

As a result, it could be inferred that the s and Z dependences of $\eta_z^{\pm 1} - \eta_{cz}$ are similar to the subtraction (24) – (23) and (26). An analytic form of $\eta_z^{\pm 1} - \eta_{cz}$ will be highly desirable for the interpretation of the scattering phase for ionized atoms.

The numerical computations were performed on a FACOM M-190 of the Kyoto University Computing Center and FACOM 230-60 of the Osaka City University Computing Center. The authors would like to thank Dr Y. Kudo for his help, since this study was carried out by improving his original programs in nuclear research. They would also like to thank S. Kodera for his help in the numerical calculations and are grateful to Professor H. Watanabe for his encouragement.

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Lattice Symmetry Determination

BY ALAN D. MIGHELL

Center for Materials Science, National Bureau of Standards, Washington, DC 20234, USA

AND JOHN R. RODGERS

University Chemical Laboratory, Cambridge CB2 1EW, England

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Abstract

Transformation matrices required to obtain a conventional cell (Crystal Data cell) from the reduced cell have been applied to 47 000 crystalline compounds in the Crystal Data file. For 97% of the compounds, the calculations from the reduced cells yield conventional cells (lattice parameters, lattice type, and crystal system) that are entirely consistent with those reported in the original literature. In a few instances in which the reduced-cell matrix indicated a higher symmetry, the author has often noted that the crystal was unusual in some way or there was an error in the reported symmetry. Some implications of the results of this survey are: (1) metric symmetry as determined from the reduced cell is usually identical to the crystal-lattice symmetry; (2) determination of precise cell parameters defining any primitive cell of the lattice is valuable because from them one can conveniently determine the

crystal system with a high degree of confidence (the results, however, should still be verified by checking equivalent intensities and systematic extinctions); (3) if the metric symmetry obtained from the reduced cell and the symmetry determined by other techniques do not agree, the reason should be sought as there are often important structural implications; (4) the sequence of steps in an automatic procedure for the determination of space groups could be: primitive cell, reduced cell, lattice metric symmetry, crystal-lattice symmetry, extinction conditions.

Introduction

Research on crystallographic data bases should lead to the discovery of new relationships, to new classification schemes and to better data evaluation. Such data bases will become increasingly important in scientific

research because they provide large representative sets of critically evaluated data which can readily be studied on the computer by sophisticated algorithms. As the data cover crystalline compounds from many branches of science, they also facilitate interdisciplinary research.

With the NBS Crystal Data file, one can systematically analyze such structural and lattice-related phenomena as: symmetry, coincidence-site lattices, derivative lattices, space groups, and twinning. Since the crystalline state is based on the lattice, a geometrical concept, the field is amenable to many kinds of mathematical analyses. New theoretical ideas on twinning, for instance, could be checked by developing algorithms and running computer programs on sample data from the file.

Two studies that demonstrate the basic importance of the metric lattice in crystallography have been carried out with the NBS Crystal Data file. In the first (J. Rodgers & A. Mighell, manuscript in preparation), we have found that the metric lattice of a substance can be used to identify and characterize materials. In this second study, we describe a classification according to the reduced form of all crystalline compounds that are listed in *Crystal Data Determinative Tables* (1972, 1973, 1978) as well as compounds that are to appear in forthcoming volumes of *Crystal Data*. This classification has allowed us to make an analysis of the relationship between lattice metric symmetry and crystal-lattice symmetry. On the basis of this analysis, we outline a symmetry determination procedure that could be adapted to an automated diffractometer.

Experimental

From the NBS Crystal Data file we have systematically classified 47 000 crystalline compounds according to reduced form and determined how accurately the Bravais lattice can be derived from any primitive cell by the following sequence:

published cell → any primitive cell → reduced cell
→ Bravais cell and lattice symmetry.

The required transformations from a given reduced cell (Niggli, 1928) to a conventional cell are presented in *International Tables for X-ray Crystallography* (1969) and are listed in the Appendix of this paper. For the calculation of the reduced cell, see Santoro & Mighell (1970).

