the matrices of the Fourier transforms of mixing energies also for the Lifshitz points. The results of such a consideration are shown in Tables 8(a)–(c), 9(a)–(c) and 10(a)–(f) for the disordered solid solutions with f.c.c., b.c.c. and h.c.p. lattices.

Each of these tables presents the fragment of the matrix $\|\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})\|$ at some given α, β and given vector $\mathbf{k}$, which corresponds to one of the Lifshitz points of the structure under consideration. The convenient designations introduced by Bouckaert, Smoluchowski & Wigner (1936) for the high-symmetry points of reciprocal lattices are used. The symbol V is used for the designation of the real quantities. The additional requirements on matrix elements $\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})$, as in the case of the non-Lifshitz points, are (12) and (13). Note that for the Lifshitz points all matrix components $\tilde{w}_{pq}^{\alpha\beta}(\mathbf{k})$ necessary are real or imaginary. Moreover, the elements belonging to the same types of position (one of m, o and t) must be real.*

The analysis carried out in this work concerns the symmetry properties of the mixing potentials of the lowest orders (unary and binary) in disordered structures. Similarly (on the basis of the approach proposed in paper 1), the study of mixing potentials of higher orders and/or for ordered structures can be performed.

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* The block $\|\tilde{w}_{m_i m_j}(\mathbf{k})\|$ of the Fourier transforms of the mixing potential corresponding to the sites of a disordered h.c.p. binary solution was obtained by Sanchez, Gratias & de Fontaine (1982) and Zhorovkov (1993) both for arbitrary and for the high-symmetry points of reciprocal space. The same results for the block $\|\tilde{w}_{o_i o_j}(\mathbf{k})\|$ corresponding to the octahedral interstices of disordered b.c.c. binary solution were given by Khachaturyan (1978, 1983) for the cases of some high-symmetry points.

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Structural Classes and Space Groups of Organic Homomolecular Crystals: New Statistical Data

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Abstract

Structural classes (SC) are very useful for the description and consideration of molecular arrangements in crystals. The distribution of 19 642 organic homomolecular crystals among SC has been investigated. 305 SC having very unequal frequencies were discovered. A full list is given.

Introduction

The concept of structural class (SC), proposed by Zorky, Belsky, Lazareva & Porai-Koshits (1967), has proved to be very convenient for describing the general features of molecular arrangements connected with space symmetry. We sometimes say that the SC reflects 'the topology' of a molecular crystal (Zorky 1991). The meaning of this

term in structural chemistry differs from that accepted in mathematics. However, as in mathematical topology, numerical values of structural parameters do not play any role in assigning a substance to a certain SC.

A SC unites crystal substances with the same space group and the same list of systems of equivalent positions (orbits) occupied by molecules.* The canonical list of space groups and orbits (*International Tables for X-ray Crystallography*, 1974) is used here. By 'the molecule occupies a position', we mean that this position is occupied by a single point of the molecule, *e.g.* by the center of mass. Two distributions of molecules throughout orbits are, of course, not regarded as different SC if one of them can be transformed into another by transferring the origin or by renaming or changing the choice of coordinate axes (without violation of rules accepted in crystallography) (*International Tables for X-ray Crystallography*, 1974).

We have more than once presented the statistical data on the SC of homomolecular organic crystals (Belsky & Zorky, 1970, 1977; Chernikova, Belsky & Zorky, 1990), considering as organic those substances that contain carbon and only the following elements: H, B, Si, N, P, As, O, S, Se, Te, F, Cl, Br, I. Organometallic and very numerous chelate compounds have been excluded from consideration in order to limit the range of objects and thus to facilitate the solution of the problem.

In essence, our aim was to reveal the general picture of the structure of organic crystals. It seems likely that the regularities established for organic substances would remain unaltered if the range of objects included molecular compounds of metals as well. At the same time, a substantial restriction lies in the fact that we have considered only homomolecular crystals, *i.e.* crystals formed by chemically identical molecules, and only such crystals will be dealt with below. The statistical investigations on heteromolecular crystals, and not only organic ones, has also been initiated (Chernikova & Zorky, 1979; Zorky & Chernikova, 1985) but has not reached the necessary level of completeness.

A SC symbol includes a space group, a number of molecules per unit cell (Z) and an indication of the orbits occupied by molecules, these orbits being written in parentheses in the form of the point-group designations characterizing the symmetry of the positions. Molecules in the crystal most often occupy one orbit (monosystem crystals, $k = 1$). In this case, there is only one point group within the parentheses in the last part of the SC symbol, *e.g.* $C2/m$, $Z = 2(2/m)$, $C2/m$, $Z = 4(m)$, $P2_1/c$, $Z = 2(\bar{1})$, $P2_1/c$, $Z = 4(1)$. If molecules occupy k orbits (polysystem crystals), then the SC symbol includes k point-group symbols, *e.g.* the classes $P2_1/c$, $Z = 6(\bar{1},1)$ and $P2_1/c$, $Z = 8(1,1)$, which comprise

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* The short term 'orbit' is very useful. It is accepted both in mathematics (Curtis & Reiner, 1962) and in crystallography (Senechal, 1975; Wondratschek, 1976). In our papers we have used this term since 1982 (Zorky, 1982).

bisystem structures, and the class $P2_1/c$, $Z = 8(\bar{1},\bar{1},1)$, which comprises trisystem structures. These examples show that molecules in the crystal can occupy positions with equal or different symmetries. For brevity, the enumeration of orbits of the same type is replaced by a superscript which indicates the number of such orbits, *e.g.* $P2_1/c$, $Z = 8(\bar{1}^2,1)$, $P2_1/c$, $Z = 16(1^4)$. We believe that, while discussing the stucture of a molecular crystal, it is much more natural to speak about the number and about the type of occupied orbits than about the number of formula units per 'asymmetric unit' (Z'), which is popular among crystallographers but unclear in respect of molecular arrangement in crystal structure.

