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On standardization of crystal-field Hamiltonians parametrization: triclinic symmetry case

J Mulak[1] **and M Mulak**[2]

[1] W Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, PO Box 1410, Poland
[2] Institute of Physics, Wrocław University of Technology, 50-370 Wrocław, Poland

E-mail: Maciej.Mulak@pwr.wroc.pl

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Abstract

The maps of magnitudes of the axial crystal-field parameters, B_{k0}, for $k = 2, 4, 6$, which enter the $\mathcal{H}_{\mathrm{CF}}$ parametrizations as functions of the z-axis spherical coordinates of the relevant reference frames are identical for all equivalent parametrizations with accuracy to the definite rotations of these frames. Therefore, it is possible to reduce all tested $\mathcal{H}_{\mathrm{CF}}$ parametrizations to the one common reference frame providing that one can find for all these parametrizations the same distinguished space direction. This condition is fulfilled by the three z-axes of the frames for which the axial parameter, B_{k0} (where $k = 2, 4, 6$ corresponds to the component multipoles), reaches its maximal value $\max B_{k0} \leqslant \left[\sum_m |B_{km}|^2\right]^{1/2}$. These maxima can serve as convenient discriminants of the entire classes of equivalent parametrizations. Based on the distinguished directions and transformational properties of $\mathcal{H}_{\mathrm{CF}}$ parametrizations with respect to the reference frame rotations, the paper presents the method how to effectively verify the equivalence of these parametrizations and postulates the way of their standardization. This method can be applied to all point symmetries of the central ion, although it seems to be particularly useful and recommended for triclinic symmetry (C_1, C_i).

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1. Introduction

The parametrizations of the crystal-field Hamiltonians $\mathcal{H}_{\mathrm{CF}}$ available from a fitting experimental data procedure always refer to some specific reference frames. However, the space orientation of these frames, e.g. relative to the crystallographic system, is principally unknown. Additionally, there exist crystal-field potentials of such symmetries that the corresponding parametrization patterns remain the same for various reference

frames, whereas the sets of the crystal-field parameters (CFPs) are different. These parametrizations, though seemingly different, are equivalent since they can be identified with each other through appropriate rotations of their reference frames. Therefore, there is a persistent demand to reduce such parametrizations to a common reference frame, i.e. to give a clear method of verification of their equivalence and postulate an unambiguous standardization.

Among the above-mentioned $\mathcal{H}_{\mathrm{CF}}$, a particular position take the potentials of the triclinic symmetry (C_1 or C_i point symmetry). This peculiarity results from the fact that they have no crystallographically distinguished reference frame (the symmetry adapted system), or in other ways, each and every reference frame is equivalently distinguished in this case. Hence, the question how to choose the reference frame common for all the tested parametrizations becomes crucial.

The conventional methods of standardization of $\mathcal{H}_{\mathrm{CF}}$ parametrizations, based on algebraic symmetry of the characteristic polynomial of the $\mathcal{H}_{\mathrm{CF}}$ matrix introduced by Clark [1] and developed by Rudowicz and Bramley for rhombic [2], and monoclinic systems [3], as well as other symmetries admitting complex-conjugate CFPs [4], do not seem to guarantee any progress while dealing with $\mathcal{H}_{\mathrm{CF}}$ of C_1 and C_i point symmetries.

Here in the paper a quite different approach is proposed. It is based on the special discriminant established separately for each of the 2^k-pole components ($k = 2, 4, 6$) in $\mathcal{H}_{\mathrm{CF}}$, i.e. on the maximal value of the axial parameter, max B_{k0}. These discriminants being the same for the entire class of the equivalent parametrizations yield directly the distinguished orientations of the relevant reference frames. In consequence, we have at our disposal three distinguished space directions for the three 2^k-poles, respectively.

Using the rotational transformation [5, 6] separately for each $\mathcal{H}_{\mathrm{CF}}$ multipole ($k = 2, 4, 6$), we are able to reduce all the tested parametrizations to a common reference frame. According to fitting procedures this shared frame, which is specific for a chosen 2^k-pole, obviously refers to the whole parametrization. Thus, comparing two different $\mathcal{H}_{\mathrm{CF}}$ parametrizations defined within two certain unknown reference frames, we are able to obtain their forms expressed within the common reference frame. It allows us to verify their equivalence and standardize them by taking the max B_{k0} value for the B_{k0} CFP. It makes no difference that the explicit space orientation of the common frame remains unknown.

Naturally, there are no limitations in applying the above method of verification and standardization of $\mathcal{H}_{\mathrm{CF}}$ parametrizations to other central-ion symmetries, however it seems to be particularly advisable for the triclinic symmetry.