First the compounds were classified into the 44 reduced forms, and the relative frequency of occurrence of each form was then determined, for organic compounds (Fig. 1) and for inorganic compounds (Fig. 2). All 44 reduced forms are represented although the distribution is uneven. Primitive lattices are the most common. Inspection of the two figures shows that the two frequencies are fundamentally different. Almost all

organic compounds (approximately 95%) fall in space groups of orthorhombic or lower symmetry. In fact, 75.7% of all organic substances crystallize in five space groups (Fig. 3): 35.5% in $P2_1/c$ (reduced forms 33, 34, 35); 12.4% in $P2_12_12_1$ (reduced form 32); 7.6% in $P2_1$ (reduced forms 33, 34, 35); 13.3% in $P\bar{1}$ (reduced forms 31, 44); and 6.9% in $C2/c$ (dispersed among 13 reduced forms). In contrast, inorganic compounds commonly crystallize in space groups (Fig. 4) of orthorhombic or higher symmetry. Thus the reduced forms 1, 3, 11, 12, 22, and 32 are commonly encountered.

Once a cell had been classified into one of the 44 reduced forms, the corresponding Bravais lattice (metric) was determined with a symmetry algorithm based on the transformation matrices given in Table 1 (see Appendix). The lattice metric symmetry was then compared with the true crystal-lattice symmetry. The crystal-lattice symmetry was that reported by the author of the original reference and was usually determined along with the space group from diffraction intensities. Lattice metric symmetry and crystal-lattice symmetry were found to be identical in over 97% of the cases. This demonstrates that the reduced cell (combined with the symmetry algorithm) can usually be relied on to determine the crystal-lattice symmetry. The number of exceptions will undoubtedly decrease with the improvement of the cell determination and refine-

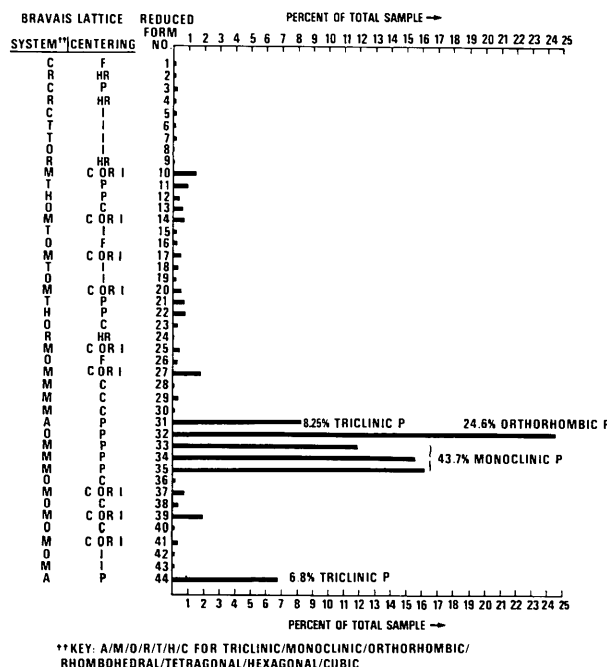


Fig. 1. Classification of organic materials and organometallic complexes by reduced form number. The figure shows the relative frequency of occurrence for each of the 44 reduced forms. Prepared from data for 21 051 compounds for which structures have been determined (to November 1978). The data are from Vols 1 and 3 of *Crystal Data* and from the structural entries in the Cambridge Data Bank.

ment procedures which would increase the precision of the unit-cell parameters.

Discussion

This symmetry analysis represents our second study on lattices from a large crystallographic data base. In our first study (manuscript in preparation), we found that the metric lattice of a crystalline compound is highly characteristic for the substance, especially for the low-symmetry organic and organometallic crystalline compounds. The first study established that highly selective identification procedures can be devised because of the uniqueness of the metric lattice. For several years, a reduced-cell file has been used in conjunction with a computer-based registration system for new compounds at the Cambridge Crystallographic Data Centre. This registration work shows that a primitive cell of the lattice (e.g. the reduced cell) could serve as the basis of a solid-state registry number.