Note that the SC symbols described above are in some cases ambiguous. For example, the symbol $Pnna$, $Z = 4(2)$ actually corresponds to two different SC, since molecules can be located on axes 2 that are parallel to either axis X or axis Z. These two cases are distinguishable and cannot be transformed into one another by means of an alteration of the crystallographic system of coordinates. In the tables of space groups, these orbits have designations c and d. Hence, for definiteness one may use symbols $Pnna$, $Z = 4(2_c)$ and $Pnna$, $Z = 4(2_d)$. Similarly, the ambiguity of the standard SC symbol $P2_1/c$, $Z = 4(\bar{1}^2)$ is removed by means of designations $P2_1/c$, $Z = 4(\bar{1}_a\bar{1}_b)$ and $P2_1/c$, $Z = 4(\bar{1}_a\bar{1}_c)$ (the other combinations of centrosymmetric positions give arrangements that can be reduced to those mentioned). However, such ambiguities occur rather rarely and there is no point in making standard symbols more complicated because of them. We use such refining designations only when this is necessary.

The SC of monosystem crystals (we shall call them monosystem SC below) fall into three types: A – all molecules in the crystal are either left (L) or right (D) (optically active crystals); B – the crystal consists of enantiomeric molecules L and D (racemates); C – molecules in the crystal are achiral (sometimes it is convenient to call such molecules 'inner racemates'). Here, we mean that the chirality of a molecule is determined by the symmetry of its position and not only by the symmetry of an isolated molecule. Accordingly, the space group included in a SC of type A is chiral, and that included in a SC of type B or C is achiral.

For polysystem crystals, the similar classification of SC presents a rather difficult problem. An attempt to solve it was made by Zorky, Razumaeva & Belsky (1977), but did not produce practical results beause, in this case, a more detailed consideration of particular structures was required.

Naturally, the study of the distribution of molecular crystals by structural classes automatically gives their distribution by space groups and by crystallographic systems (syngonies). Such data are interesting and perhaps even instructive, but they hardly have deep physical meaning. The point is that the molecular arrangements described by the same space group are in

many cases very different (examples are the above SC belonging to the space group $P2_1/c$), and *vice versa*, SC belonging to entirely different space groups, and even to different syngonies, may be closely related. For example, crystals of the classes $P2_1$, $Z = 2(1)$ and $P2_12_12_1$, $Z = 4(1)$ are often made up of chains of the same type, arranged parallel in the former case and antiparallel in the latter. In this work, we have not considered it reasonable to present the distribution of homomolecular organic crystals by space groups but it can be easily derived from the data given below.

The space group by itself is, therefore, not an adequate characteristic of the arrangement of molecules in a crystal. Hence, it cannot serve as the starting point for the interpretation of this arrangement. By adding the list of occupied orbits to the space group we come to a substantially more meaningful description of the structure of the molecular crystal. Therefore, we had started using structural classes very early in our studies on this matter (Zorky, Belsky, Lazareva & Porai-Koshits, 1967).

In his monographs, Kitaigorodskii (1961, 1973) spoke about space groups but in effect he usually meant some more precise information about the arrangement of molecules. The representations of molecular packings that he used correspond, in reality, to structural classes. In their statistical studies, other authors (Padmaya, Ramakumar & Viswamitra, 1990; Scaringe, 1991; Wilson, 1988, 1990, 1991, 1993; Brock & Dunitz, 1994) tried to take into account the specific features of crystal structure that are not reflected in the space group as such, by considering the number of molecules in the 'asymmetric unit' (Z'). However, this criterion has too general a character. We believe that only the SC symbol, in which the orbits occupied by molecules are explicitly enumerated, gives the possibility of an adequate consideration of the crystal structure (naturally, this gives the information about Z' too).

It is important to ensure the uniformity of the objects of statistical investigation. However, very different distributions by space groups may occur for different classes of chemical compounds. For example, cubic, hexagonal and tetragonal symmetry is very common or even prevails in binary compounds AX and AX_2, where A is a metal and X is a nonmetal, while for organic substances high symmetry is not typical. Significant specific features will also be found in the salts of organic acids with alkaline and alkaline-earth metals [in Chernikova & Zorky (1979), Zorky & Chernikova (1985), we class them as heteromolecular], while quite different structural features will be characteristic of the salts of transition metals (very often such substances can in no way be classed as molecular crystals).

In our opinion, there is no point in seeking common features of distribution by space groups or by SC for objects that have a completely dissimilar crystallo-chemical nature. In this work, we attempt to deal with the substances composed of physically, not formally, distinguishable molecules. Accordingly, we find ways of treating the cases noted by Brock & Dunitz (1994):

(1) $NaH(CH_3COO)_2$ crystals are not homomolecular; they can be considered only within a set of objects of their type. Such a consideration is undoubtedly of much interest, but it is beyond the purpose of our work. Moreover, according to the formal criterion we have accepted, these crystals are not organic.

(2) $Be_4O(CH_3COO)_6$ crystals also are not organic according to our system and hence do not appear in our statistics. However, they are typical homomolecular crystals and in principle they can be treated within the set of such objects, being attributed to the class $Fd3$, $Z = 8(23)$.

Apparently, the statistical approach to revealing any regularities will be effective only if the method of selection and classification of the material implies, in a somewhat definite form, a method of interpretation based on physical principles. As such a physical basis, Kitaigorodski (1961, 1973) used the theory of dense molecular packing, whereas we used the method of potential-function symmetry (MPFS) (Zorky, 1968, 1982; Zorky, Potekhin & Dashevskaya, 1993).

