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SHORT COMMUNICATIONS

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Improvement of the tangent formula by constraints based on additional information.

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Abstract

The first part of this communication describes a simple procedure by which the non-centrosymmetric form of the tangent formula is adapted to incorporate the 'centrosymmetry constraint' for centrosymmetric structures, thus allowing refinement of phases uniformly distributed from 0 to 2π to the expected values 0 or 2π. The convergence of the resulting formula is illustrated with two structures. In the second part, a modified tangent formula including the constraint based on the zero points of the Patterson function is derived. To do this, both the Cochran integral $\int_v \rho^3\,dV$ and the sum over all zero points of the Patterson function of ρ^2 are expressed in terms of the phases of the strong E's. The modified tangent formula is then obtained assuming that the difference between the two corresponds to a large positive maximum for the correct phases. Finally, it is shown how the information supplied by the weak E's and by the zero points can be treated in an unified way, so that a combined tangent formula can be derived.

Introduction

As is well known, the integral (Cochran, 1952; Hauptman & Karle, 1953)

$$V^2 \int_v \rho^3(\mathbf{r})\,d\mathbf{r} = \text{large magnitude}, \tag{1}$$

including the 'positivity criterion' of the electron-density distribution, can be expressed as the sum of the triplets

$$\sum_{\mathbf{h}} \sum_{\mathbf{h}'} \mathbf{E}_{-\mathbf{h}} \mathbf{E}_{\mathbf{h}'} \mathbf{E}_{\mathbf{h}-\mathbf{h}'}. \tag{2}$$

As shown by Debaerdemaeker, Tate & Woolfson (1985), a way of deriving the tangent formula (Karle & Hauptman, 1956)

$$\varphi(\mathbf{h}) = \text{phase of} \left\{ \sum_{\mathbf{h}'} \mathbf{E}_{\mathbf{h}'} \mathbf{E}_{\mathbf{h}-\mathbf{h}'} \right\} \tag{3}$$

is to assume that the true phase angles $\varphi(\mathbf{h})$ of the normalized structure factors correspond to a maximum of the double summation (2). However, by refining phases with the tangent formula, it is also possible to reach, besides the correct maximum, false maxima. This may happen for several reasons, such as the effect of space-group symmetry, size of the structure and special features in the atomic positions (Schenk, 1988). By using additional information *e.g.* the weak E's found from the diffraction experiment (Debaerdemaeker, Tate & Woolfson, 1985) or the minimum interatomic separation derived from the atomic size (Rius & Miravitlles, 1989), constraints can be added to (1) in order to reduce the number of such false maxima. In this communication, the constraints based on the centrosymmetry of the electron-density distribution and on the zero points of the Patterson function are investigated.

The centrosymmetry constraint

A special case of the conventional tangent formula results from introducing the centrosymmetry constraint explicitly in (1), *i.e.* in the form of an integral:

$$I = V^2 \int_v \rho(-\mathbf{r})\rho^2(\mathbf{r})\,d\mathbf{r}. \tag{4}$$

The integrals (4) and (1) will only be equivalent for a

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Table 1. *Evolution of the phase values* (°) *for some reflections of ALC*2 *during the refinement of* 200 *initially random phases with the centrosymmetric tangent formula*

			Cycle no.					
Reflection			0	1	2	3	4	11 (correct)
1	5	5	−52	−53	9	9	8	0
1	3	1	58	141	125	177	174	180
0	8	0	−140	−9	161	−176	−18	1
1	3	3	−178	174	−123	153	169	180
0	4	10	9	48	−16	5	0	0
1	4	6	−120	161	127	178	−175	180
−11	1	3	30	−20	−93	−61	−24	0
−8	9	4	−58	−145	−97	−164	−172	180
−9	3	4	−102	−27	3	−5	−3	0
−4	4	10	79	−141	−12	13	11	0
0	3	12	−54	−141	29	99	172	−179

Table 2. *Evolution of the phase values* (°) *for some reflections of BNA during the refinement of* 150 *initially random phases with the centrosymmetric tangent formula*