In this symmetry study, it was found that the lattice metric symmetry is closely correlated with the crystal-lattice symmetry. Thus any primitive cell of the lattice is sufficient not only to identify (register) a compound but also to determine its metric symmetry. Use of

reduced-cell techniques can save considerable time and prevent errors in symmetry determination, and they can reveal special structural features. For example, from the reduced cell, the experimentalist can quickly deduce whether he is dealing with a crystal of triclinic symmetry. If the reduced form is No. 31 or No. 44, the crystal lattice must be triclinic because its symmetry cannot exceed the metric symmetry. Sometimes a given reduced form may have more specialization than required. Such specialization can occur if one has determined a derivative lattice rather than the correct lattice or if the material has some unusual structural feature. In our evaluation of crystallographic data in the NBS and Cambridge Crystallographic Data Centers, we have noted that in some cases the correct symmetry is missed. For example, rhombohedral symmetry may be incorrectly reported as monoclinic. In our work, we have found that reduced-cell files ordered on the magnitude of the cell parameters are useful in symmetry evaluation because isostructural compounds will be grouped together. Other modes of sorting and various computer checks are also invaluable in the evaluation of the symmetry of a new compound with respect to existing substances.

This symmetry survey shows that methods based on the reduced cell are practical and efficient in the first step in the determination of crystal-lattice symmetry. A procedure that could be adapted to an automated diffractometer is summarized in Fig. 5. In this procedure, the diffractometer must first obtain a primitive cell of the lattice. Without special precautions, one may obtain a supercell in reciprocal space rather than the correct cell. Methods to check systematically for a primitive cell (once a supercell has been determined) have been briefly discussed by Mighell (1976). A

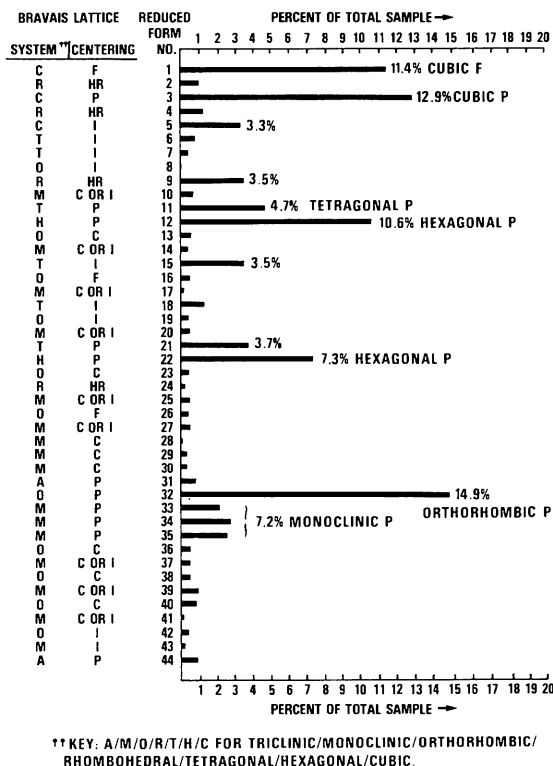


Fig. 2. Classification of inorganic materials by reduced form number. The figure shows the relative frequency of occurrence for each of the 44 reduced forms. Prepared from data for approximately 26 000 compounds in Vols 2 and 4 of *Crystal Data*.

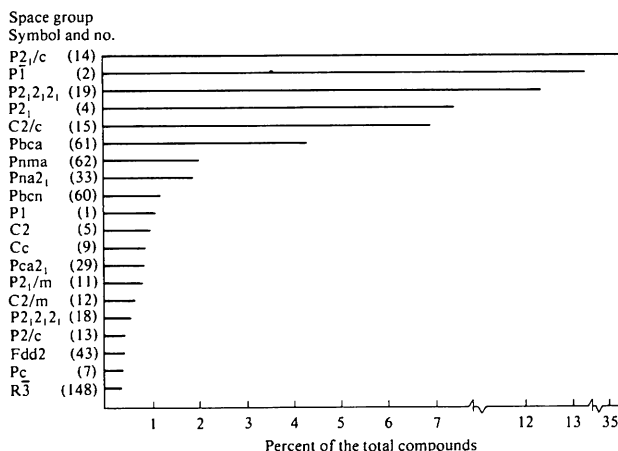


Fig. 3. Relative frequency of space-group occurrence for 21 051 organic crystalline compounds (compounds from same source as in Fig. 2). Our analysis shows that 75.7% of organic compounds crystallize in five space groups and that many space groups are uninhabited.

convenient algorithm for the calculation of the required subcells has been published in the appendix of a paper by Santoro & Mighell (1973).