Sources of statistical data and the technique of their processing

The data on organic homomolecular crystal structures published in 1929–1973 have been collected and distributed among SC in reference books (Kitaigorodskii, Zorky & Belsky, 1980, 1982). The main source of information for compiling these books, as well as of the information on the structures studied in 1974–1992, was the journal of abstracts *Khimiya* (RZhKhim) published by the All-Russian Institute of Scientific and Technical Information (VINITI). Issues of the journal up to and including No. 7, 1993, have been processed and used for statistical calculations. This allowed us to work with the data on 19 642 structures [in Belsky & Zorky (1977), 5022 structures were considered, and Chernikova, Belsky & Zorky (1990) dealt with 15 282 structures].

The data on the distribution of organic crystals are accumulated in two files. The first one is in the Crystal Chemistry Laboratory of the Chemistry Department of Moscow University (at different times it was worked on by N. Yu. Chernikova, E. E. Dashevskaya, Ya. M. Nesterova, and O. N. Zorkaya). It contains the data on the structures published in 1974–1992 subdivided into SC. For the period from 1974 to 1987, the file contains data on all discovered SC; for the period from 1988 to 1991, the structures belonging to the 14 most common SC, called 'giants', were excluded (the contribution of every such SC is over 1%); for 1992, the 'giants', as well as 12 other SC, called 'big' (the contribution of each of them is over 0.25%), were excluded too. These

exclusions were due to the loss of interest in typical ways of formation of molecular arrangements, as their contribution to the general picture of the structure of molecular crystals is already well studied (their frequencies practically do not change with the increase of the number of considered objects) and has been successfully interpreted on the basis of MPFS (Zorky & Belsky, 1972).

The second file (and the corresponding computer database) is being built up by V. K. Belsky at L. Ya. Karpov Institute of Physical Chemistry, Moscow. In this file, substances are arranged according to their chemical features in compliance with the Beilstein System (Prager, Stern & Ilberg, 1929), which we have used in a reference book (Kitaigorodskii, Zorky & Belsky, 1984). The file is, in effect, the continuation of this book. At the same time, every object put into the file is taken into account in the statistical calculations of SC frequencies. These calculations have formed the factual basis of the present work. In V. K. Belsky's database (VBD), particular attention is given to anomalous SC, which are represented by no more than five compounds. The register of anomalous SC, as well as the Moscow University file, are planned to be used in the future for a more detailed study of molecular arrangements in crystals.

In many cases, when an RZhKhim abstract did not give unambiguous information about the SC, we had to consult primary sources, i.e. journal papers. However, even the original paper does not always give all the necessary information. In some cases, original studies were inaccessible for us. As a result, our work has inevitable omissions; their number, however, is apparently very low. Besides, since in most cases the assigning of a substance to a particular SC was not accompanied by a thorough study of the primary source, in the future there may be some refinements of the data presented here.

It was not our aim to establish the exact relationship between our database and the Cambridge Stuctural Database (CSD) (Allen, Kennard & Taylor, 1983). This would be difficult to achieve, as the CSD contains data not only on molecular crystals and homomolecular crystals are in no way differentiated.

The statistical data on which we based the present work cover publications of structural studies up to 1991 inclusive and more than half of the 1992 publications.

Results and discussion

As a result of our work, 305 SC have been discovered. There were 190 SC in Belsky & Zorky (1977) and 283 SC in Chernikova, Belsky & Zorky (1990). We noted (Chernikova, Belsky & Zorky, 1990) that the number of SC continued to grow fairly rapidly: 5–10 (on average about 7) new SC were discovered annually from 1974 to 1987. In the following five years, there appeared a trend towards the reduction of this number: about five new SC

were added each year [authors of X-ray structural studies still do not notice the appearance of a new way of molecular arrangement in the crystal, although Chernikova, Belsky & Zorky (1990), as well as the present work, seem to offer such a possibility]. There are strong reasons to believe that, in the future, new SC will be found still more rarely.

As has long been known, crystal structures are very unevenly distributed among classes. Fourteen of the most typical SC (Table 1) contain 85% of crystals (we call these SC 'giants'). The first six 'supergiants' account for 69% of organic homomolecular crystals, and the SC with the greatest number of representatives, which is the class $P2_1/c, Z = 4(1)$, contains almost one third of the crystals under consideration. It is curious that the share of this class slightly increases as years pass. However, the frequencies of occurence of 'giants' have changed very little compared with Chernikova, Belsky & Zorky (1990). This indicates that the volume of statistical data is sufficently large, and that these data adequately reflect the general picture of the structure of homomolecular crystals.

Besides 'giants', it is convenient to distinguish 'big' SC, each having more than 49 representatives of structures, and 'small' SC, containing no fewer than 20 representatives, as well as 'rare' and 'anomalous' SC (Table 2). Among anomalous SC, also called 'monsters', there are 117 'unique' SC, each being represented by only one structure.

The full list of SC that we have registered is given in Table 3. The sequence of the SC is determined by the numeration of space groups (*International Tables for X-ray Crystallography*, 1974) (the extreme left column). Within each group, SC are arranged in order of increasing Z, and at a given Z the SC with molecules in special positions are listed first, the SC with molecules in general positions next.

The SC that have been added to the list of Chernikova, Belsky & Zorky (1990) are marked + (after the SC symbol), ambiguous symbols are marked * (before the SC symbol). The systemization of SC according to their occurence is reflected by means of marks prefixing the number of known representatives in the following way: !! supergiants, ! other giants, oo big classes, o small classes.