			Cycle no.				
Reflection			0	1	2	3	5 (correct)
4	4	2	−109	−113	−147	−4	0
10	4	4	105	152	9	1	0
4	8	6	101	−10	0	−2	0
10	0	4	−125	172	180	180	180
0	4	4	−41	0	−2	0	0
12	4	0	161	139	179	180	180
2	8	0	55	−10	−1	0	0
4	4	4	64	73	173	178	180
6	4	6	−18	38	175	180	180
0	12	4	−25	−8	0	0	0
10	4	0	−79	178	180	180	180

centrosymmetric structure having the unit-cell origin on an inversion centre of the crystal. In reciprocal space,

$$I=\sum_{\mathbf{h}}\sum_{\mathbf{h}'}|E_{-\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|\cos(\varphi_{\mathbf{h}}+\varphi_{\mathbf{h}'}+\varphi_{\mathbf{h}-\mathbf{h}'}) \qquad (5)$$

and, obviously, (5) will be a maximum for a correct phase set corresponding to a centrosymmetric structure with the cell origin on an inversion centre. As shown in the Appendix, (5) can be maximized as a function of the phases by means of the centrosymmetric tangent formula:

$$\varphi_{\mathbf{h}}=\text{phase of}\left\{-\sum_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'}\right\}. \qquad (6)$$

Notice that since the centrosymmetry condition has already been considered in the derivation of (6), the symmetry operations generating equivalent positions related by the centre of symmetry need not be included in the crystal-structure-determination process and, consequently, the phase values will not be algebraically restricted to 0 or π. This allows refinement of initial random phases distributed between 0 and 2π. Consequently, and except for the minus sign in (6), a unique algorithm can treat both noncentrosymmetric and centrosymmetric structures, *i.e.* during the phase refinement of a centrosymmetric structure with (6), the new phase estimate $\varphi_{-\mathbf{h}}$ is $-\varphi_{\mathbf{h}}$ and not $\varphi_{\mathbf{h}}$. Our experience with the centrosymmetric tangent formula indicates that it is a useful tool for solving centrosymmetric structures of normal complexity.

To illustrate the use of the centrosymmetric tangent formula, two structures (one equal-atom structure and one containing medium heavy atoms) have been selected:

(1) Code name: ALC2, an imidazolium benzimidazolate compound (Alcalde, Dinares, Miravitlles & Rius, 1990). Formula: $C_{11}H_{10}N_4.H_2O$, $P2_1/a$, $Z=8$; $a=12{\cdot}225\,(8)$, $b=14{\cdot}090\,(3)$, $c=12{\cdot}890\,(8)$ Å, $\beta=99{\cdot}54\,(4)^{\circ}$, $V=2190$ Å^3. In this example, only the symmetry operations corresponding to the identity and the 2_1 axis at $(\frac{1}{4},.,\frac{1}{2})$ were introduced. From 40 sets of initially random phases refined with the centrosymmetric tangent formula, three show the complete structure. To illustrate the convergence of the random phases to 0 and π at the end of a successful phase-refinement trial, the evolution of the phase values for some reflections at different refinement stages is given (Table 1).

(2) Code name: BNA, a macrocycle incorporating a *nido*-carborane cage (Teixidor, Viñas, Rius, Miravitlles & Casabo, 1990).
Formula: $Na[B_9C_{10}H_{25}O_3S_2]$, *Pnma*, $Z=4$; $a=15{\cdot}615\,(2)$, $b=13{\cdot}851\,(3)$, $c=9{\cdot}076\,(1)$ Å, $V=1963$ Å^2. Only the symmetry operations corresponding to the identity and the three 2_1 axes at $(.,\frac{1}{4},\frac{1}{4})$, $(0,.,0)$ and $(\frac{1}{4},0,.)$ are introduced. 13 sets out of the 40 refined sets are successful. The convergence of the refinement is illustrated in Table 2.

The constraint based on the zero points of the Patterson function

Another way of obtaining a modified tangent formula is based on satisfying the Sayre equation (Sayre, 1952) for both strong and weak E's (Debaerdemaeker *et al.*, 1985). This leads to the derivation of the Sayre-equation tangent formula that makes active use during the phase-refinement process of the known weak E's. For a set of correct phases, a reduced form of the Sayre tangent formula is obtained (Debaerdemaeker, Tate & Woolfson, 1988) that in the words of the authors is almost as effective as the full form in refining random phases and nearly twice as fast. This reduced form is essentially based on the expression

$$V^2\int_v \rho^3(\mathbf{r})\,d\mathbf{r}-c_wV^{-2}\sum_{\mathbf{l}}\left|\sum_{\mathbf{h}}\mathbf{E}_{-\mathbf{h}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}\right|^2$$
$$=\text{large magnitude} \qquad (7)$$

with $\mathbf{l}$ being the indices of the weak E's, c_w being a scaling constant and $\mathbf{E}_{-\mathbf{h}}$ and $\mathbf{E}_{-\mathbf{l}+\mathbf{h}}$ belonging to the set of strong E's. The second term can be alternatively expressed in the form

$$\sum_{\mathbf{l}}\left|\sum_{\mathbf{h}}\mathbf{E}_{-\mathbf{h}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}\right|^2 \qquad (8)$$

$$=\sum_{\mathbf{l}}\left(\sum_{\mathbf{h}}\mathbf{E}_{-\mathbf{h}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}\right)\left(\sum_{\mathbf{h}''}\mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{l}-\mathbf{h}''}\right) \qquad (9)$$

$$=\sum_{\mathbf{h}}\mathbf{E}_{-\mathbf{h}}\sum_{\mathbf{l}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}\sum_{\mathbf{h}''}\mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{l}-\mathbf{h}''}. \qquad (10)$$

