explained by the omission of the slight correlation between the structure factors in the least-squares analysis. The agreement of the estimated standard deviations is of great importance. In the integrated intensity method the e.s.d.'s are evaluated from the least-squares residuals whereby the uniform underestimation of the variances is insignificant. Hence, the variance estimates obtained by the profile-refinement method are reasonable, which can be explained by a diminution of the influence of the correlation when the spectrum comprises a large number of separated peaks.

6. Conclusions

The results of the present paper demonstrate that reverse time-of-flight diffractometers with Fourier choppers offer a useful means for structure analysis. The ultimate accuracy obtainable with this white-beam technique is determined by the precision of the incident neutron flux estimate, which must, therefore, be taken into account in a proper analysis.

The theoretically rigorous method for the refinement of diffraction data measured with the correlation technique was considered impracticable, for which reason the ordinary method was applied yielding unreliable estimates for parameters evaluated from only one reflection. Fortunately, a powder diffraction pattern contains a large number of peaks so that reliable estimates can be obtained for structural parameters, but nevertheless part of the high efficiency of correlation methods will be lost on account of the cautious interpretations.

References

ABRAHAMS, S. C. (1969). *Acta Cryst.* A25, 165–172.
BALAGUROV, A. M., BORCA, E., DLOUHA, M., GHEORGHIU, Z., MIRONOVA, G. M. & ZLOKAZOV, V. B. (1979). *Acta Cryst.* A35, 131–136.
BURAS, B. (1969). Report INR 1108/II/PS. Institute of Nuclear Research, Warzawa.
BURAS, B. & HOLAS, A. (1968). *Nukleonika*, 13, 591–619.
CHEETHAM, A. K. & TAYLOR, J. C. (1977). *J. Solid State Chem.* 21, 253–275.
COOPER, M. J. & TAYLOR, R. I. (1969). *Acta Cryst.* A25, 714–715.
DRAPER, N. R. & SMITH, H. (1966). *Applied Regression Analysis*, pp. 77–81. New York: John Wiley.
HIISMÄKI, P., JUNTTILA, J. & PIIRTO, A. (1975). *Nucl. Instrum. Methods*, 126, 435–443.
HUBBARD, C. R., QUICKSALL, C. O. & JACOBSON, R. A. (1972). *Acta Cryst.* A28, 236–245.
INKINEN, O. & SUORTTI, P. (1964). *Ann. Acad. Sci. Fenn. Ser. A6*, p. 147.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
MARSHALL, W. & LOVESEY, S. W. (1971). *Theory of Thermal Neutron Scattering*, p. 35. Oxford Univ. Press.
PAAKKARI, T. (1974). *Acta Cryst.* A30, 83–86.
PÖYRY, H. (1978). *Nucl. Instrum. Methods*, 156, 499–514.
PÖYRY, H., HIISMÄKI, P. & VIRJO, A. (1975). *Nucl. Instrum. Methods*, 126, 421–433.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.
ROULT, G. & BUÉVOZ, J. L. (1977). *Rev. Phys. Appl.* 12, 581–590.
TIITTA, A. & HIISMÄKI, P. (1979). *Nucl. Instrum. Methods*, 163, 427–436.
WILSON, S. A. & COOPER, M. J. (1973). *Acta Cryst.* A29, 90–91.
WINDSOR, C. G. & SINCLAIR, R. N. (1976). *Acta Cryst.* A32, 395–409.
WORLTON, T. G., JORGENSEN, J. D., BEYERLEIN, R. A. & DECKER, D. L. (1976). *Nucl. Instrum. Methods*, 137, 331–337.

Statistics of Ion Distribution in 1D and 2D Mixed Crystals

BY CLAUS FRIEBEL

Sonderforschungsbereich 127 (Kristallstruktur und chemische Bindung) und Fachbereich Chemie der Universität Marburg, Lahnberge, D-3550 Marburg, Federal Republic of Germany

Abstract

A statistical distribution of ions M in lattices or partial lattices $_\infty[A_{1-x}M_xL_m]$ of mixed crystals being assumed, the probability functions $P_j^{(\nu)}(x)$ for single coordination polyhedra ML_n ($j = 1$), pairs ($j = 2$) and larger clusters of ML_n groups ($j > 2$) in 1D ($\nu = 2$) and ν-connected 2D systems ($\nu = 3, 4, 6$) are calculated. On raising the connecting number ν, increasing cluster probabilities are distinctly shifted to lower concentrations x of the foreign ion M. For a relation between the numerical values $P(x)$ and experimental results, the

mixed-crystal series $(BaF)_2[Zn_{1-x}Cu_xF_4]$ of a four-connected 2D structure is given as an illustrative example.