Within the scope of this work, it was not possible to remove the ambiguity that exists in the asterisked symbols, for this would require a far more detailed analysis of each particular structure. We should note, however, that a more scrupulous approach to these cases can slightly change some of the above figures. For example, the total number of SC known for the considered substances will most probably increase a little. This is evident from the fact that some of the ambiguous symbols can correspond to two or more SC. However, this increase cannot be large. Table 3 has 36 ambiguous symbols but only in 20 cases can such

Table 1. *Typical structural classes*

Structural class	Number of structures	% of structures of named type	% of total number of structures 1977*	1990†	This work
Monosystem classes					
Type A					
$P2_12_12_1, Z = 4(1)$	2795	59.9	16.0	14.7	14.2
$P2_1, Z = 2(1)$	1327	28.5	7.0	7.1	6.8
Type B					
$P2_1/c, Z = 4(1)$	5951	54.9	28.6	29.7	30.3
$P\bar{1}, Z = 2(1)$	1796	16.6	5.8	8.7	9.1
$Pbca, Z = 8(1)$	827	7.6	4.1	4.3	4.2
$C2/c, Z = 8(1)$	587	5.4	2.7	2.9	3.0
$C2/c, Z = 4(2)$	365	3.4	2.6	1.9	1.9
$Pna2_1, Z = 4(1)$	367	3.4	2.1	2.0	1.9
Type C					
$P2_1/c, Z = 2(\bar{1})$	828	42.0	6.2	4.4	4.2
$P\bar{1}, Z = 1(\bar{1})$	269	13.6	1.9	1.5	1.4
$Pnma, Z = 4(m)$	241	12.2	1.9	1.3	1.2
Bisystem classes					
$P2_1/c, Z = 8(1^2)$	594	–	2.5	2.9	3.0
$P\bar{1}, Z = 4(1^2)$	398	–	–	1.8	2.0
$P2_1, Z = 4(1^2)$	289	–	1.3	1.4	1.5

* Belsky & Zorky (1977).
† Chernikova, Belsky & Zorky (1990).

Table 2. *The systematization of structural classes in accordance with their frequencies*

Groups of SC	Range	Number of SC	Number of structures	Total contribution (%)
Supergiants	More than 4%	6	13524	68.9
Other giants	More than 1%	8	3110	15.8
Big SC	0.25–1.0%	13	1285	6.5
Small SC	0.10–0.25%	24	782	4.0
Rare SC	6–19 structures	55	587	3.0
Anomalous SC (monsters)	No more than 5 structures	199	354	1.8
Total		305	19642	100

Table 3. *Structural classes of organic homomolecular crystals*

	Structural class		Number of structures
1	$P1, Z = 1(1)$	oo	90
	$P1, Z = 2(1^2)$	oo	55
	$P1, Z = 3(1^3)$		7
	$P1, Z = 4(1^4)$		9
	$P1, Z = 6(1^6)+$		1
	$P1, Z = 8(1^8)$		3
	$P1, Z = 16(1^{16})$		1
2	$P\bar{1}, Z = 1(\bar{1})$	!	269
	$P\bar{1}, Z = 2(\bar{1}^2)$	oo	56
	$P\bar{1}, Z = 2(1)$	!!	1796
	$P\bar{1}, Z = 3(\bar{1}^3)$		1
	$P\bar{1}, Z = 3(\bar{1}, 1)$		9
	$P\bar{1}, Z = 4(\bar{1}^4)$		4
	$P\bar{1}, Z = 4(\bar{1}^2, 1)$		1
	$P\bar{1}, Z = 4(1^2)$	!	398
	$P\bar{1}, Z = 6(1^3)$	o	27
	$P\bar{1}, Z = 8(1^4)$		16
	$P\bar{1}, Z = 12(1^6)$		2
	$P\bar{1}, Z = 16(1^8)$		1
3	$*P2, Z = 2(2^2)$		1
4	$P2_1, Z = 2(1)$	!!	1327
	$P2_1, Z = 4(1^2)$	!	289
	$P2_1, Z = 6(1^3)$		14
	$P2_1, Z = 8(1^4)$		16
	$P2_1, Z = 12(1^6)$		1
5	$C2, Z = 2(2)$		18
	$*C2, Z = 4(2^2)$		5
	$C2, Z = 4(1)$	oo	109
	$C2, Z = 6(2, 1)$		3
	$C2, Z = 8(1^2)$		15
	$C2, Z = 12(1^3)$		1
	$C2, Z = 16(1^4)+$		1
6	$*Pm, Z = 4(m^4)$		1
7	$Pc, Z = 2(1)$	oo	58
	$Pc, Z = 4(1^2)$		14
	$Pc, Z = 6(1^3)$		1
	$Pc, Z = 8(1^4)$		2
8	$Cm, Z = 2(m)$		6
	$Cm, Z = 6(m, 1)$		1
9	$Cc, Z = 4(1)$	oo	144
	$Cc, Z = 8(1^2)$		18
	$Cc, Z = 12(1^3)$		2
	$Cc, Z = 16(1^4)$		3
10	$P2_1/m, Z = 2(m)$		1
11	$P2_1/m, Z = 2(m)$	oo	87
	$P2_1/m, Z = 4(m^2)$		3
12	$C2/m, Z = 2(2/m)$	o	20
	$*C2/m, Z = 4[(2/m)^2]$		4
	$C2/m, Z = 4(2)$		1
	$C2/m, Z = 4(m)$		16
	$C2/m, Z = 6(2/m, m)$		1
	$C2/m, Z = 8(m^2)+$		1
13	$P2/c, Z = 2(\bar{1})$		2
	$P2/c, Z = 2(2)$		12
	$*P2/c, Z = 4(2^2)$		6
	$P2/c, Z = 4(\bar{1}, 2)$		1
	$P2/c, Z = 4(1)$		11
	$P2/c, Z = 6(2, 1)$		1
	$*P2/c, Z = 8(2^2, 1)$		1
	$P2/c, Z = 8(1^2)+$		2
14	$P2_1/c, Z = 2(\bar{1})$	!!	828
	$*P2_1/c, Z = 4(\bar{1}^2)$	o	44
	$P2_1/c, Z = 4(1)$	!!	5951
	$*P2_1/c, Z = 6(\bar{1}^3)+$		1
	$P2_1/c, Z = 6(\bar{1}, 1)$		13
	$*P2_1/c, Z = 8(\bar{1}^2, 1)$		3
	$P2_1/c, Z = 8(1^2)$	!	594
	$P2_1/c, Z = 12(1^3)$	o	24
	$P2_1/c, Z = 16(1^4)$		13
	$P2_1/c, Z = 24(1^6)$		1