Taking (10) into account, it can be shown that (7) may be maximized as a function of the phases of the strong E's by means of the improved tangent formula (11)

$$\varphi(\mathbf{h})=\text{phase of}\left\{\sum_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'}-c_wV^{-2}\sum_{\mathbf{l}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}\sum_{\mathbf{h}''}\mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{l}-\mathbf{h}''}\right\} \qquad (11)$$

that essentially coincides with the reduced form of the Sayre-equation tangent formula of Debaerdemaeker *et al.* (1988). For incorrect phase values of the strong E's, the summation $\sum_{\mathbf{l}}|\sum_{\mathbf{h}} \mathbf{E}_{-\mathbf{h}}\mathbf{E}_{-\mathbf{l}+\mathbf{h}}|^2$ will be, in general, much greater than zero, thus preventing (7) from being a large magnitude, *i.e.* the slightly modified ψ_0 test function of Cochran & Douglas (1957) is actively incorporated in the phase-refinement process.

The weak E's are not the only source of additional information. The zero points in the Patterson function, for example, can also be readily obtained from the experimental data. Methods applying zero points have been described, for example, by Anzenhoffer & Hoppe (1962), Hoppe (1962, 1963), Main & Woolfson (1962, 1963) and Allegra (1979). Most of them derive the phase values from this information. Here, however, the zero points are used to reduce the number of possible solutions given by the tangent-formula refinement. Effectively, in parallel with (7), the following expression including the zero points can be derived for space group $P1$:

$$V^2 \int_v \rho^3(\mathbf{r})\,\mathrm{d}\mathbf{r} - c_z \sum_j \mathscr{P}(\mathbf{u}_j) = \text{large magnitude} \qquad (12)$$

where $\mathscr{P}(\mathbf{u})$ is the Patterson function computed with the squared electron-density function, *i.e.*

$$\mathscr{P}(\mathbf{u}) = V \int_v \rho^2(\mathbf{r}+\mathbf{u})\rho^2(\mathbf{r})\,\mathrm{d}\mathbf{r}, \qquad (13)$$

and with $\mathbf{u}_j$ and c_z being the position vector of the j zero point and a scaling constant, respectively. By definition, (13) must always be greater than or equal to zero and will display zero values at the same positions as the normal Patterson function (Patterson, 1935).

Suppose that the $\mathbf{G}_\mathbf{k}(\mathbf{u})$ denote the Fourier coefficients of the periodic function

$$\rho(\mathbf{r},\mathbf{u}) = \rho(\mathbf{r}+\mathbf{u})\rho(\mathbf{r}). \qquad (14)$$

Then, from (13),

$$\mathscr{P}(\mathbf{u}) = \sum_\mathbf{k} |\mathbf{G}_\mathbf{k}(\mathbf{u})|^2 \qquad (15)$$

and (12) can also be written in the form

$$V^2 \int_v \rho^3(\mathbf{r})\,\mathrm{d}\mathbf{r} - c_z \sum_\mathbf{k}\sum_j |\mathbf{G}_\mathbf{k}(\mathbf{u}_j)|^2. \qquad (16)$$

Since $\mathscr{P}(\mathbf{u}_j) \simeq 0$ for each j zero point, (15) implies

$$|\mathbf{G}_\mathbf{k}(\mathbf{u}_j)|^2 \simeq 0 \quad \text{for each } \mathbf{k}, \qquad (17)$$

i.e. the double summation in (16) can only vanish if all the $|\mathbf{G}_\mathbf{k}(\mathbf{u}_j)|^2$ are simultaneously zero.