Introduction

Replacement of closed-shell cations in a matrix compound by transition-metal ions is a useful means of inspecting the symmetry of lattice sites by spectroscopic techniques. This method is valid if the transition-metal ions with their specific electronic properties are able to accommodate themselves to the symmetry of the lattice sites into which they are incorporated. If these ions, however, by virtue of a peculiar electronic configuration, exhibit an obstinate symmetry behaviour (well known as the Jahn–Teller effect), cooperative interactions between them may result in a macroscopic distortion of the given host structure at higher concentrations. Symmetry effects of such a kind have been found, for instance, by Reinen and co-workers in Cu^{2+}-containing mixed crystals such as $Sr_2Zn_{1-x}Cu_xWO_6$ (Reinen, 1968; Friebel & Reinen, 1969), $Cr_2Zn_{1-x}Cu_xO_4$ (Reinen & Grefer, 1973), or $Ba_2Zn_{1-x}Cu_xF_6$ (Friebel, Propach & Reinen, 1976). Here the question arises as to which kind of clusters and which distributions of clusters are present in the concentration range where cooperative Jahn–Teller interactions between the Cu^{2+} ions start. This question suggests a general mathematical treatment of the problem of ion distributions in different structure types.

Provided that the distribution of cations incorporated into well defined sites of a host structure obeys the laws of statistics, the probabilities of obtaining isolated coordination polyhedra of these ions and smaller groups consisting of two to about six polyhedra linked by common corners, edges or faces can be determined without too much exertion. The calculation of these probabilities as a function of the structure type and the ratio of the mixed ions has yielded some remarkable results, presented in this paper. Restricting ourselves to mixed crystals of one- and two-dimensional structure types, we define these as containing infinite structural units $_\infty[A_{1-x}M_xL_m]$ (neutral or charged), forming chains and nets, respectively, in which the ions A of a matrix compound are substituted partially by foreign ions M (L being any ligand coordinated to the mixed ions). The more sophisticated statistics of ion distribution in three-dimensional mixed crystals (framework structures), which would find a useful application, for instance, in the widely investigated perovskite ferroelectric $PbZr_{1-x}Ti_xO_3$, will be discussed in a later article.

Ion distribution in 1D mixed crystals

If the very simple case of a mixed crystal containing infinite chains $_\infty^1[A_{1-x}M_xL_m]$ of two-connected coor-

dination groups of mixed ions A and M in statistical distribution is taken as the starting point, the probability P_j of finding units of isolated ($j = 1$) or linked ML_n polyhedra ($j > 1$) is given by the simple expression

$$^1P_j^{(2)} = jx^{j-1}(1-x)^2; \quad 0 < x < 1. \tag{1}$$

P_j is marked by a prefix giving the dimension of the structural unit and a superscript to the right giving the connecting number v, i.e. the number of equivalent sites adjacent to the coordination polyhedra $A(M)L_n$ (cf. Fig. 2).

If M belongs to a finite chain of j ions M, $j - 1$ sites of this chain adjacent to M are occupied by M also and two adjacent sites by A; hence these two quantities appear as exponents of x and $1 - x$, respectively. The additional factor j in equation (1) arises because each M of the chain may be considered as the original M. The summation of the probabilities with respect to j necessarily results in

$$\sum_{j=1}^{\infty} {}^1P_j^{(2)} = 1. \tag{2}$$

$^1P_j^{(2)}$ as a function of x is drawn in Fig. 1 for the first seven j values. The remaining probability for all M belonging to chains of more than seven coordination groups is shown in Fig. 5 and will be discussed below.

Fig. 1. The probability functions $^1P_j^{(2)}(x)$ for single coordination polyhedra ML_n ($j = 1$) as well as for pairs ($j = 2$) and clusters of $2 < j \leq 7$ ML_n groups in chain structures $_\infty^1[A_{1-x}M_xL_m]$.
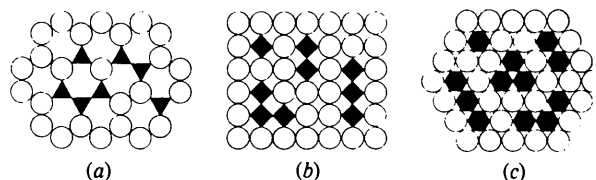
Fig. 2. Isolated sites, pairs of two and clusters of three sites occupied by ions M (black v-gons) instead of A (open circles) in v-connected layer structures $_\infty^2[A_{1-x}M_xL_m]$: (a) $v = 3$, (b) $v = 4$, (c) $v = 6$.

Ion distribution in 2D mixed crystals

If lattices with a two-dimensional network containing the mixed ions A and M are considered, three main cases of connecting numbers, $v = 3$, 4, and 6, have to be distinguished. Restricting ourselves to the simplest periodic networks of v-connected systems in which all the polyhedra are topologically equivalent (Fig. 2), these three cases are represented by the hexagon, the square, and the triangular net, respectively. At each point of these nets one could place a v-gon (triangle, square, hexagon) or any topologically equivalent coordination polyhedron such as a tetrahedron sharing three or four vertices or an octahedron sharing four vertices or three or six edges (cf. Table 1).