2. Basic theoretical approach

2.1. The rotational transformation of $\mathcal{H}_{\mathrm{CF}}$ parametrizations

We need the transformational properties of any $\mathcal{H}_{\mathrm{CF}}$ parametrization, $[B_{km}]$, induced by the reference frame rotation. Throughout the paper the tensor (Wybourne) notation [7] for the B_{km} CFPs is consistently used ($B_{km} = \mathrm{Re}\, B_{km} + \mathrm{i}\, \mathrm{Im}\, B_{km}$; $B^*_{km} = (-1)^m B_{k,-m}$). In the most general case three-dimensional rotations of the reference frame, $O^+(3)$ group, induce the transformations of $(2k + 1)$ components (constituting the 2^k-pole) according to the kth-order irreducible representations of the rotation group $\mathcal{D}^{(k)}(\alpha, \beta, \gamma)$, where (α, β, γ) are the three Euler angles [5, 6].

Representing the set of $2k + 1$ CFPs, including one real axial parameter B_{k0} and k pairs of complex-conjugate parameters, by a one-column vector, the effect of the rotation can be

described by means of the following matrix equation,

$$\begin{bmatrix} \mathcal{D}^{(k)}_{-k,-k} & \mathcal{D}^{(k)}_{-k,-k+1} & \cdots & \mathcal{D}^{(k)}_{-k,0} & \cdots & \mathcal{D}^{(k)}_{-k,k} \\ \vdots & \vdots & & \vdots & & \vdots \\ \mathcal{D}^{(k)}_{0,-k} & \mathcal{D}^{(k)}_{0,-k+1} & \cdots & \mathcal{D}^{(k)}_{0,0} & \cdots & \mathcal{D}^{(k)}_{0,k} \\ \vdots & \vdots & & \vdots & & \vdots \\ \mathcal{D}^{(k)}_{k,-k} & \mathcal{D}^{(k)}_{k,-k+1} & \cdots & \mathcal{D}^{(k)}_{k,0} & \cdots & \mathcal{D}^{(k)}_{k,k} \end{bmatrix} \cdot \begin{bmatrix} B_{k,-k} \\ \vdots \\ B_{k,0} \\ \vdots \\ B_{k,k} \end{bmatrix} = \begin{bmatrix} B'_{k,-k} \\ \vdots \\ B'_{k,0} \\ \vdots \\ B'_{k,k} \end{bmatrix}, \tag{1}$$

where the matrix elements $\mathcal{D}^{(k)}_{mn}(\alpha, \beta, \gamma)$ are defined as [5, 6]

$$\mathcal{D}^{(k)}_{mn}(\alpha, \beta, \gamma) = \exp \mathrm{i}(m\gamma + n\alpha) \left[\frac{(k+m)!(k-m)!}{(k+n)!(k-n)!} \right]^{\frac{1}{2}} \sum_{\sigma} \binom{k+n}{k-m-\sigma} \times \binom{k-n}{\sigma} (-1)^{k-m-\sigma} \left(\cos \frac{\beta}{2} \right)^{2\sigma+m+n} \left(\sin \frac{\beta}{2} \right)^{2k-2\sigma-m-n}. \tag{2}$$

The sum in the above expression is extended for those values of σ for which both Newton symbols hold their sense.

Since the description of real crystal-field effects must be independent of the reference system choice, all the $\mathcal{H}_{\mathrm{CF}}$ parametrizations related to each other by equation (1), as $[B_{km}]$ and $[B'_{km}]$, are equivalent. Owing to the unitarity of transformations $\mathcal{D}^{(k)}(\alpha, \beta, \gamma)$, the square roots of the sums of the CFPs moduli squares, $M_k = \left[\sum_m |B_{km}|^2 \right]^{1/2}$, are their invariants.

Now, within these various reference frames related to the original one by the above-mentioned rotations the axial CFP B_{k0} takes, according to equation (1), the value

$$B'_{k0} = \sum_{m=-k}^{k} \mathcal{D}^{(k)}_{0m}(\alpha, \beta, 0) B_{km} = \sum_{m=-k}^{k} C^{(k)}_{m}(\beta, \alpha) B_{km}, \tag{3}$$

since $\mathcal{D}^{(k)}_{0m}(\alpha, \beta, 0) = C^{(k)}_{m}(\beta, \alpha)$ [5, 6], and where the B_{km} CFPs correspond to the original reference frame.