symbols correspond to two different SC (and not more, for in most such cases only two SC corresponding to a given symbol are possible, and when there are more such SC, only two representatives are known). Hence, there will be no more than 20 additional SC. In actual fact, their number is certain to be substantially smaller. The probability of realization of different SC corresponding to the same ambiguous symbol is by no means the same, and most probably all (or nearly all) representatives corresponding to this symbol will prove to be 'classmates'. Thus, in Zorky & Kukina (1981), we have considered 19 structures with the symmetry $P2_1/c$, in which molecules occupy two systems of inversion centers. They have all been found to belong to the class $P2_1/c$, $Z = 4(\bar{1}_a, \bar{1}_b)$, and no representative of the class $P2_1/c$, $Z = 4(\bar{1}_a, \bar{1}_c)$ has been found.

Yet another circumstance that should be noted while discussing Table 3 is that in some cases the structural class (and the space group) is only an effective, an average, characteristic of the substance. Such cases are structures with partial disorder. On the basis of X-ray

Table 3 (*cont.*)

	Structural class		Number of structures
15	$C2/c, Z = 4(\bar{1})$	oo	93
	$C2/c, Z = 4(2)$	!	365
	*$C2/c, Z = 8(\bar{1}^2)$		2
	$C2/c, Z = 8(2^2)$		4
	$C2/c, Z = 8(1)$	!	587
	$C2/c, Z = 12(\bar{1}, 1)+$		2
	$C2/c, Z = 12(2, 1)$		10
	$C2/c, Z = 16(\bar{1}, 2, 1)$		1
	$C2/c, Z = 16(2^2, 1)+$		1
	$C2/c, Z = 16(1^2)$	o	37
	$C2/c, Z = 24(1^3)$		8
	$C2/c, Z = 32(1^4)$		3
	$C2/c, Z = 40(1^5)$		1
	$C2/c, Z = 48(1^6)$		1
18	$P2_12_12, Z = 2(2)$	o	25
	$P2_12_12, Z = 4(1)$	o	30
	$P2_12_12, Z = 8(1^2)+$		1
19	$P2_12_12_1, Z = 4(1)$	!!	2795
	$P2_12_12_1, Z = 8(1^2)$	oo	177
	$P2_12_12_1, Z = 12(1^3)$		14
	$P2_12_12_1, Z = 16(1^4)$		7
20	$C222_1, Z = 4(2)$		5
	*$C222_1, Z = 8(2^2)$		2
	$C222_1, Z = 8(1)$		11
	$C222_1, Z = 12(2, 1)$		1
	$C222_1, Z = 16(1^2)$		1
23	$I222, Z = 4(2)$		1
26	*$Pmc2_1, Z = 4(m^2)$		5
27	$Pcc2, Z = 4(1)+$		1
29	$Pca2_1, Z = 4(1)$	oo	153
	$Pca2_1, Z = 8(1^2)$	o	42
	$Pca2_1, Z = 12(1^3)$		1
30	*$Pnc2, Z = 4(2^2)$		1
	$Pnc2, Z = 4(1)$		1
	$Pnc2, Z = 8(1^2)+$		1
31	$Pmn2_1, Z = 2(m)$		16
	$Pmn2_1, Z = 8(m^2, 1)$		1
32	*$Pba2, Z = 4(2^2)$		1
	$Pba2, Z = 4(1)$		1
	$Pba2, Z = 8(1^2)$		1
33	$Pna2_1, Z = 4(1)$	!	367
	$Pna2_1, Z = 8(1^2)$	o	36
	$Pna2_1, Z = 12(1^3)$		2
	$Pna2_1, Z = 16(1^4)$		1
34	$Pnn2, Z = 2(2)$		2
	$Pnn2, Z = 4(1)$		1
36	$Cmc2_1, Z = 4(m)$	o	34
	$Cmc2_1, Z = 8(m^2)$		1
	$Cmc2_1, Z = 12(m, 1)$		1
37	$Ccc2, Z = 4(2)$		1
39	$Abm2, z = 4(m)$		2
41	$Aba2, Z = 4(2)$		9
	$Aba2, Z = 8(1)$		11
	$Aba2, Z = 12(2, 1)+$		1
	$Aba2, Z = 16(1^2)$		1
42	$Fmm2, Z = 4(mm)$		2
43	$Fdd2, Z = 8(2)$	o	44
	$Fdd2, Z = 16(1)$	o	35
45	$Iba2, Z = 4(2)$		2
	$Iba2, Z = 8(1)$		14
	$Iba2, Z = 16(1^2)$		2
	$Iba2, Z = 32(1^4)$		1
52	*$Pnna, Z = 4(2)$		4
	*$Pnna, Z = 8(2^2)$		1
	$Pnna, Z = 8(1)$		1
53	*$Pmna, Z = 8(2, m)$		2
54	*$Pcca, Z = 4(2)$		2
	*$Pcca, Z = 8(\bar{1}, 2)$		1
	$Pcca, Z = 8(1)$		3
55	$Pbam, Z = 4(m)$		2
	$Pbam, Z = 4(2)$		1
	*$Pbam, Z = 8(m^2)$		1