As illustrated in Figs. 2(b,c) and 3 the arrangement of $j \geq 3$ neighbouring sites can be different, giving for each v and j a specific number of configurations. All possible configurations $k_j^{(v)}$ must be taken into consideration, rendering the procedure of calculating $^2P_j^{(v)}(x)$ for higher j values rather sophisticated. From Figs. 2(b,c) and 3 it can further be seen that the number u of 'unoccupied' sites (A) adjacent to a cluster of j ions

M is a variable depending on its specific configuration. A principal characteristic of each configuration is its point symmetry. Different point symmetries render possible several non-equivalent orientations of identical configurations; hence the probabilities $^2P_j^{(v)}$ are modified by a 'symmetry factor' f as an additional variable which depends on $k_j^{(v)}$. Both parameters u and f are listed in Fig. 3, where all configurations for groups of $j = 4$ neighbouring sites with the connecting number $v = 4$ are given. The following general expression for the functions ^2P_j giving the probabilities for clusters of j neighbouring sites occupied by ions of the same kind in 2D mixed crystals is valid:

$$^2P_j^{(v)} = jx^{j-1} \sum_K f(K)(1-x)^{u(K)}$$

$$= jx^{j-1}(1-x)^w \sum_K f(K)(1-x)^{-\Delta u(K)}, \quad (3)$$

Table 1. *Representative examples, with structures based on v-connected systems $_\infty[AL_m]$, of coordination groups AL_n linked to infinite chains ($v = 2$) and nets ($v = 3, 4, 6$), respectively (cf. Wells, 1975)*

v	Coordination groups AL_n	Connected by sharing v...	m of resulting $_\infty[AL_m]$ system[a]	Examples[b]
2	Tetrahedra	Vertices	2/2 + 2	Na[PO₃], pyroxenes, Pb[GeS₃][c], Ba₂[MnS₃]
		Edges	4/2 + 0	Tl[FeS₂][d], Ba₆[FeS₂]₁₆[e]
	Squares	Adjacent centres	0 + 4	[Pd(NH₃)₄]Cl₂·H₂O
		Edges	4/2 + 0	Li₂[NiO₂][f]
	Octahedra	trans-Vertices	2/2 + 4	Tl₂[AlF₅], (SrF)[PbF₅]
		cis-Vertices		K₂[FeF₅][g], Mn[CrF₅][h]
		Opposite edges	4/2 + 2	Na₂[MnCl₄], Ca₂[SnO₄]
		Non-opposite edges		[ZrI₄][i], Ca[TeO₄][j]
		Faces	6/2 + 0	Cs[NiF₃], Ba[CoO₃][k]
	Elongated octahedra	Vertices	2/2 + 4	Cs₂[MnF₄]·H₂O[l]
		Edges	4/2 + 2	Na₂[CuF₄]
		Faces	6/2 + 0	Cs[CuCl₃]
	Dodecahedra	Edges	4/2 + 4	K₂[ZrF₆]
3	Tetrahedra	Vertices	3/2 + 1	Rb[Be₂F₅], Na₂[Si₂O₅], Al₂(OH)₄[Si₂O₅]
	Octahedra	cis-Vertices	3/2 + 3	Cs₃[Bi₂Br₉][m]
		Edges	6/2 + 0	[CrCl₃], [Al(OH)₃] (SiO₁.₅)[AlO(OH)₂]
4	Dumb-bells	Adjacent centres	0 + 2	Na₂[HgO₂], K₂[NiO₂][n]
	Tetrahedra	Vertices	4/2 + 0	Sr[ZnO₂]
	Octahedra	Vertices	4/2 + 2	Tl[AlF₄], α-Sn[WO₄][o], K₂[NiF₄], (BaF)₂[ZnF₄], Rb₃[MnBr₄][p]
6	Octahedra	Edges	6/3 + 0	[CdCl₂], (LaS)[CrS₂][q]
	Trigonal prisms	Edges	6/3 + 0	[MoS₂]

(a) Specified as sum of shared and unshared ligand atoms L. (b) References, unless otherwise cited, are given by Wells (1975). (c) Ribes, Olivier-Fourcade, Philippot & Maurin (1974). (d) Zabel & Range (1979). (e) Hoggins & Steinfink (1977). (f) Rieck & Hoppe (1972). (g) Vlasse, Matejka, Tressaud & Wanklyn (1977). (h) Férey, de Pape & Boucher (1978). (i) Krebs, Henkel & Dartmann (1979). (j) Hottentot & Loopstra (1979). (k) Taguchi, Takeda, Kanamaru, Shimada & Koizumi (1977). (l) Kaučič & Bukovec (1978). (m) Lazarini (1977). (n) Rieck & Hoppe (1973). (o) Jeitschko & Sleight (1974). (p) Goodyear, Ali & Sutherland (1979). (q) Kato & Kawada (1977).