2.2. *Maximal values of B_{k0} CFPs for $k = 2, 4, 6$ in parametrized $\mathcal{H}_{\mathrm{CF}}$*

Since for the triclinic symmetry there is no crystallographically distinguished direction, one may suspect that the standardization of equivalent parametrizations of the involved $\mathcal{H}_{\mathrm{CF}}$ is principally impossible to obtain. Fortunately, this pessimistic conclusion is not true. It turns out that for each separate 2^k-pole component of the $\mathcal{H}_{\mathrm{CF}}$, the maximal magnitude of B_{k0}, $\max B_{k0}$ (that for the particularly orientated reference frame), does not generally reach the modulus value $M_k = \left[\sum_{m=-k}^{k} |B_{km}|^2 \right]^{1/2}$. Therefore, the $\max B_{k0}$ can be treated as a well-defined discriminant of the equivalent $\mathcal{H}_{\mathrm{CF}}$ parametrizations. Similarly, the minimal value of B_{k0}, $\min B_{k0}$, could be used. The use of $\max|B_{k0}|$ magnitude needs to respect the B_{k0} sign.

Knowing the spherical coordinates $(\bar{\alpha}_k, \bar{\beta}_k)$ of the distinguished z-axis (related to $\max B_{k0}$) for all the tested $\mathcal{H}_{\mathrm{CF}}$ parametrizations, one may reduce them to the one common reference frame, consequently proving their equivalence, and finally standardize them by taking the $\max B_{k0}$ as the B_{k0} for a fixed k. For $\mathcal{H}_{\mathrm{CF}}$ of C_1 or C_i point symmetries no other distinguished space direction comes to mind.

The maximal magnitudes of the axial CFPs, $\max B_{k0}$, along with the orientations of the relevant z-axes, $(\bar{\alpha}_k, \bar{\beta}_k)$, can be found either by means of the extremum calculus in which we are looking for the zero points of the partial derivatives of the right side of equation (3) with respect to α and β rotation angles, or directly from the $B_{k0}(\alpha, \beta)$ maps within the whole range

of the angles $0 \leqslant \alpha \leqslant 2\pi$ and $0 \leqslant \beta \leqslant \pi$, identifying the highest summits (or the deepest valleys).

Based on max B_{k0} points on the maps, we can find the three respective distinguished directions defined within the same initial reference frame. Then, the mutual orientation of the distinguished z-axes can be found from the expression for the angle between the vectors knowing their components. Since the unit vector along the distinguished z-axis of 2^k-pole has, within the initial (Cartesian) reference frame, the following components $(\sin\bar{\beta}_k \cos\bar{\alpha}_k, \sin\bar{\beta}_k \sin\bar{\alpha}_k, \cos\bar{\beta}_k)$, the angle ω_{kl} between the distinguished z-axes of 2^k- and 2^l-poles can be calculated as

$$\omega_{kl} = \arccos[\sin\bar{\beta}_k \sin\bar{\beta}_l \cos\bar{\alpha}_k \cos\bar{\alpha}_l + \sin\bar{\beta}_k \sin\bar{\beta}_l \sin\bar{\alpha}_k \sin\bar{\alpha}_l + \cos\bar{\beta}_k \cos\bar{\beta}_l]. \tag{4}$$

If for one of the component multipoles, e.g. the 2^k-pole, the initial frame is optimal (i.e. $\sin\bar{\beta}_k = 0$), then $\omega_{kl} = \bar{\beta}_l$.

3. The standardization procedure

3.1. Mapping of the $B_{k0}(\alpha, \beta)$ CFPs as a function of the reference frame rotation angles

The plots of the B_{k0} maps for all possible orientations of the related reference frame z-axis are directly feasible by using basic computational programs like MathCad. In the case of the triclinic symmetry, due to the lack of any symmetry elements, the maps ought to be plotted within the full range of the angles, $0 \leqslant \alpha \leqslant 2\pi$, $0 \leqslant \beta \leqslant \pi$. As an example, figure 1 shows three such maps for one out of two crystallographically different U^{4+} ions in UF_4, i.e. that of C_1 symmetry [8, 9]. The solid lines on the maps (figure 1) refer to the constant values of the B_{k0} (i.e. the iso-B_{k0} lines).

Eight out of twelve U^{4+} ions in the UF_4 unit cell possess C_1 site symmetry. The complete set of 27 CFPs (thoroughly given in the last column of table IV in [9]) was estimated for the simple one-parameter version of the angular overlap model (AOM) [10], where $e_\sigma = 1800\ \mathrm{cm}^{-1}$, $e_\sigma/e_\pi = 2.88$.