Table 3 (*cont.*)

	Structural class		Number of structures
56	$Pccn, Z = 4(\bar{1})$		7
	$Pccn, Z = 4(2)$		19
	*$Pccn, Z = 8(2^2)$		1
	$Pccn, Z = 8(1)$	o	37
	$Pccn, Z = 12(2, 1)$		1
	$Pccn, Z = 16(1^2)$		4
57	$Pbcm, Z = 4(m)$		17
58	$Pnnm, Z = 2(2/m)$		4
	$Pnnm, Z = 4(m)$		1
	$Pnnm, Z = 6(2/m, m)+$		1
59	$Pmmn, Z = 2(mm)$		3
	*$Pmmn, Z = 4[(mm)^2]$		1
60	$Pbcn, Z = 4(\bar{1})$		6
	$Pbcn, Z = 4(2)$	oo	101
	$Pbcn, Z = 8(1)$	oo	60
	$Pbcn, Z = 12(\bar{1}, 1)$		1
	$Pbcn, Z = 12(2, 1)$		3
	$Pbcn, Z = 16(1^2)$		2
	$Pbcn, Z = 24(1^3)$		2
61	$Pbca, Z = 4(\bar{1})$	oo	102
	$Pbca, Z = 8(1)$	!!	827
	$Pbca, Z = 16(1^2)$	o	41
	$Pbca, Z = 24(1^3)$		1
	$Pbca, Z = 40(1^5)$		1
62	$Pnma, Z = 4(m)$	!	241
	$Pnma, Z = 8(m^2)$		6
	$Pnma, Z = 12(m, 1)$		1
	$Pnma, Z = 36(m, 1^4)+$		1
63	$Cmcm, Z = 4(2/m)$		1
	$Cmcm, Z = 4(mm)$		16
64	$Cmca, Z = 4(2/m)$	o	20
	$Cmca, Z = 8(m)$		9
68	$Ccca, Z = 4(222)$		4
70	$Fddd, Z = 8(222)$		2
	$Fddd, Z = 16(2)$		4
	$Fddd, Z = 32(1)$		2
72	$Ibam, Z = 4(2/m)$		3
	$Ibam, Z = 8(m)$		4
73	$Ibca, Z = 8(\bar{1})$		1
	$Ibca, Z = 8(2)$		1
76	$P4_1, Z = 4(1)$	o	40
	$P4_1, Z = 8(1^2)$		5
77	$P4_2, Z = 4(1)$		1
79	$I4, Z = 2(4)$		1
	$I4, Z = 8(1)$		3
80	$I4_1, Z = 4(2)$		2
	$I4_1, Z = 8(2^2)$		1
	$I4_1, Z = 8(1)$		3
	$I4_1, Z = 16(1^2)$		3
81	$P\bar{4}, Z = 8(1^2)$		1
82	$I\bar{4}, Z = 2(4)$		6
	$I\bar{4}, Z = 4(2)$		1
	$I\bar{4}, Z = 8(1)$		7
84	$P4_2/m, Z = 4(m)$		1
85	$P4/n, Z = 2(4)$		2
	$P4/n, Z = 2(\bar{4})$		1
	$P4/n, Z = 4(\bar{4}^2)$		1
	$P4/n, Z = 8(1)+$		1
86	$P4_2/n, Z = 2(\bar{4})$		3
	$P4_2/n, Z = 4(\bar{4}^2)$		6
	$P4_2/n, Z = 4(2)$		5
	$P4_2/n, Z = 8(1)$	o	20
	$P4_2/n, Z = 10(\bar{4}, 1)$		1
87	$I4/m, Z = 2(4/m)+$		1
88	$I4_1/a, Z = 4(\bar{4})$		12
	$I4_1/a, Z = 8(\bar{1}^2)$		4
	$I4_1/a, Z = 8(2)$		6
	$I4_1/a, Z = 16(1)$	o	29
91	$P4_122, Z = 8(1)$		1
92	$P4_12_12, Z = 4(2)$	o	42
	$P4_12_12, Z = 8(2^2)$		1
	$P4_12_12, Z = 8(1)$	o	49
	$P4_12_12, Z = 12(2, 1)+$		1
	$P4_12_12, Z = 16(1^2)$		1
	$P4_12_12, Z = 32(1^4)$		1

Table 3 (cont.)