Fig. 3. Complete set of configurations $k_j^{(v)}$ in a tetragonal 2D system ($v = 4$) for $j = 4$ [u = number of 'unoccupied' sites adjacent to $k_j^{(v)}$, s = point symmetry of $k_j^{(v)}$ (Schoenflies symbols), f = number of possible non-equivalent orientations of $k_j^{(v)}$ (dependent on s)].

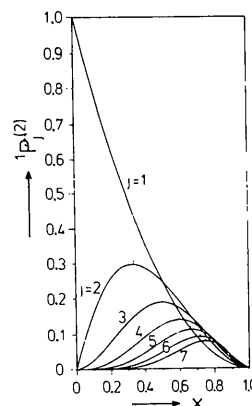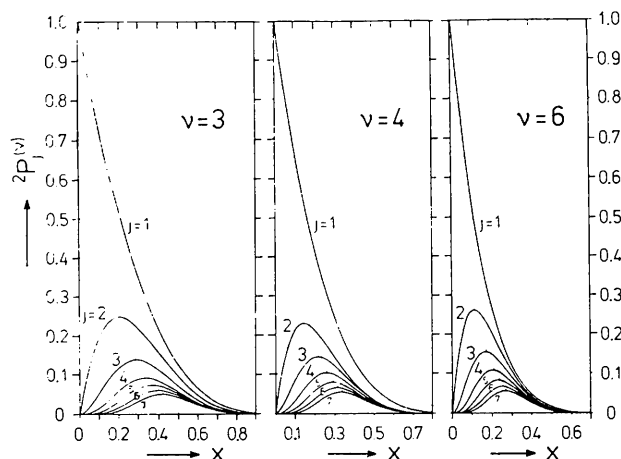| u	$k_4^{(4)}$	s	f
10		C_{2v}	2
9		C_1	4
		C_s	4
8		C_2	2
		C_{4v}	1

Fig. 4. The probability functions $^2P_j^{(v)}(x)$ for single coordination polyhedra ML_n ($j = 1$) as well as for pairs ($j = 2$) and clusters of $2 < j \leq 7$ ML_n groups in v-connected layer structures $_\infty^2[A_{1-x}M_xL_m]$.

where

$$K = k_j^{(v)}, \quad u = u_j^{(v)}, \quad w = w_j^{(v)}.$$

Moreover the parameter $u(K)$ has been separated into one part (w) independent of $k_j^{(v)}$ and a second component (Δu) dependent on $k_j^{(v)}$; w is the maximal number of unoccupied sites adjacent to the cluster. Admitting linear configurations only, one obtains:

v	2	3	4	6
$w_j^{(v)}$	2	$j + 2$	$2j + 2$	$2j + 4$

Equation (3) differs from equation (1) merely in the additional summation over all possible configurations and their orientations. It should be mentioned that the number f of non-equivalent orientations of any configuration $k_j^{(v)}$ is correlated directly to the Schoenflies symbols C_n and C_{nv} (the symmetry C_s corresponding to $n = 1$) by $v/n = f$ (Fig. 3 and Table 2). The increasing complexity of the numerical expressions of equation (3), if j is increased, becomes evident from Table 2 in the Appendix where the sums over all configurations having identical numbers of unoccupied adjacent sites and identical symmetries are given. On the basis of this table the probabilities $^2P_j^{(v)}$ have been computed as functions of x and drawn in Fig. 4.

Discussion

Figs. 1 and 4 demonstrate how the probability for isolated coordination polyhedra ML_n in a matrix compound decreases with $(1 - x)^v$ if the concentration x of M is raised. The probabilities for pairs of two and for clusters of $j \geq 3$ coordination groups run through maximal values of $P_j^{(v)}$ at definite concentrations $x_j^{(v)}$ which increase if j is raised. The corresponding data are indicated in the graphs (Figs. 1 and 4). With increasing v the probability of cluster formation is shifted signifi-

cantly to lower x values and this is demonstrated in Fig. 5 $(c = 7)$ by the probability functions

