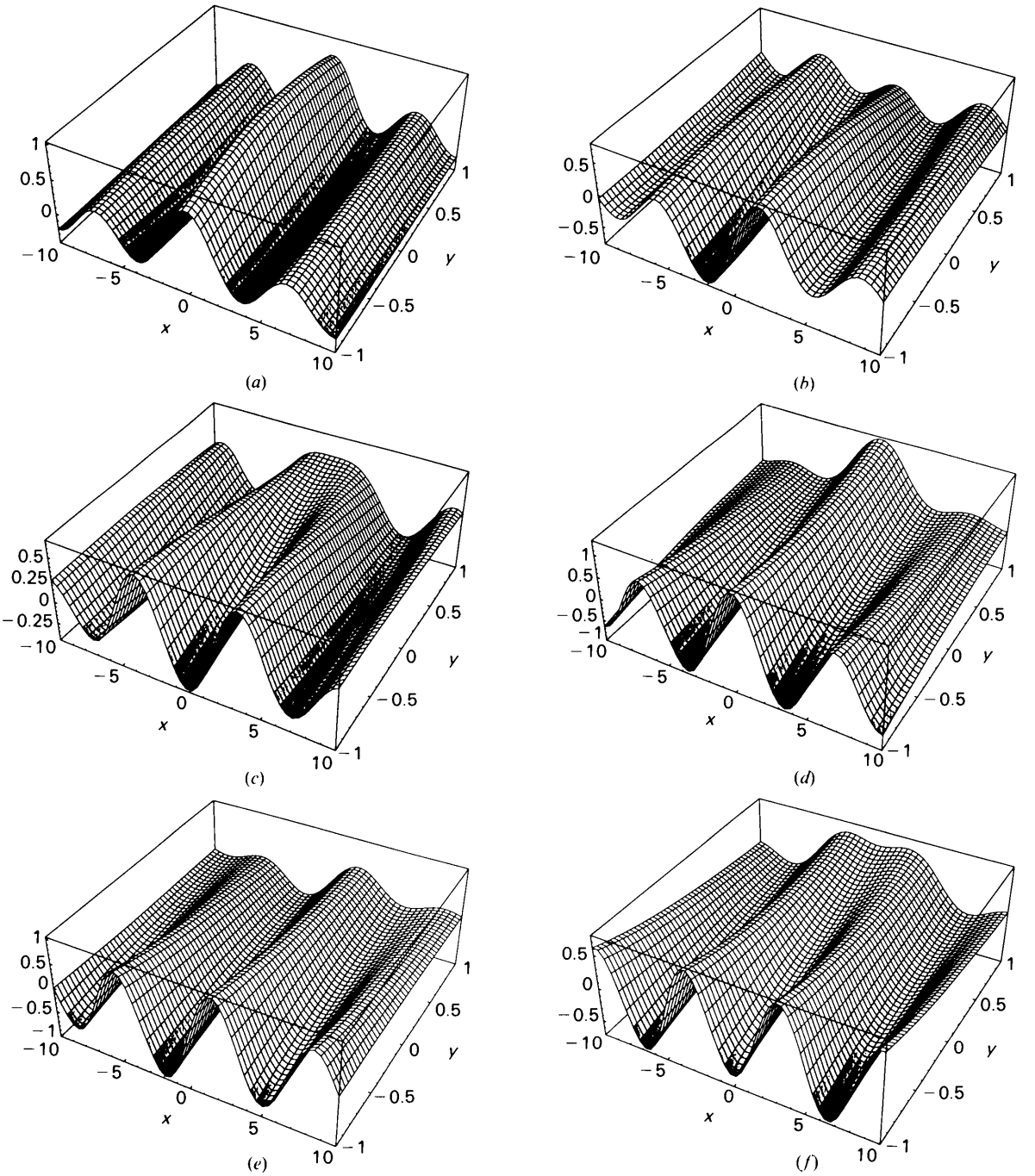

Fig. 1. Generalized Bessel functions $J_n(x,y)$, $n = 0, 1, 2$ [(a), (b), (c)] and $\tilde{J}_n(x,y)$, $n = 0, 1, 2$ [(d), (e), (f)]. If $y = 0$, both reduce to the well known $J_n(x)$.

parameters are

$$\frac{\partial Z_k^{\mu,g}}{\partial x_{i,k}^{\mu,s}} = \frac{\partial z_k^{\mu,g}}{\partial x_{i,k}^{\mu,c}} = 2\pi H_i^g, \tag{6.14}$$

$$\frac{\partial Z_k^{\mu,g}}{\partial B_{ij,k}^{\mu,s}} = \frac{\partial z_k^{\mu,g}}{\partial B_{ij,k}^{\mu,c}} = i\, H_i^g H_j^g. \tag{6.15}$$

Note that the part of the SF depending on the modulation of atomic coordinates and thermal displacements is now

$$\tilde{F}^{\mu,g} = \exp(i\tilde{\chi}^{\mu,g} - \tilde{\beta}^{\mu,g}) \tag{6.16}$$

and has precisely the form of a generating function for the GBF studied in detail in § 3. This function can replace an ordinary BF used so far.