Conclusion

Some recommendations based on this study are: (1) far more emphasis should be placed on cell determination and refinement algorithms, because of the basic importance of the metric lattice in crystallography; (2) errors in the cell parameters must be appropriately determined and treated (preferably by statistical methods) so that one obtains the correct reduced form and reduced form number; (3) one should prove that the angles fixed by symmetry (*e.g.* α and γ in the monoclinic system with b the unique axis) are at the required values by metric means as well as by analysis of equivalent intensities; (4) in those exceptional cases in which the lattice metric symmetry exceeds the crystal-lattice symmetry, structural reasons for the pseudo-symmetry should be sought; (5) as part of editorial review procedures (*e.g.* in crystallographic compilation work), the reported symmetry of the crystals should be

checked routinely by reduction procedures; (6) automated diffractometer procedures used in the determination of symmetry should be backed by traditional optical methods.

Finally, we wish to emphasize that it is the metric lattice of a crystalline compound that is so very important (with respect to characterization, symmetry determination, *etc.*) and that the reduced cell is only one way, although practical and convenient, to describe it. Various other methods to study the metric lattices will undoubtedly be developed. For example, a general procedure to study lattice and interlattice relationships has been devised which does not depend on reduction but rather on transformation matrices relating lattices (Santoro, Mighell & Rodgers, to be submitted to *Acta Crystallographica*).

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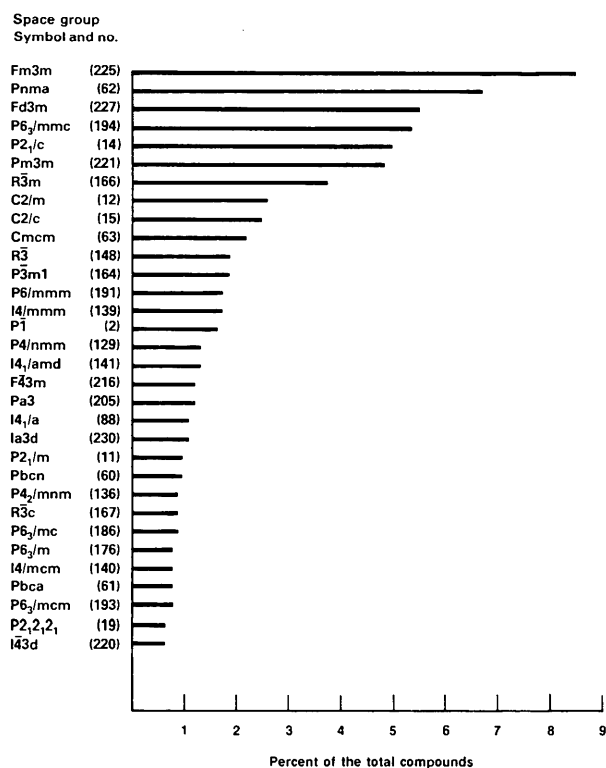


Fig. 4. Relative frequency of space-group occurrence for 11641 inorganic crystalline compounds (whose space groups are reported in the 3rd edition of *Crystal Data*). Our analysis shows that inorganic compounds are concentrated in relatively few space groups and that many space groups are uninhabited or sparsely populated. However, the concentration is not as great as with organic substances.