$$P_c^{(v)} = 1 - \sum_{j=1}^{c} P_j^{(v)}. \tag{4}$$

This expression gives the probabilities for clusters consisting of $j > c$ coordination polyhedra. From Fig. 5 a relative statement can be made about those 'critical' ion concentrations in mixed crystals, at which cooperative interactions between linked ML_n groups increase to an extent that results in macroscopic distortion effects: The steep slope of the probability curves $P_c^{(v)}(x)$ suggests a definition of the x values, at which just half of all ions M belong to clusters with $j > c$ ML_n polyhedra, as 'critical' concentrations $x_c^{(v)}$ for cooperative effects. The concentration values thus defined are illustrated in Fig. 6 with their dependence on c. Postulating a specific c value to define a critical cluster size would be presumptuous. Nevertheless, the x_c values for a given v draw considerably closer if c is taken in the range $\gtrsim 4$. These findings allow the following conclusion, based on the assumption of a statistical distribution of foreign ions M incorporated into a matrix compound: Clusters which contain half of the ions M (corresponding to a molar fraction $x_c/2$) and have sizes $j > c$ of at least 5 to 9 linked ML_n groups, exist in the concentration ranges of $x_c \simeq$ 75 ($\mp$6), 47 ($\mp$4), 37 ($\mp$4), and 30 ($\mp$3)% in two-, three-, four- and six-connected systems (1D and 2D structures), respectively (Fig. 6). These results may be applied to a series of model compounds containing chains of two-connected or nets of v-connected coordination groups (Table 1).
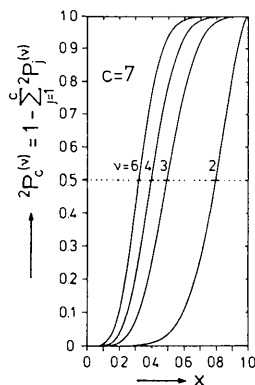

Fig. 5. The probability functions $P_c^{(v)}(x)$ for all clusters consisting of more than $c = 7$ coordination polyhedra ML_n in 1D $(v = 2)$ and 2D $(v = 3, 4, 6)$ mixed crystals containing chains and layers, respectively, of $_\infty[A_{1-x}M_xL_m]$ units.
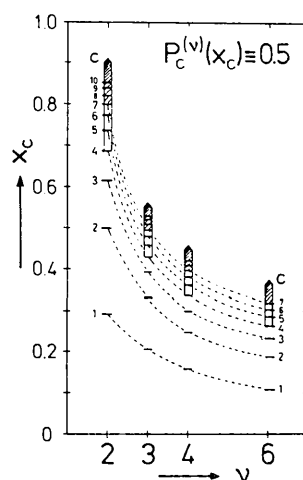

Fig. 6. Concentrations $x_c^{(v)}$, where just $x_c/2$ of M belong to clusters of more than c coordination polyhedra ML_n in 1D $(v = 2)$ and 2D $(v = 3, 4, 6)$ mixed crystals containing chains and layers, respectively, of $_\infty[A_{1-x}M_xL_m]$ units [ranges of increasing cluster probabilities $(c \geq 7)$ are emphasized by hatching].

Application

In Table 1 some examples of structure types containing ν-connected coordination groups of various geometrical shapes are collected. Not all of them may be suitable as model compounds for the incorporation of obstinate foreign ions inducing specific cooperative effects. Nevertheless, sufficient examples remain for investigations of relations between experimental data and the statistical results obtained on ion distribution in mixed crystals.

One example of Cu^{2+}-containing solid solutions exhaustively investigated by Friebel, Propach & Reinen (1976) is the mixed-crystal series $Ba_2Zn_{1-x}Cu_xF_6$ containing four-connected nets of coordination octahedra sharing four vertices (Table 1). Whereas in the host lattice Ba_2ZnF_6 (space group $I422$) the ZnF_6 octahedra are tetragonally compressed in the direction perpendicular to the layers (von Schnering, 1967), the compound Ba_2CuF_6 (space group $Bbam$) contains elongated CuF_6 octahedra in a disturbed type of
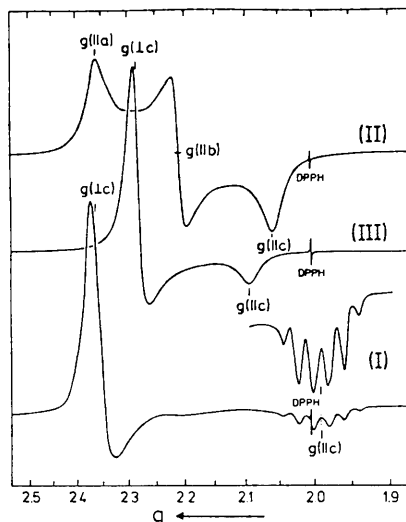

Fig. 7. EPR spectra (35 GHz, 295 K) of $Ba_2Zn_{0.9}Cu_{0.1}F_6$ (I) with isolated tetragonally compressed CuF_6 octahedra. Ba_2CuF_6 (II) and K_2CuF_4 (III) with elongated CuF_6 octahedra in disturbed (II) and non-disturbed (III) antiferrodistortive order (Reinen & Friebel, 1979).