These graphical representations lead to two observations worth noting:

- The common feature of these three cases is the $\max|B_{k0}|$ and the modulus M_k proximity: $\max|B_{k0}|/M_k$ amounts to $\frac{1448}{1501} = 0.964$, $\frac{7205}{7755} = 0.929$, $\frac{4011}{4574} = 0.877$, for $k = 2, 4, 6$, respectively.
- The angles between the distinguished directions (equation (4)) are: $\omega_{24} = 14.3^\circ$, $\omega_{26} = 13.2^\circ$, $\omega_{46} = 1.6^\circ$; so the directions are fairly focused especially those for the 2^4- and 2^6-poles which are almost collinear.

Taking into account these two facts, one can conclude that the $\mathcal{H}_{\mathrm{CF}}$ of the $U^{4+}(C_1)$ ion in UF_4 has distinctly axial character. It is not surprising since this crystal-field potential can be roughly approximated by that of the Archimedean antiprism symmetry (D_{4d}) with a pure axial $\mathcal{H}_{\mathrm{CF}}$ [11, 12]. The approximate $\bar{8}$ axis stands for the average distinguished direction. Thus, the model considered above gains convincing ground.

To obtain the maps we begin with an initial, in general unknown, reference system in which the considered $\mathcal{H}_{\mathrm{CF}}$ parametrization $[B_{km}]$ is defined. Then, we carry out all rotational transformations according to equation (3). The third Euler angle γ, inessential to this procedure, is assumed to be zero: the rotation by γ does not affect the axial B_{k0} CFPs.

In order to be able to compare the $B_{k0}(\alpha, \beta)$ maps for any two different parametrizations, i.e. for any two different reference frames, one needs the trigonometrical relations between the angle spherical coordinates of unit radius vectors in both the frames. By analogy, it can be

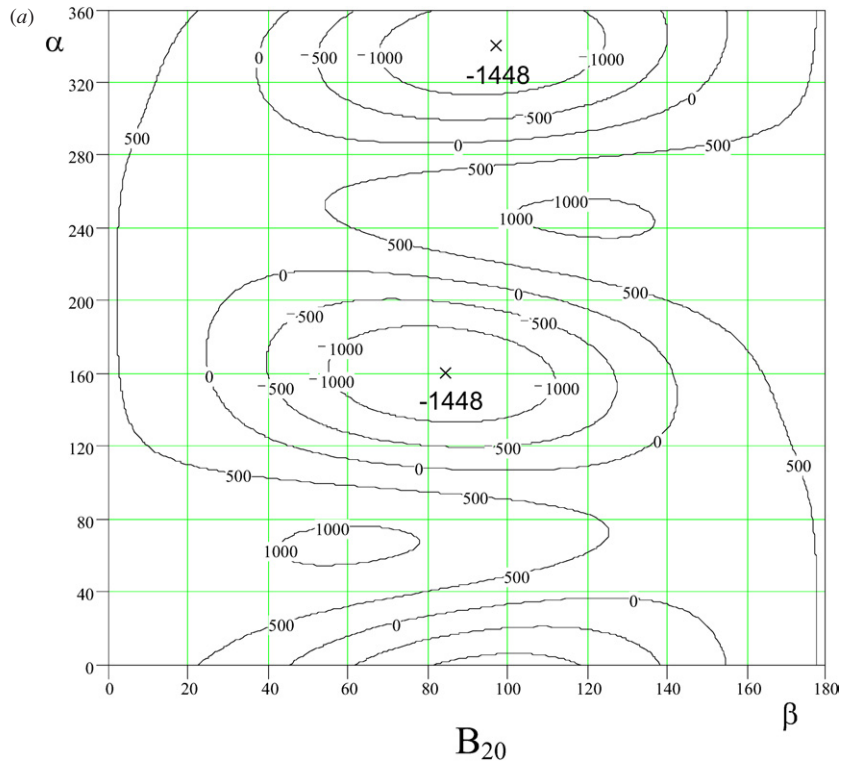

Figure 1. The maps of values of B_{20} (*a*), B_{40} (*b*) and B_{60} (*c*) CFPs (in cm^{-1}) for $UF_4(C_1)$:UF_4 [9] as functions of the reference frame rotation angles α and β within their ranges $0 \leqslant \alpha \leqslant 2\pi$, $0 \leqslant \beta \leqslant \pi$. The pairs of characteristic $\max|B_{k0}|$ are denoted by the crosses with their exact values (bold-faced).

referred to the relationship between the latitude and longitude of any point on the Earth within the conventional coordinate system (the polar axis, Greenwich meridian) and those within another system based on a new 'polar axis' and a new zero-meridian.