	Structural class	Number of structures
94	$P4_22_12, Z = 8(1)+$	1
101	$P4_2cm, Z = 4(m)$	2
102	$P4_2nm, Z = 4(m)$	1
104	$P4nc, Z = 2(4)$	1
106	$P4_2bc, Z = 4(2)$	1
	$P4_2bc, Z = 8(1)+$	1
109	$P4_1md, Z = 8(m)$	1
110	$I4_1cd, Z = 8(2)$	5
	$I4_1cd, Z = 16(1)$	5
113	$P\bar{4}2_1m, Z = 2(mm)$	4
	$P\bar{4}2_1m, Z = 4(m)$	2
114	$P\bar{4}2_1c, Z = 2(4)$	17
	$*P\bar{4}2_1c, Z = 4(2)$	2
	$P\bar{4}2_1c, Z = 8(1)$	12
	$*P\bar{4}2_1c, Z = 12(2^3)+$	1
115	$*P\bar{4}m2, Z = 32[(mm)^4, m^4, 1]$	1
118	$P\bar{4}n2, Z = 2(222)$	2
121	$I\bar{4}2m, Z = 2(\bar{4}2m)$	3
122	$I\bar{4}2d, Z = 4(4)$	1
	$*I\bar{4}2d, Z = 8(2)$	2
126	$P4/nnc, Z = 2(422)$	1
	$P4/nnc, Z = 4(4)$	1
128	$P4/mnc, Z = 8(m)$	1
130	$P4/ncc, Z = 4(222)$	1
135	$*P4_2/mbc, Z = 4(2/m)+$	1
	$P4_2/mbc, Z = 8(m)$	1
136	$P4_2/mnm, Z = 2(mmm)$	6
137	$P4_2/nmc, Z = 2(\bar{4}2m)$	2
139	$I4/mmm, Z = 2(4/mmm)$	1
141	$I4_1/amd, Z = 4(\bar{4}2m)$	2
142	$I4_1/acd, Z = 8(222)$	3
	$I4_1/acd, Z = 8(\bar{4})$	1
	$*I4_1/acd, Z = 16(2)$	2
144	$P3_1, Z = 3(1)$ ○	33
	$P3_1, Z = 6(1^2)$	1
	$P3_1, Z = 9(1^3)$	2
	$P3_1, Z = 27(1^9)$	1
146	$R3, Z = 3(3)$	8
	$R3, Z = 9(1)$	11
	$R3, Z = 18(1^2)$	2
147	$*P\bar{3}, Z = 2(3)$	9
	$*P\bar{3}, Z = 6(3^3)$	3
	$P\bar{3}, Z = 6(1)$	1
	$P\bar{3}, Z = 18(1^3)$	1
148	$R\bar{3}, Z = 3(3)$	6
	$R\bar{3}, Z = 6(3)$ ○	21
	$R\bar{3}, Z = 9(1)$	5
	$R\bar{3}, Z = 12(3^2, 3)$	1
	$R\bar{3}, Z = 18(1)$ ○	30
	$R\bar{3}, Z = 54(1^3)$	1
152	$P3_121, Z = 3(2)$	8
	$P3_121, Z = 6(1)$	10
160	$R3m, Z = 3(3m)$	10
161	$R3c, Z = 6(3)$	11
	$R3c, Z = 18(1)$	7
163	$P\bar{3}c1, Z = 2(3)$	1
	$P\bar{3}c1, Z = 6(2)$	1
	$P\bar{3}c1, Z = 18(2, 1)+$	1
166	$R\bar{3}m, Z = 3(3m)$	2
	$R\bar{3}m, Z = 6(3m)+$	1
167	$R\bar{3}c, Z = 6(3)$	2
	$R\bar{3}c, Z = 6(32)$	5
	$R\bar{3}c, Z = 18(2)$	1
169	$P6_1, Z = 6(1)$ ○	22
	$P6_1, Z = 12(1^2)$	1
171	$*P6_2, Z = 3(2)$	1
	$P6_2, Z = 6(1)$	1
173	$*P6_3, Z = 2(3)$	7
176	$*P6_3/m, Z = 2(\bar{6})$	12
	$P6_3/m, Z = 6(m)$	7
178	$*P6_122, Z = 6(2)$	4
	$P6_122, Z = 12(1)$	2
182	$P6_322, Z = 12(1)$	1
185	$P6_3cm, Z = 2(3m)$	1

Table 3 (cont.)

	Structural class	Number of structures
186	$*P6_3mc, Z = 2(3m)$	3
190	$P\bar{6}2c, Z = 6(m)$	3
192	$P6/mcc, Z = 36(m^3)$	1
194	$*P6_3/mmc, Z = 2(\bar{6}m2)$	1
198	$P2_13, Z = 4(3)$	2
202	$Fm3, Z = 4(m3)$	2
204	$Im3, Z = 6(mmm)$	1
205	$Pa3, Z = 4(\bar{3})$	7
	$Pa3, Z = 8(3)$	2
217	$I\bar{4}3m, Z = 2(\bar{4}3m)$	4
218	$P\bar{4}3n, Z = 8(23, \bar{4})+$	1
219	$F\bar{4}3c, Z = 8(23)$	1
225	$Fm3m, Z = 4(m3m)$	9
229	$Im3m, Z = 2(m3m)$	2
	$Im3m, Z = 16(3m)$	1

analysis, such disorder is described as a statistical arrangement of some fragments of molecules (and in some cases of whole molecules) in two or more positions, which most often differ from each other by a rotation about some straight line, e.g. about a single bond. However, this picture is often incorrect. In reality, the crystals consist of completely ordered coherently conjugated domains of two types. The real SC of the crystal substance within a domain differs from the effective SC, which is attributed to the crystal on the basis of the diffraction picture produced by different domains. Examples of this kind are described by Zorky & Nesterova (1986, 1990). A similar situation may occur due to intralayer polytypism (Zorky & Nesterova, 1993). In all these cases, the effective SC of the crystal does not reflect its structure adequately.

Although the mentioned nuances require, strictly speaking, some corrections, they cannot substantially influence the picture of the structure of organic homomolecular crystals that we derive from Table 3. Let us note some general features of this picture.

Table 4 shows the distribution of the crystals under consideration by crystallographic systems (syngonies) compared with the data of other authors. It is remarkable that in comparison with the distribution given by Belsky & Zorky (1977), where four times fewer structures had been used, the only appreciable difference is that the share of the triclinic syngony has increased by 4% exclusively at the expense of the orthogonal system. We are inclined to attribute this to the fact that in the 1950s and 1960s, when most of these 5000 structures were studied, the analysis of triclinic systems presented a difficult problem for many researchers and they preferred to deal with orthogonal crystals.