Next, let the Fourier coefficients of $\rho(\mathbf{r},\mathbf{u})$ be related to those of $\rho(\mathbf{r}+\mathbf{u})$ and $\rho(\mathbf{r})$. One obtains

$$\mathbf{G}_\mathbf{k}(\mathbf{u}) = V^{-1} \sum_{\mathbf{h}''} \mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{k}-\mathbf{h}''} \exp[-i2\pi\mathbf{h}''\mathbf{u}] \qquad (18)$$

so that

$$\sum_\mathbf{k} |\mathbf{G}_\mathbf{k}(\mathbf{u})|^2 = \sum_\mathbf{k} \mathbf{G}_{-\mathbf{k}}(\mathbf{u})\mathbf{G}_\mathbf{k}(\mathbf{u}) \qquad (19)$$

$$= V^{-2} \sum_\mathbf{k} \left\{ \left[\sum_\mathbf{h} \mathbf{E}_{-\mathbf{h}}\mathbf{E}_{-\mathbf{k}+\mathbf{h}} \exp(i2\pi\mathbf{h}\mathbf{u}) \right] \right. \qquad (20)$$

$$\left. \times \left[\sum_{\mathbf{h}''} \mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{k}-\mathbf{h}''} \exp(-i2\pi\mathbf{h}''\mathbf{u}) \right] \right\} \qquad (21)$$

$$= V^{-2} \sum_\mathbf{h} \mathbf{E}_{-\mathbf{h}} \sum_\mathbf{k} \mathbf{E}_{-\mathbf{k}+\mathbf{h}} \sum_{\mathbf{h}''} \mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{k}-\mathbf{h}''}$$

$$\times \exp[-i2\pi(\mathbf{h}''-\mathbf{h})\mathbf{u}]. \qquad (22)$$

By substituting (22) and (2) in (16), the resulting expression can be maximized as a function of the phases $\varphi(\mathbf{h})$ of the strong E's by means of the following tangent formula (hereafter called ZP tangent formula; ZP = zero point):

$$\varphi(\mathbf{h}) = \text{phase of} \left\{ \sum_{\mathbf{h}'} \mathbf{E}_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'} - c_z V^{-2} \sum_\mathbf{k} \mathbf{E}_{-\mathbf{k}+\mathbf{h}} \sum_{\mathbf{h}''} \mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{k}-\mathbf{h}''} \right.$$

$$\left. \times \sum_j \exp[-i2\pi(\mathbf{h}''-\mathbf{h})\mathbf{u}_j] \right\}. \qquad (23)$$

Unlike the simpler Ω tangent formula, the ZP tangent formula can handle more than one zero point. In principle, inorganic compounds are the most favourable cases for its application. In such compounds, the electron density tends to be concentrated at a reduced number of positions in the cell, so that the corresponding Patterson function contains a large proportion of regions for which its value is very low. Owing to the minimum interatomic separation and for sufficient resolution, a zero region around the Patterson origin peak will always exist.

In addition, a new figure of merit, the ZP_0 test function, can be derived from (17) and (18):

$$\mathrm{ZP}_0 = V \sum_\mathbf{k}\sum_j |\mathbf{G}_\mathbf{k}(\mathbf{u}_j)|$$

$$= \sum_\mathbf{k}\sum_j \left| \sum_{\mathbf{h}''} \mathbf{E}_{\mathbf{h}''}\mathbf{E}_{\mathbf{k}-\mathbf{h}''} \exp[-i2\pi\mathbf{h}''\mathbf{u}_j] \right|. \qquad (24)$$

The correct sets of refined phases will be those with the lower values of ZP_0.

Finally, it is worth mentioning the possibility of deriving a combined tangent formula including both 'the weak E's' and 'the zero points' constraints from the following expression

$$V^2 \int_v \rho^3(\mathbf{r})\,\mathrm{d}\mathbf{r} - c_w \sum_\mathbf{l} |\mathbf{G}_\mathbf{l}(0)|^2 - c_z \sum_\mathbf{k}\sum_j |\mathbf{G}_\mathbf{k}(\mathbf{u}_j)|^2$$

$$= \text{large magnitude} \qquad (25)$$

in a similar way as for (11) or (23).

Since no practical application of this method has been carried out as yet, this is to be regarded as a preliminary theoretical investigation.

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APPENDIX

Derivation of the centrosymmetric form of the tangent formula

As indicated in the text, the true set of phases corresponds to a maximum of the function

$$I = \sum_\mathbf{h}\sum_{\mathbf{h}'} |E_{-\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}| \cos(\varphi_\mathbf{h} + \varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'}). \qquad (A1)$$

The condition for an extremum is then

$$\partial I/\partial\varphi_\mathbf{h} = 0 \text{ for each } \mathbf{h} \qquad (A2)$$

and consequently

$$0=\sum_{\mathbf{h}'}|E_{-\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|$$
$$\times\{\sin(\varphi_{\mathbf{h}}+\varphi_{\mathbf{h}'}+\varphi_{\mathbf{h}-\mathbf{h}'})+\sin(\varphi_{\mathbf{h}}+\varphi_{\mathbf{h}'}+\varphi_{-\mathbf{h}+\mathbf{h}'})$$
$$+\sin(\varphi_{\mathbf{h}}+\varphi_{-\mathbf{h}'}+\varphi_{\mathbf{h}-\mathbf{h}'})\}. \qquad (A3)$$