'antiferrodistortive order' (von Schnering, 1973; Friebel, 1974; Reinen & Weitzel, 1977) (see Fig. 8b).

In all cases of cubic site symmetry a tetragonal *elongation* of the regular CuL_6 octahedron is favoured, though a compression of the coordination octahedron would also lift the twofold orbital degeneracy of the ^2E_g ground state of the Cu^{2+} ion (Friebel & Reinen, 1974). The present symmetry of the Zn^{2+} sites in Ba_2ZnF_6 forces the Cu^{2+} ions into *tetragonally compressed* octahedral coordination as long as cooperative interactions between several CuF_6 polyhedra are to be neglected or weak. From the EPR data a striking difference is to be found between the spectra of isolated Cu^{2+} centres in tetragonally compressed octahedral coordination and those of clusters with elongated CuF_6 octahedra in (disturbed) antiferrodistortive order (Fig. 7). Referring to the experimental results (Friebel, Propach & Reinen, 1976) cooperative effects have not been observed at Cu^{2+} concentrations $x \leq 0.30$. In the range $0.30 < x < 0.45$, however, the beginning of a transition from isolated compressed to elongated octahedra, which are cooperatively ordered, is indicated by an orthorhombic symmetry component of the CuF_6 polyhedra. Then, at concentrations $x > 0.45$, the elongated distortion becomes predominant as a consequence of increasing cooperative Jahn–Teller interactions. This transition may take place simply by shifting the F^- ligands of four connected compressed CuF_6 octahedra in such a way that alternately two of the four long Cu–F bonds would be lengthened and the other two shortened (Fig. 8).

It is of interest to state that the concentration range $0.3 < x < 0.45$, in which cooperative effects become effective, is in agreement with $x_c^{(4)}$ in the range $3 \lesssim c \lesssim 12$ (Fig. 6). An investigation of $K_2Zn_{1-x}Cu_xF_4$ mixed crystals (K_2NiF_4 lattice type, Table 1) has yielded similar results (Krause & Reinen, 1979).
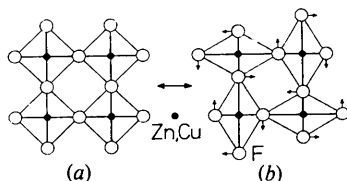
Fig. 8. The change from (a) ferrodistortively ordered tetragonally compressed to (b) antiferrodistortively ordered elongated coordination octahedra in mixed crystals $(BaF)_2[Zn_{1-x}Cu_xF_4]$ of a four-connected 2D structure [view into (001) plane of Ba_2ZnF_6 structure; the arrows indicate additional rotations of the CuF_6 polyhedra around [001] in Ba_2CuF_6 yielding a disturbance of the antiferrodistortive order].

APPENDIX
Procedure for calculating $^2P_j^{(\nu)}(x)$

For computing numerically the probability functions $^2P_j^{(\nu)}(x)$ [equation (3)], the calculation of

$$\sum_K f(K)(1-x)^{-\Delta u(K)} = U \qquad (5)$$

is performed in three steps.

(1) After noting down the complete set of $K = k_j^{(v)}$ (cf. Fig. 3) the sum total $\sum K$ (Table 2) is separated into partial sums $K(s, \Delta u)$, representing the numbers of all configurations $k_j^{(v)}$ having equal symmetry s, and the same number u of unoccupied adjacent sites; accordingly the same parameter

$$\Delta u(K) = w - u(K), \qquad (6)$$

used in equation (3).

(2) The partial sums $K(s, \Delta u)$ listed in Table 2(a), (b) and (c) for $v = 3$, 4, and 6, respectively, render feasible the summations of the products $K(s, \Delta u) . f(s)$ with

Table 2. *Classification of the sum $(\sum K)$ of all configurations $[K = k_j^{(v)}]$ of j v-connected ML_n groups in 2D mixed crystals into partial sums $K(s, \Delta u)$*

s = symmetry of K; f = number of non-equivalent orientations of K; Δu = difference between the maximal number (w) and the actual one (u) of sites adjacent to K and occupied by ions A of the matrix compound [equation (6)]; boxed numbers = parameters $F(\Delta u)$ resulting from equation (7).