The main result of this study can thus be expressed in the form

$$F(\mathbf{h}) = \sum_{\mu,g} M^\mu f^\mu \Omega^s \bar{F}^{\mu,g} W^{\mu,g}, \tag{6.17}$$

$$W^{\mu,g} = \sum_{n=-M}^{M} P_n^\mu \, \nu_{-m(g)-n}(\{Z^{\mu,g}, z^{\mu,g}\}_N) \tag{6.18}$$

and all nontrivial partial derivatives are derived from

$$\frac{\partial \nu_m}{\partial Z_k^{\mu,g}} = (1/2)(\nu_{m-k} - \nu_{m+k}) \tag{6.19}$$

$$\frac{\partial \nu_m}{\partial z_k^{\mu,g}} = (i/2)(\nu_{m-k} + \nu_{m+k}), \tag{6.20}$$

where $m = -m(g) - n$, $n = 1, \ldots, M$ and $k = 1, \ldots, N$.

The above expressions constitute an analytical solution for the SF and all its partial derivatives with respect to both average structure and all MF parameters for all one-dimensional IC structures studied so far. The only restriction is that the number of harmonics in the MFs is finite.

The SF formula derived above has the same simple form as for harmonic displacive modulation. If the first harmonic is to be added to the thermal displacement parameters, the only change is to use BFs of complex rather than real argument. If higher harmonics are to be added, the ordinary BFs are to be replaced by (suitable) GBFs.

The evaluation of BFs is not particularly difficult (see Press, Flannery, Teukolsky & Vetterling, 1992), even in the case of complex variables. We expect similar algorithms for GBFs in the near future, especially for the first few harmonics.

To illustrate GBFs suitable for crystallographic applications, two such functions (see § 2) are presented in Fig. 1. The first one, $J_n(x,y)$ can be an aid to study the influence of the second harmonic in atomic displacements. The second one, $\tilde{J}_n(x,y)$, plays a similar role in the study of the effect of the second harmonic on the thermal displacement parameters.

7. Concluding remarks

The application of the GBFs in IC-structure analysis as proposed here can be potentially useful in several areas of research. The obvious application is to improve further the commonly used computing procedures, where an efficient evaluation of the SF is important (*e.g.* structure refinement).

de Wolff's formula, recast in terms of GBFs, retains its former simplicity but gains a novel mathematical interpretation. Many new formulas and techniques offered by the GBF theory can lead to better understanding of IC structures, as described by the superspace-group approach.

The possibility is not excluded that the availability of an analytical formula can be useful in the solution of other problems. We mention here the open questions in the formulation of direct-methods theory for IC structures, where even the SF normalization is a quite complicated problem. The very rich GBF theory can probably be useful here.

Conversely, IC-structure analysis is another field where GBFs can be very useful and even some new suggestions for further studies within this theory can be inferred. GBFs could perhaps be used in other areas of computational crystallography. Work is in progress on the applications of GBFs in crystallographic statistics.

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References

Aalst, W. van, den Hollander, J., Peterse, W. J. A. M. & de Wolff, P. M. (1976). *Acta Cryst.* **B32**, 47–58.

Dattoli, G., Chiccoli, C., Lorenzutta, S., Maino, G., Richetta, M. & Torre, A. (1991). *Nuovo Cimento B*, **106**, 1159–1166.

Dattoli, G., Chiccoli, C., Lorenzutta, S., Maino, G., Richetta, M. & Torre, A. (1992). *J. Math. Phys.* **33**(1), 25–36.

Dattoli, G., Giannessi, L., Mezi, L. & Torre, A. (1990). *Nuovo Cimento B*, **105**, 327–348.

Dattoli, G., Mari, C., Torre, A., Chiccoli, C., Lorenzutta, S. & Maino, G. (1992). *J. Sci. Comput.* **7**(2), 175–196.

Dattoli, G., Torre, A., Lorenzutta, S., Maino, G. & Chiccoli, C. (1991). *Nuovo Cimento B*, **106**, 21–51.

Giacovazzo, C. (1980). *Direct Methods in Crystallography*. New York: Academic Press.