After some algebraic manipulation, the following tangent formula results:

$$\varphi_{\mathbf{h}}=\text{phase of}\left\{-\sum_{\mathbf{h}'}[\mathbf{E}_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'}+\mathbf{E}_{\mathbf{h}'}\mathbf{E}_{-\mathbf{h}+\mathbf{h}'}+\mathbf{E}_{-\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'}]\right\}. \qquad (A4)$$

Since for the correct phase $\varphi_{-\mathbf{h}'}=\varphi_{\mathbf{h}'}$ and $\varphi_{-\mathbf{h}+\mathbf{h}'}=\varphi_{\mathbf{h}-\mathbf{h}'}$, ($A4$) can be further reduced to

$$\varphi_{\mathbf{h}}=\text{phase of}\left\{-\sum_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}'}\mathbf{E}_{\mathbf{h}-\mathbf{h}'}\right\}. \qquad (A5)$$

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Strukturverfeinerung des Kompositkristalls im mehrdimensionalen Raum: Kommensurabler Kompositkristall.

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Abstract

The superspace-group approach formulated for incommensurate composite crystals by Janner & Janssen [*Acta Cryst.* (1980), A36, 408-415] is applicable to the structure refinement of commensurate composite crystals, if the number and the coordinates of summation points in the structure-factor formula are determined through an algorithm given in the text.

Die mehrdimensionale Darstellung des Kompositkristalls wurde von Janner & Janssen (1980) entwickelt. Kürzlich hat Kato (1990) anhand von zwei Anwendungsbeispielen gezeigt, daß sie für die Strukturverfeinerung derartiger Kristalle sehr geeignet ist. Inzwischen ist die mehrdimensionale Verfeinerungsmethode auf einen neuen Kompositkristall $(PbS)_{1,12}VS_2$ erfolgreich angewandt worden (Onoda, Kato, Gotoh & Oosawa, 1990). Obwohl diese Methode vorerst für nicht-kommensurable Kompositkristalle gedacht war, läßt sie sich auch auf einen kommensurablen anwenden. Im folgenden soll kurz beschrieben werden, wie sie gehandhabt wird.

Einbettung eines Atoms in den $(3+d)$-dimensionalen Raum erfolgt nach Janner & Janssen (1980) mit Hilfe einer linearen Abbildung π_ν. Das eingebettete Atom wird mittels eines beliebigen d-dimensionalen Vektors $\mathbf{t}$ wie $(\mathbf{x}-\pi_\nu\mathbf{t},\mathbf{t})$ dargestellt. Kato (1990) hat hierzu eine Matrix P (Eigentlich P^ν; auf ν, die Nummer des betreffenden Teilsystems, wird allgemein verzichtet) eingeführt, welche die gleiche Einbettung durch $P(\mathbf{x},\mathbf{t})$ bewirkt. Das hierdurch entstandene Atombild stellt ein unendlich ausgedehntes, periodisches Gebilde im $(3+d)$-dimensionalen Raum dar. Wenn man eine Lage-Modulation des Atoms außer acht läßt, so ist das Atombild eine d-dimensionale Hyperebene.

Sind alle Elemente der σ-Matrix (Janner & Janssen, 1980) rationale Zahlen, so liegt ein kommensurabler Kompositkristall vor. Aus der $(3+i)$-ten Zeile $(i=1,\ldots,d)$ von P^{-1} leitet man einen Vektor h^i her, indem man die Zeilenelemente zunächst als reduzierte Brüche darstellt und dann mit dem kleinsten gemeinsamen Vielfachen der Nenner multipliziert. Die $(3+d)$-dimensionalen Indexvektoren $h+\sum_{i=1}^{d}p_ih^i$ mit beliebigem ganzzahligen p_i beziehen sich auf ein und denselben Reflex im dreidimensionalen Raum. Yamamoto (1982) hat gezeigt, daß in kommensurablen Fällen die Integration in der Strukturfaktorformel einer gewöhnlichen modulierten Struktur in eine Summation übergeht. Die Strukturfaktorformel eines kommensurablen Kompositkristalls läßt sich im wesentlichen wie folgt niederschreiben:

$$F(h)=\sum_j[f_j/M\,\mathrm{Det}(P)]\sum_{m=1}^{M}\exp[2\pi ihP(\mathbf{x},\mathbf{t}_m)_j].$$

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