(a) $v = 3$

j	ΣK	s	f^*	0	1	2	3	4
1	1	3m	1	1				
				☐1				
2	1	mm2	3/2	1				
				☐1·5				
3	1	m	3	1				
				☐3				
4	4	m	3	1				
		2	3/2	2				
		3m	1	1				
				☐7				
5	6	1	3	4	–			
		m	3	1	1			
				☐15	☐3			
6	19	1	3	6	4	–		
		m	3	2	1	–		
		2	3/2	4	–	–		
		mm3	3/2	1	–	–		
		6mm	1/2	–	–	1		
				☐31·5	☐15	☐0·5		
7	43	1	3	18	18	–		
		m	3	2	2	1		
		3	1	2	–	–		
				☐62	☐60	☐3		
8	120	1	3	32	56	6		
		m	3	4	3	4		
		2	3/2	10	–	4		
		mm2	3/2	–	–	1		
				☐123	☐177	☐37·5		
9	307	1	3	78	152	60	4	
		m	3	4	5	3	–	
		3m	1	–	–	1	–	
				☐246	☐471	☐190	☐12	
10	866	1	3	150	384	226	34	–
		m	3	7	5	12	2	–
		2	3/2	20	–	18	–	–
		mm2	3/2	–	–	2	–	1
		3	1	2	–	–	2	–
		3m	1	–	–	–	1	–
				☐503	☐1167	☐744	☐111	☐1·5

*The occurrence of half numbers for f results from the fact that trigonally coordinated points of the hexagon net belong to triangles, the apices of which point on the one side upwards and on the other side downwards (Fig. 2a). Rotations of K resulting in identical configurations with oppositely arranged triangles are not allowed to be counted.

Table 2 (cont.)

(b) $v = 4$

j	ΣK	s	f	0	1	2	3	4	5	6	7	8	9
1	1	4mm	1	1									
				☐1									
2	1	mm2	2	1									
				☐2									
3	2	m	4	–	1								
		mm2	2	1	–								
				☐2	☐4								
4	7	1	4	–	2	–							
		m	4	–	–	1							
		2	4	–	–	2							
		mm2	2	1	–	–							
		4mm	1	–	–	1							
				☐2	☐8	☐9							
5	18	1	4	–	2	4	4	–					
		m	4	–	1	2	1	–					
		2	2	–	–	2	–	–					
		mm2	2	1	–	–	–	–					
		4mm	1	–	–	–	–	1					
				☐2	☐12	☐28	☐20	☐1					
6	60	1	4	–	4	10	20	6	–				
		m	4	–	–	3	–	4	1				
		2	2	–	–	4	–	6	–				
		mm2	2	1	–	–	–	1	–				
				☐2	☐16	☐60	☐80	☐54	☐4				
7	196	1	4	–	4	20	54	54	32	4			
		m	4	–	1	3	3	6	2	1			
		2	2	–	–	4	–	4	–	–			
		mm2	2	1	–	–	–	2	–	1			
				☐2	☐20	☐100	☐228	☐252	☐136	☐22			
8	704	1	4	–	6	30	120	184	194	80	18	–	
		m	4	–	–	5	–	10	2	9	2	–	
		2	2	–	–	6	–	16	–	14	–	–	
		mm2	2	1	–	–	1	–	1	–	2		
		4	1	–	–	–	–	–	2	–	–		
		4mm	1	–	–	–	–	1	–	–	–		
				☐2	☐24	☐152	☐480	☐810	☐785	☐388	☐80	☐4	
9	2483	1	4	–	6	46	208	494	682	588	282	64	6
		m	4	–	1	5	4	13	11	15	6	7	1
		2	2	–	–	6	–	16	–	12	–	4	–
		mm2	2	1	–	–	–	2	–	–	–	1	–
		4mm	1	–	–	–	–	1	–	–	–	–	–
				☐2	☐28	☐216	☐848	☐2065	☐2774	☐2436	☐1152	☐295	☐28

(c) $v = 6$

j	ΣK	s	f	0	1	2	3	4	5	6
1	1	6mm	1	1						
				☐1						
2	1	mm2	3	1						
				☐3						
3	3	m	6	1	–					
		mm2	3	1	–					
		3m	2	–	1					
				☐9	☐2					
4	10	1	6	2	2	–				
		m	6	1	–	–				
		2	3	2	–	–				
		mm2	3	1	–	1				
		3m	2	1	–	–				
				☐29	☐12	☐3				
5	33	1	6	10	8	2	–			
		m	6	4	3	1	1			
		2	3	2	–	–	–			
		mm2	3	1	–	1	–			
				☐93	☐66	☐21	☐6			
6	147	1	6	40	48	20	6	–		
		m	6	6	1	3	1	1		
		2	3	8	–	4	–	2		
		mm2	3	2	–	1	–	–		
		3	2	–	2	–	–		
		3m	2	–	–	–	1		
		6mm	1	–	–	–	1	–		
				☐306	☐298	☐153	☐43	☐14		
7	620	1	6	152	206	126	54	16	4	–
		m	6	11	9	11	7	2	1	–
		2	3	8	–	6	–	–	–	–
		mm2	3	2	–	–	–	1	–	–
		3	2	2	–	–	–	–	–	–
		3m	2	1	–	–	–	–	–	–
		6mm	1	–	–	–	–	–	–	1
				☐1014	☐1290	☐840	☐366	☐111	☐30	☐1

respect to s. By this procedure one obtains the parameters

$$\sum_s K(s, \Delta u) . f(s) = F(\Delta u), \tag{7}$$

specified in Table 2 by boxes.