Giacovazzo, C. (1992). *Fundamentals of Crystallography*, edited by C. Giacovazzo, pp. 61–137. IUCr/Oxford Univ. Press.

Hadamard, J. (1945). *The Psychology of Invention in the Mathematical Field*, p. 54. New Jersey: Princeton Univ. Press.

Janner, A. (1972). *Acta Cryst.* A**28**, S111.

Janssen, T. (1992). *Condens. Matter News*, **1**(8), 7–12.

Janssen, T., Janner, A., Looijenga-Vos, A. & de Wolff, P. M. (1992). *International Tables for Crystallography*, Vol. C, pp. 797–844. Dordrecht: Kluwer Academic Publishers.

Maino, G. (1993). Personal communication.

PACIOREK, W. A. & CHAPUIS, G. (1992). *J. Appl. Cryst.* **25**, 317–322.
PACIOREK, W. A. & KUCHARCZYK, D. (1985). *Acta Cryst.* A**41**, 462–466.
PETRIČEK, V. & COPPENS, P. (1988). *Acta Cryst.* A**44**, 235–239.
PETRIČEK, V., COPPENS, P. & BECKER, P. (1985). *Acta Cryst.* A**41**, 478–483.
PETRIČEK, V., MALÝ, K. & CÍSAŘOVÁ, I. (1991). *Methods of Structural Analysis of Modulated Structures and Quasicrystals*, edited by J. M. PÉREZ-MATO, F. J. ZÚÑIGA & G. MADARIAGA, pp. 262–267. Singapore: World Scientific.
PRESS, W. H., FLANNERY, B. P., TEUKOLSKY, S. A., VETTERLING, W. T. (1992). *Numerical Recipes: the Art of Scientific Computing*, 2nd ed. Cambridge Univ. Press.
REISS, H. R. (1980). *Phys. Rev. A*, **22**, 1786–1813.
WATSON, G. N. (1958). *A Treatise on the Theory of Bessel Functions*, 2nd ed. Cambridge Univ. Press.
WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.
WOLFF, P. M. DE & VAN AALST, W. (1972). *Acta Cryst.* A**28**, S111.
WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625–636.

Acta Cryst. (1994). A**50**, 203–210

Structure Solution by Minimal-Function Phase Refinement and Fourier Filtering. I. Theoretical Basis

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Abstract

Eliminating the N atomic position vectors $\mathbf{r}_j$, $j = 1, 2, \ldots, N$, from the system of equations defining the normalized structure factors $E_{\mathbf{H}}$ yields a system of identities that the $E_{\mathbf{H}}$'s must satisfy, provided that the set of $E_{\mathbf{H}}$'s is sufficiently large. Clearly, for fixed N and specified space group, this system of identities depends only on the set $\{\mathbf{H}\}$, consisting of n reciprocal-lattice vectors $\mathbf{H}$, and is independent of the crystal structure, which is assumed for simplicity to consist of N identical atoms per unit cell. However, for a fixed crystal structure, the magnitudes $|E_{\mathbf{H}}|$ are uniquely determined so that a system of identities is obtained among the corresponding phases $\varphi_{\mathbf{H}}$ alone, which depends on the presumed known magnitudes $|E_{\mathbf{H}}|$ and which must of necessity be satisfied. The known conditional probability distributions of triplets and quartets, given the values of certain magnitudes $|E|$, lead to a function $R(\varphi)$ of phases, uniquely determined by magnitudes $|E|$ and having the property that $R_T < \frac{1}{2} < R_R$, where R_T is the value of $R(\varphi)$ when the phases are equal to their true values, no matter what the choice of origin and enantiomorph, and R_R is the value of $R(\varphi)$ when the phases are chosen at random. The following conjecture is therefore plausible: the global minimum of $R(\varphi)$, where the phases are constrained to satisfy all identities among them that are known to exist, is attained when the phases are equal to their true values and is thus equal to R_T. This 'minimal principle' replaces the problem of phase determination by that of finding the global minimum of the function $R(\varphi)$ constrained by the identities that the phases must satisfy and suggests strategies for determining the values of the phases in terms of N and the known magnitudes $|E|$. Equivalently, the minimal principle leads to the solution of the (in general redundant) system of equations satisfied by the phases φ_H.

Introduction

The structure invariants, in this paper only triplets and quartets, link the observed magnitudes $|E|$ with the desired phases φ of the normalized structure factors E. The traditional techniques of direct methods use the conditional probability distributions of the structure invariants to obtain estimates of their values and thus relationships among the individual phases having probabilistic validity. These rela-

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