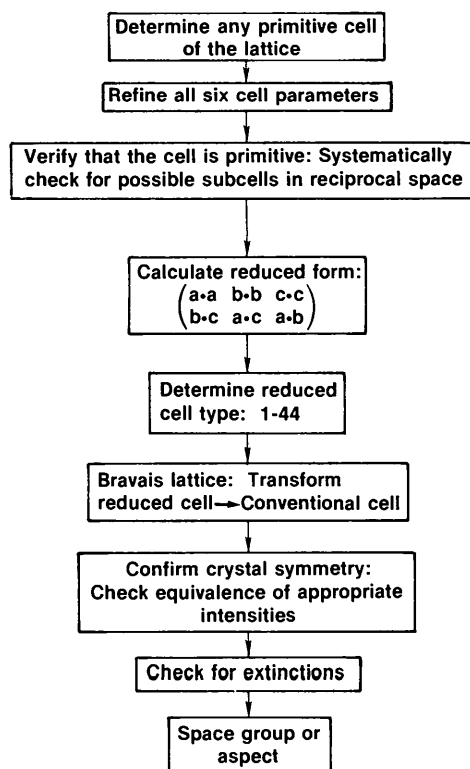


Fig. 5. Symmetry determination: the reduced cell as a routine tool. The crystal-lattice symmetry can never exceed the metric symmetry determined from the reduced cell, but it may be less. If the reduced form corresponds to a triclinic lattice, the crystal-lattice symmetry can only be triclinic; if the reduced form corresponds to a monoclinic lattice, the crystal system must be monoclinic or triclinic. This survey shows, however, that in most cases (97%) the reduced form leads directly to the correct crystal lattice.

Table 1. Metric classification

Reduced Form No.	Reduced Form Matrix			Reduced Form Type	Bravais Lattice	Cell Transformation Reduced → Conventional
	First Row	Second Row	Third Row			
a=b=c 1	a a b c c	b c	a b	+	Cubic	111/111/111
a=b≠c 2	a a a a a	a a / 2	a a / 2	+	Rhombohedral hR	110/101/111
3	a a a a a	b c	b c	+	Cubic	100/010/001
4	a a a a a	0	0	-	Rhombohedral hR	110/101/111
5	a a a a a	- b-c	- b-c	-	Cubic	101/110/011
6	a a a a a	a a / 3	a a / 3	-	Tetragonal	011/101/110
7	a a a a a	-a a + a b / 2	- a b	-	Tetragonal	101/110/011
8	a a a a a	-a a + b c / 2	- a a + b c / 2	-	Orthorhombic I	110/110/011
a=b 9	a a a a c c	a a / 2	a a / 2	+	Rhombohedral hR	100/110/113
10	a a a a c c	b c	b c	+	Monoclinic C**	110/110/001
11	a a a a c c	0	0	-	Tetragonal	100/010/001
12	a a a a c c	0	0	-	Hexagonal	100/010/001
13	a a a a c c	0	0	-	Orthorhombic C	110/110/001
14	a a a a c c	- b-c	- b-c	-	Monoclinic C**	110/110/001
15	a a a a c c	a a / 2	a a / 2	-	Tetragonal	100/010/112
16	a a a a c c	- b-c	- b-c	-	Orthorhombic F	110/110/112
17	a a a a c c	- b-c	- b-c	-	Monoclinic I††	101/110/011
b=c 18	a a b b b b	a a / 4	a a / 2	+	Tetragonal	011/111/100
19	a a b b b b	b c	a a / 2	+	Orthorhombic I	100/011/111
20	a a b b b b	b c	a c	+	Monoclinic C†	011/011/100
21	a a b b b b	0	0	-	Tetragonal	010/001/100
22	a a b b b b	b b / 2	0	-	Hexagonal	010/001/100
23	a a b b b b	- b-c	0	-	Orthorhombic C	011/011/100
24	a a b b b b	b b - a a / 3	-a a / 3	-	Rhombohedral hR	121/011/100
25	a a b b b b	- b-c	- a-c	-	Monoclinic C†	011/011/100

Reduced Form No.	Reduced Form Matrix			Reduced Form Type	Bravais Lattice	Cell Transformation Reduced → Conventional
	First Row†††	Second Row	Third Row			
a c b c c	a a b b c c	b c	a c	+	Orthorhombic F	100/120/102
26	a a b b c c	a a / 4	a a / 2	+	Monoclinic I***	011/100/111
27	a a b b c c	b c	a a / 2	+	Monoclinic C	100/102/010
28	a a b b c c	a b / 2	a b / 2	+	Monoclinic C	100/120/001
29	a a b b c c	a c / 2	a c / 2	+	Monoclinic C	010/012/100
30	a a b b c c	b b / 2	a b / 2	+	Monoclinic C	100/010/001
31	a a b b c c	b c	a c	+	Triclinic P	100/010/001
32	a a b b c c	0	0	-	Orthorhombic P	100/010/001
33	a a b b c c	0	- a-c	-	Monoclinic P	100/010/001
34	a a b b c c	0	0	-	Monoclinic P	100/001/010
35	a a b b c c	- b-c	0	-	Monoclinic P	010/100/001
36	a a b b c c	0	a a / 2	-	Orthorhombic C	100/102/010
37	a a b b c c	- b-c	a a / 2	-	Monoclinic C*	102/100/010
38	a a b b c c	0	0	-	Orthorhombic C	100/20/001
39	a a b b c c	- b-c	0	-	Monoclinic C**	120/100/001
40	a a b b c c	b b / 2	0	-	Orthorhombic C	010/012/100
41	a a b b c c	b b / 2	- a-c	-	Monoclinic C†	012/010/100
42	a a b b c c	b b / 2	a a / 2	-	Orthorhombic I	100/010/112
43	a a b b c c	b b - a b / 2	a a - a b / 2	-	Monoclinic I	100/112/010
44	a a b b c c	- b-c	- a-c	-	Triclinic P	100/010/001