(3) Henceforth, with regard to the relation of

$$\sum_{\Delta u} F(\Delta u)(1 - x)^{-\Delta u} = U \tag{8}$$

to equation (5) the calculation of U is easily completed.

Selecting, for example, the probability $^2P_7^{(3)}$ one obtains from Table 2(a)

$$U_7^{(3)} = 62 + 60(1 - x)^{-1} + 3(1 - x)^{-2}. \tag{9}$$

Taking $w_7^{(3)} = 9$ the complete numerical expression

$$^2P_7^{(3)} = 7x^6(1 - x)^7[62(1 - x)^2 + 60(1 - x) + 3] \tag{10}$$

is obtained from equation (3).

References

FÉREY, G., DE PAPE, R. & BOUCHER, B. (1978). Acta Cryst. B34, 1084–1091.

FRIEBEL, C. (1974). Z. Naturforsch. Teil B, 29, 634–641.

FRIEBEL, C., PROPACH, V. & REINEN, D. (1976). Z. Naturforsch. Teil B, 31, 1574–1584.

FRIEBEL, C. & REINEN, D. (1969). Z. Naturforsch. Teil A, 24, 1518–1525.

FRIEBEL, C. & REINEN, D. (1974). Z. Anorg. Allg. Chem. 407, 193–200.

GOODYEAR, J., ALI, E. M. & SUTHERLAND, H. H. (1979). Acta Cryst. B35, 456–457.

HOGGINS, J. T. & STEINFINK, H. (1977). Acta Cryst. B33, 673–678.

HOTTENTOT, D. & LOOPSTRA, B. O. (1979). Acta Cryst. B35, 728–729.

JEITSCHKO, W. & SLEIGHT, A. W. (1974). Acta Cryst. B30, 2088–2094.

KATO, K. & KAWADA, I. (1977). Acta Cryst. B33, 3437–3443.

KAUČIČ, V. & BUKOVEC, P. (1978). Acta Cryst. B34, 3337–3339.

KRAUSE, S. & REINEN, D. (1979). To be published.

KREBS, B., HENKEL, G. & DARTMANN, M. (1979). Acta Cryst. B35, 274–278.

LAZARINI, F. (1977). Acta Cryst. B33, 2961–2964.

REINEN, D. (1968). Z. Naturforsch. Teil A, 23, 521–529.

REINEN, D. & FRIEBEL, C. (1979). Struct. Bonding (Berlin), 37. 1–60.

REINEN, D. & GREFER, J. (1973). Z. Naturforsch. Teil A, 28, 1185–1192.

REINEN, D. & WEITZEL, H. (1977). Z. Naturforsch. Teil B, 32, 476–478.

RIBES, M., OLIVIER-FOURCADE, J., PHILIPPOT, E. & MAURIN, M. (1974). Acta Cryst. B30, 1391–1395.

RIECK, H. & HOPPE, R. (1972). Z. Anorg. Allg. Chem. 392, 193–196.

RIECK, H. & HOPPE, R. (1973). Z. Anorg. Allg. Chem. 400, 311–320.

SCHNERING, H. G. VON (1967). Z. Anorg. Allg. Chem. 353, 13–25.

SCHNERING, H. G. VON (1973). Z. Anorg. Allg. Chem. 400, 201–207.

TAGUCHI, H., TAKEDA, Y., KANAMARU, F., SHIMADA, M. & KOIZUMI, M. (1977). Acta Cryst. B33, 1299–1301.

VLASSE, M., MATEJKA, G., TRESSAUD, A. & WANKLYN, B. M. (1977). Acta Cryst. B33, 3377–3380.

WELLS, A. F. (1975). Structural Inorganic Chemistry, 4th ed. Oxford: Clarendon Press.

ZABEL, M. & RANGE, K.-J. (1979). Z. Naturforsch. Teil B, 34, 1–6.

Temperature Dependence of the Atomic Thermal Displacements in UO₂: A Test Case for the Rietveld Profile-Refinement Procedure

By A. Albinati

Institute of Chemistry, The Polytechnic, Milan, Italy

and M. J. Cooper, K. D. Rouse, M. W. Thomas and B. T. M. Willis

Materials Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, England

Abstract

The neutron diffraction powder pattern of UO_2 has been recorded at five temperatures between 293 and 1733 K, and the data have been analysed by two methods: the Rietveld profile-refinement procedure and the more conventional approach based on independent integrated intensities. The structural parameters (i.e. the thermal amplitudes of the U and O atoms) derived by the two methods do not differ significantly, but the e.s.d.'s of the parameters given by the Rietveld treatment differ at some temperatures from those obtained