Let us denote the coordinates of a chosen radius vector in the initial frame as (θ, φ) and then rotate the frame by $(\alpha, \beta, 0)$. Between the coordinates of the considered point within the transformed (θ', φ') and initial (θ, φ) frames, the following relationships hold:

$$\theta' = \arccos[-\sin\beta\cos\varphi\sin\theta + \cos\beta\cos\theta]$$

$$\varphi' = \arctan\left[\frac{\sin\alpha\cos\beta\cos\varphi\sin\theta + \cos\alpha\sin\varphi\sin\theta - \sin\alpha\sin\beta\cos\theta}{\cos\alpha\cos\beta\cos\varphi\sin\theta - \sin\alpha\sin\varphi\sin\theta - \cos\alpha\sin\beta\cos\theta}\right]. \tag{5}$$

Knowing for the corresponding points (e.g. for the max B_{k0}) (θ, φ) from the first map, and (θ', φ') from the second map, the angles of the mutual rotation of the frames (α, β) can be found. The maps $B_{k0}(\alpha, \beta)$ reflect to some extent the central-ion point symmetry. Namely, such a map orientated with respect to an accidental z-axis of its initial reference frame (according to the choice of the $(0, 0)$ point) cannot straightforwardly reveal the central-ion point symmetry. However, the multiplicity of identical B_{k0} values occurring due to the present axes and planes of symmetry has to be the same for all other orientations of the

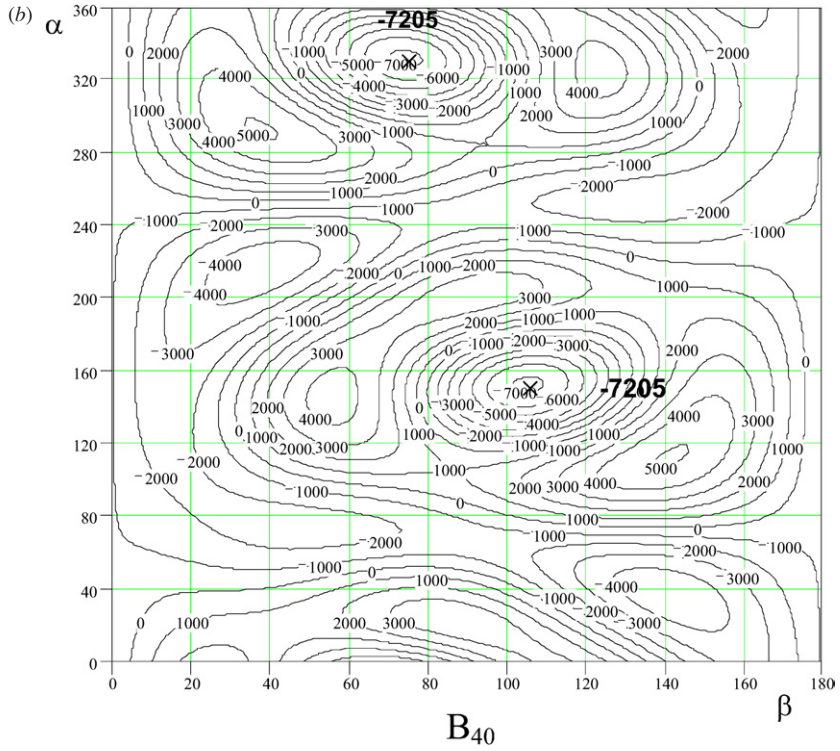

Figure 1. (Continued.)

reference frame including the symmetry adapted system. When $\beta = 0$, then the α angle becomes inessential for an arbitrary choice of the reference frame. Consequently, all points of the α-axis correspond to the $(0, 0)$ point, and everywhere along this axis $B_{k0} = \text{const}$. It manifests itself on the maps as a constant height of the surface plot for $\beta = 0$, and similarly for $\beta = \pi$.

Since the sign of B_{k0} CFPs does not depend on the sense of the reference system z-axis, their identical values occur for each pair of points (α, β) and $(\alpha + \pi, \pi - \beta)$ (see figure 1). This property can be proven based on equation (3). In other words, the B_{k0} CFPs depend only on the even powers of the z coordinates of the ligands (or charge density) in the central-ion surroundings. This imposes the characteristic symmetry of the maps (figure 1) in spite of the lack of any crystallographic elements of symmetry. Thus, even in the case of triclinic symmetry the corresponding pairs of B_{k0} points occur on the maps. If the z-axis of the applied reference frame is the $C_{\infty v}$ symmetry axis, then all the iso-B_{k0} lines on the maps are vertical, straight lines parallel to the α-axis ($\beta = \text{const}$) . Finally, a constant function, $B_{k0}(\alpha, \beta) = \text{const}$, would correspond to the spherical symmetry of the central ion.