Our data differ, also mainly in the ratio between the numbers of triclinic and orthogonal crystals, from the results of Padmaya, Ramakumar & Viswamitra (1990) and Brock & Dunitz (1994), where the share of triclinic structures was found to be still larger. This fact is apparently due to the contribution of heteromolecular crystals for which a higher (in comparison with

Table 4. *The distribution of organic crystals by crystallographic systems (%)*

Crystallographic system	Belsky & Zorky (1977)	Padmaya et al. (1990)	Brock & Dunitz (1994)	This work
Triclinic	9.6	18.1	21	14.0
Monoclinic	55.9	53.8	55	55.0
Orthogonal (orthorhombic)	31.2	24.4	21	27.7
Tetragonal	1.8	2.3	2	1.8
Hexagonal	1.4	–	–	–
Trigonal	–	1.5	1	1.0
Proper hexagonal	–	0.5	<1	0.3
Cubic	0.1	0.4	<1	0.2

homomolecular crystals) share of triclinic structures was noted by Chernikova & Zorky (1979) and Zorky & Chernikova (1985), as well as to the contribution of nonmolecular crystals.

The distribution by chiral types has changed little in comparison with our work of 1990 (%):

	A	B	C
1990	27.3	60.8	11.9
1994	26.7	62.0	11.3.

The contribution of type C will probably gradually decrease in the future, since molecules with an inversion center or with a mirror plane are being studied less often, giving way to natural chiral molecules. The ratio between the frequencies of occurrence of types A and B could undoubtedly be of interest if it indicated how frequently the mixture of right and left crystals of type A, and not racemic crystals of type B, precipitates from a solution containing equal numbers of enantiomeric molecules. However, a considerable percentage of the structures of type A that we know has arisen not because the separation of L and D molecules was advantageous as regards the energy but because the source solution contained either only left or only right molecules. Such conditions of crystallization occur especially commonly since natural compounds, where usually only one of enantiomers is represented, have become the objects of very numerous investigations. As a consequence, statistical data (and most often original X-ray studies too) do not provide the possibility of studying the conditions of formation or disintegration of racemic phases and relative advantageousness (or disadvantageousness) of chiral space groups. It is worth noting that transitions L $\rightleftarrows$ D occur if the energy barrier separating enantiomeric molecules is low and a mixture of left and right crystals, and under certain conditions a racemate too, can crystallize from a solution prepared by dissolving only left (or only right) crystals.

A steady tendency towards slow increase is found for the share of polysystem crystal structures. According to the data of our studies, it changed as follows: Belsky & Zorky (1977) 8.3% (only 413 structures), Chernikova, Belsky & Zorky (1990) 10.4% (1590 structures), the present work (1994) 11.0% (2170 structures). The increase of this share, as well as the increase of the

share of triclinic structures that took place in the 1970s, is apparently due to the increase of automation, of the availability of computer hardware and software and of the level of X-ray analysis. The distribution of polysystem crystals by numbers of orbits occupied by molecules (k) as compared with the data of the previous work is as follows (the number of structures is given):

k	2	3	4	5	6	8	9	16
1990	1433	91	55	2	4	3	2	–
1994	1951	124	78	2	5	4	2	1

In Zorky & Dashevskaya (1992), it has been proposed to call the homomolecular crystals in which more than two orbits are occupied 'multisystem'. We shall call 'multimultisystem' those very rare crystals in which molecules occupy more than four orbits. Up to now, we know of only 14 such substances. In conclusion, we list the unique structures in which molecules occupy 8, 9 and 16 systems of equivalent positions:

$P1, Z = 8(1^8)$	cholesterol	Shieh et al. (1977, 1981)
	4,6-dimethyl-1,2,3-triazine-2-imine	Yamaguchi et al. (1988)
	diphenylamine	Mornon et al. (1977)
$P\bar{1}, Z = 16(1^8)$	triphenylsilanol	Puff et al (1991)
$P3_1, Z = 27(1^9)$	selenourea	Kondrashev & Andreeva (1963)
		Rütherford & Calvo (1969)
$P\bar{4}m2, Z = 32[(mm)^4, m^4, 1]$	α-deuteromethane	Prokhvatilov & Isakina (1980)
$P1, Z = 16(1^{16})$	2,2-aziridine-dicarboxamide	Brückner (1982)

The above circumstances show that the statistical data on crystal structures also reflect the level of development of X-ray analysis as well as (varying with time) trends in the choice of objects. Therefore, one should be cautious when attempting to derive the regularities of formation of crystal structures from these data. In the future, the engineering of molecular crystals will probably allow researchers to make at will any number of structures belonging to a particular class. Therefore, strictly speaking, the presented statistics characterize not the laws of formation of crystal structures but the existing set of X-ray data. However, taking a thoughtful approach to these statistics, one can certainly obtain valuable information about the principles of the structure of molecular crystals.

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Microdiffraction and CBED Crystal Structure Determination of the Si-Rich Phase in Laser-Clad Ni Alloy FP-5

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Abstract

This paper demonstrates an example of using kinematical microdiffraction to solve an unknown Si-rich phase of micrometer size in a laser-clad Ni alloy FP-5 on Al alloy AA333. The composition of the Si-rich phase obtained by energy-dispersive X-ray spectroscopy (EDX) analysis in a transmission electron microscope is approximately 0.7wt% Al, 71wt% Si, 3.3wt% Cr, 0.8wt% Fe, 21wt% Ni and 2.7wt% Cu. The point group was identified by the standard convergent-beam symmetry analysis to be $P6_3/mmc$ (No. 194). Structure analysis by microdiffraction (MD) indicates that the Si-rich phase is a close-

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