† If a=a, 4|a-c|
 * If b=b, 4|b-c|
 ** If c=c, 4|b-c|
 †† If 3a=a', c=c+2|a-c|
 ††† If 3b=b', c=c+2|b-c|
 †††† No required relationships between symmetrical scalars for reduced forms 26-44.

Source: Table 5.1.3.1 prepared by Mighell, Santoro & Donnay for *International Tables for X-ray Crystallography* (1969). Revisions included.

Seidel for his assistance with the computer coding of the symmetry routines used in this analysis.

APPENDIX

In Table 1, the 44 reduced forms and the corresponding conventional cells are presented in a simple format. This table is a slight modification [*i.e.* it is a shortened version with appropriate *errata* and *addenda* (see Mighell, Santoro & Donnay, 1971, 1975, and Parthé & Hornstra, 1973)] of Table 5.1.3.1 which was prepared by A. D. Mighell, A. Santoro and J. D. H. Donnay for *International Tables for X-ray Crystallography* (1969). We have found a computer algorithm based on the table convenient for the critical evaluation of symmetry in our crystal-data work.

This table gives the transformation matrices relating the reduced cell to the corresponding conventional cell. For convenience, the reduced forms are first grouped in $a = b = c$, $a = b$, $b = c$, and $a \leq b \leq c$ (*i.e.* no special conditions other than those required for the reduced cell) categories and then further divided into positive and negative reduced forms. Also, we have found an alternative format, in which the reduced forms are arranged according to the Bravais lattice, to be convenient for the determination of symmetry.

Table conventions

The following conventions apply: (1) in the orthorhombic system, the axes of the primitive, body-centered, and face-centered lattices are labeled to obey $a < b < c$. The side-centered lattice is taken as *C* centered with $a < b$. (2) In the monoclinic system, b is taken as the unique axis, and a and c are chosen coincident with the shortest two translations in the net $(010)_0$. (To assure the shortest translations, the conditions in the footnote for the specified monoclinic lattices must be checked. In those cases for which the transformation matrix in the footnote premultiplies a given table matrix, the resultant lattice centering is indicated in parentheses following the transformation matrix.) The angle β is taken to be non-acute. This choice allows primitive, side-centered, and body-centered lattices. In the primitive and body-centered lattices a and c obey $a < c$. The side-centered lattice is taken as *C* centered. In the triclinic system, $a \leq b \leq c$.

Crystal-Data cell: For identification purposes, the cell obtained by applying the table matrix can be converted to the cell used in *Crystal Data* by applying one of the following transformations: Triclinic system; type I cell: $0\bar{1}0/00\bar{1}/100$; type II cell: $010/001/100$. Monoclinic system: *P* and *I* lattices: $00\bar{1}/0\bar{1}0/\bar{1}00$; *C* lattice: $100/010/001$ if $c < a$, $00\bar{1}/0\bar{1}0/\bar{1}00$ if $c > a$ (the resulting cell is *A* centered). Orthorhombic system: *P*, *I*, and *F* lattices: $010/001/100$; *C* lattice: $100/010/001$ if $c < a < b$, $00\bar{1}/0\bar{1}0/\bar{1}00$ if $a < c < b$ (the resulting cell is *A* centered), $010/001/100$ if $a < b < c$ (the resulting cell is *B* centered). No transformations are required in the hexagonal, tetragonal, and cubic systems. In the case of the rhombohedral lattice, note that the hexagonal coordinate axes (*hR*) are used.

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