After the above-described reduction of any two considered maps to the two coordinate frames sharing the same z-axis, the subsequent rotation of one of them about this z-axis which leads to their total overlapping (and which corresponds to the third Euler angle γ) is equivalent to the parallel shift of the transformed map along its α-axis. In this way, having the maps for two different but equivalent $\mathcal{H}_{\text{CF}}$ parametrizations one can reduce them to the common reference frame, showing their compatibility.

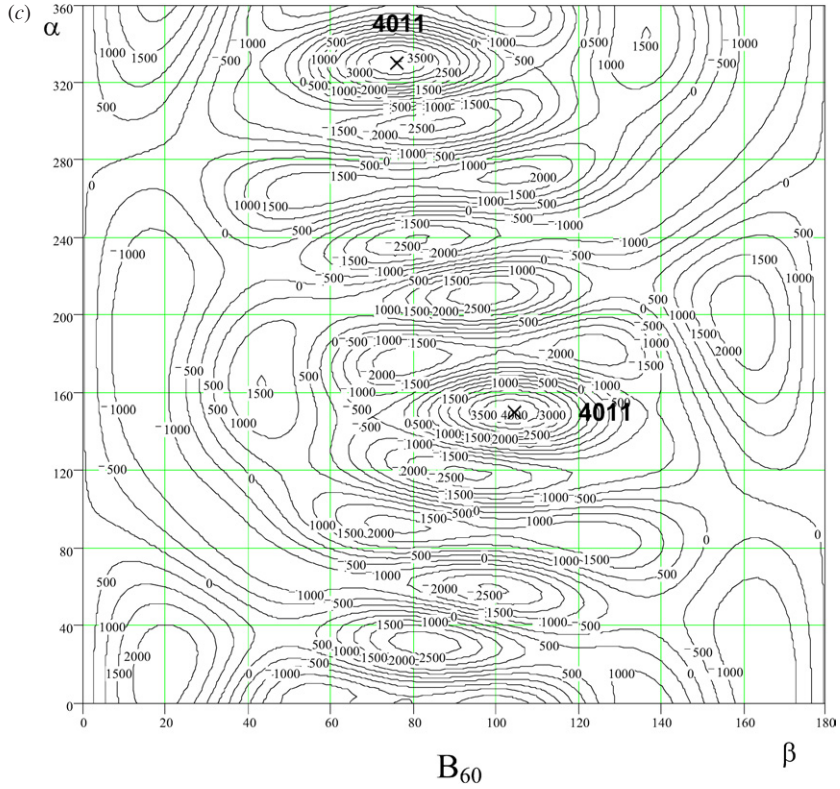

Figure 1. (Continued.)

3.2. Verification of the $\mathcal{H}_{\mathrm{CF}}$ parametrization equivalence

Let us assume that one needs to compare two different parametrizations $\left[B_{km}^{(1)}\right]$ and $\left[B_{km}^{(2)}\right]$ of the same $\mathcal{H}_{\mathrm{CF}}$ at a triclinic symmetry site. These parametrizations are obtained from fitting certain available experimental data. Eliminating one out of the 27 CFPs nominally assigned to this symmetry (e.g. Im B_{21}) by means of the virtual rotations of the reference systems (corresponding to $\left[B_{km}^{(1)}\right]$ and $\left[B_{km}^{(2)}\right]$, respectively), about their z-axes by strictly defined angles $\chi^{(i)} = \arctan\left(\mathrm{Im}\ B_{21}^{(i)}/\mathrm{Re}\ B_{21}^{(i)}\right)$, where $i = 1, 2$, the applied parametrization pattern should be based on the 26 independent CFPs.

Although the compared $\mathcal{H}_{\mathrm{CF}}$ parametrizations describe the same physical reality, they differ from each other since they are defined within different reference frames. However, only those $\mathcal{H}_{\mathrm{CF}}$ parametrizations which are mutually related through equation (1) belong to the one class of equivalent parametrizations. Unfortunately, we do not know the mutual orientation of the involved reference frames and this prevents us from verifying their equivalence in such a direct manner.

Therefore, let us consider, in detail, the conditions which have to be fulfilled by the equivalent $\mathcal{H}_{\mathrm{CF}}$ parametrizations. It may happen that their inequivalence (if any) is revealed already at these preliminary stages of the investigation.

- Since the individual 2^k-poles ($k = 2, 4, 6$) in $\mathcal{H}_{\mathrm{CF}}$ become transformed under the separate irreducible representations $\mathcal{D}^{(k)}$ of the three-dimensional rotation group, the moduli of the

particular multipoles, $M_k = \left[\sum_m |B_{km}|^2\right]^{1/2}$, have to be the invariants of these rotations. Thus, for both the considered $\mathcal{H}_{\mathrm{CF}}$ parametrizations they have to be the same. This is the first necessary condition, but not a sufficient one, of their equivalence.

- The maps of $B_{k0}(\alpha, \beta), k = 2, 4, 6$, for both the $\mathcal{H}_{\mathrm{CF}}$ parametrizations after their appropriate conversion into a common reference system have to be identical. The magnitude $\max B_{k0} \leqslant M_k$ can serve as a convenient discriminant of the reconciliation procedure.
- The mutual orientation of the component 2^k-poles has to be identical. This refers not only to the distinguished z_k-axes (the z-axes for which B_{k0} reach their maxima) but also to the x- and y- axes in the planes perpendicular to the distinguished z-axes.

The proposed verification procedure of the equivalence of two $\mathcal{H}_{\mathrm{CF}}$ parametrizations (this is the transitive property) can follow the scheme:

1. The moduli $M_k, k = 2, 4, 6$, for both the parametrizations are calculated. They have to be equal for the equivalent parametrizations.
2. The maps of $B_{k0}(\alpha, \beta), k = 2, 4, 6$, within the whole ranges of the angles $0 \leqslant \alpha \leqslant 2\pi$ and $0 \leqslant \beta \leqslant \pi$ are plotted. Based on these maps the top points $\left(\bar{\alpha}_k^{(1)}, \bar{\beta}_k^{(1)}\right)$, $\left(\bar{\alpha}_k^{(2)}, \bar{\beta}_k^{(2)}\right)$, for $\max B_{k0}^{(1)}$ and $\max B_{k0}^{(2)}$, respectively, are found. For the equivalent parametrizations the relationship $\max B_{k0}^{(1)} = \max B_{k0}^{(2)}$ must hold. This constitutes the second criterion of the equivalence. Additionally, the coordinates of the corresponding z_k-axes, i.e. $\left(\bar{\alpha}_k^{(1)}, \bar{\beta}_k^{(1)}\right)$ and $\left(\bar{\alpha}_k^{(2)}, \bar{\beta}_k^{(2)}\right)$, allow us, by means of equation (4), to find out the mutual space orientation of the distinguished z_k-axes of the three component multipoles. This is only a roughly established orientation of the reference systems ignoring their rotations about these distinguished axes. These orientations have to be the same for both examined parametrizations if they are to be equivalent. This may be treated as the third criterion of the equivalence.
3. The initial (unknown) reference frame relevant to the first parametrization $\left[B_{km}^{(1)}\right]$ is rotated by $\left(\bar{\alpha}_k^{(1)}, \bar{\beta}_k^{(1)}, 0\right)$ for a chosen k (one out of the three) to point its z-axis along the distinguished direction. As a consequence of this rotation, the new transformed set of all 27 CFPs of the first parametrization, $[B_{km}^{\prime(1)}]$, is obtained according to equation (1). Similarly, the reference frame relevant to the second parametrization, $\left[B_{km}^{(2)}\right]$, is rotated by $\left(\bar{\alpha}_k^{(2)}, \bar{\beta}_k^{(2)}, 0\right)$ in order to point its z-axis in the same distinguished direction. As previously, the second transformed complete set of 27 CFPs, $\left[B_{km}^{\prime(2)}\right]$, is obtained. Let us emphasize that both the parametrizations $\left[B_{km}^{\prime(1)}\right]$ and $\left[B_{km}^{\prime(2)}\right]$ correspond to the two reference frames with the same z-axis. If they are to be equivalent, they can differ from each other only in their off-axial CFPs in such a way that a plane rotation of, e.g., the second frame about the common z-axis by a certain angle $\bar{\gamma}_k^{(2)}$ leads to the total identity of both the parametrizations. The transformation of $\left[B_{km}^{\prime(2)}\right]$ as a result of the last rotation has the form

$$\left[B_{km}^{\prime\prime(2)}\right] = \left[B_{km}^{\prime(2)}\right] \exp\left(\mathrm{i}m\bar{\gamma}_k^{(2)}\right), \tag{6}$$

where

$$\left[B_{km}^{\prime\prime(2)}\right] \equiv \left[B_{km}^{\prime(1)}\right] \qquad \text{or} \qquad \left[B_{km}^{\prime\prime(2)}\right] \equiv \left[(-1)^m B_{km}^{\prime(1)*}\right], \tag{7}$$

i.e. for all k and m; the second equation refers to the opposite sense of the z-axis.
Hence, based on equations (6) and (7), the $\bar{\gamma}_k^{(2)}$ angle for the equivalent parametrizations can be found directly.

4. There still remains the last step which is the elimination, at our own request, one out of the Im B_{km} CFPs, e.g. the Im B_{21}. This is attainable transforming the last parametrization, i.e. $\left[B'^{(1)}_{km}\right] \equiv \left[B''^{(2)}_{km}\right]$, due to the rotation $(0, 0, \chi_{21})$, where $\chi_{21} = \arctan(\text{Im } B_{21}/\text{Re } B_{21})$.

4. Complementary comments

The idea underlying the method presented is the rotation invariant defined for any entire class of equivalent $\mathcal{H}_{\text{CF}}$ parametrizations instead of a single parametrization. Therefore, the postulated invariants, max B_{k0}, can be treated as a generalization of the previously introduced crystal-field invariants [13] and exploited in the case of individual parametrizations [14, 15]. The examples of such single parametrization invariants are the M_k magnitudes, the crystal-field strength parameters s_k, as well as the angles between the distinguished directions of component multipoles in $\mathcal{H}_{\text{CF}}$. In fact they can be helpful in verification of compatibility and reliability of $\mathcal{H}_{\text{CF}}$ parametrizations, but their utility is rather limited: for instance the s_k parameters render the shifts of the centres of gravity of the free-ion levels caused by J-mixing or the second moment of Stark levels in the absence of J-mixing [13].

In *ab initio* or model calculations of $\mathcal{H}_{\text{CF}}$ parametrizations, the relevant axis system is *a priori* assumed and all the CFPs admitted by group theory are unambiguously determinable—27 in the case of triclinic $\mathcal{H}_{\text{CF}}$'s. This is not the case, however, for parametrizations of fitting origin. As results from the analysis of $\mathcal{H}_{\text{CF}}$ algebraic symmetry, not all the admissible CFPs can be determined unambiguously [1–4], and in consequence several, and often an infinite number of equivalent parametrizations coexist. The corresponding axis systems called by Rudowicz [16] 'nominal' ones remain unknown, but it does not prevent us from rotating them. To obtain reliable $\mathcal{H}_{\text{CF}}$ parametrization, we also face the next problem. The number and choice of independent CFPs (forming the fitting pattern) play a crucial role in the procedure. In addition to this comes the adjustment of the free-ion parameters with the CFPs.

By means of rotation of any initial (nominal) axis system by appropriate Euler angles, one can always reduce the fitting pattern by one to three parameters for the specific orientations of the axis system [3, 4, 17]. However, such procedures should be supplemented by the convention clearly stating the CFPs to be removed. An essential reduction in the number of independent CFPs can be achieved only by interrelating the involved CFPs based on the superposition model (SM) [18], the angular overlap model (AOM) [19], or using, e.g., the point charge model (PCM) B_{kq}/B_{k0} ratios [20].

Unfortunately, as is seen from the literature data [17, 20] the reliable $\mathcal{H}_{\text{CF}}$ parametrization of triclinic symmetry constitutes a difficult task indeed. In order to ensure compatibility and reliability of the parametrizations, a broad basis treatment [16, 20] is required. Fortunately, such tools as the computer package CST (conversions, standardization and transformations) [16] and the multipole correlated fitting technique (MCFT) [16] come to our aid.

5. Summary

The $\left(\bar{\alpha}^{(1)}_k, \bar{\beta}^{(1)}_k, 0\right)$ rotation of the reference frame relative to the first parametrization $\left[B^{(1)}_{km}\right]$ leads to the $\left[B'^{(1)}_{km}\right]$ parametrization, and analogously, the $\left(\bar{\alpha}^{(2)}_k, \bar{\beta}^{(2)}_k, \bar{\gamma}^{(2)}_k\right)$ rotation of the reference frame relative to the second parametrization $\left[B^{(2)}_{km}\right]$ leads to the $\left[B''^{(2)}_{km}\right]$ parametrization. For the equivalence of the $\left[B^{(1)}_{km}\right]$ and $\left[B^{(2)}_{km}\right]$ parametrizations the identity of the $\left[B'^{(1)}_{km}\right]$ and $\left[B''^{(2)}_{km}\right]$ parametrizations is necessary.

Thus, the method of reduction of two different but corresponding to the same $\mathcal{H}_{\mathrm{CF}}$ parametrizations to the common reference frame is proposed. It enables us to verify their equivalence and introduce the standardization which consists in taking the max B_{k0} as the B_{k0} CFP (for a fixed k). So, there are three possibilities ($k = 2, 4, 6$) to choose the distinguished axis as the z-axis. General standardization should be defined for commonly fixed k, e.g. $k = 2$. Then, the distinguished axis of the quadrupole component of the $\mathcal{H}_{\mathrm{CF}}$ would be the z-axis of the standard reference system.

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