In the case of the form I crystals, ε indeed seems to be very small because the reflections were seen up to 5.5 Å resolution along **c**. For the assumption that $\cos(2\pi l\varepsilon)$ is close to 1 and $l_{\max}$ is $(165\text{ Å})/(5.5\text{ Å}) = 30$ to hold, the value of ε for any two successive *ab* planes cannot be larger than 0.04 (or $0.04\times 165 = 7$ Å) for $0.99 \leq \cos(2\pi l\varepsilon)$. Because of this statistical property of the random displacement errors in *c* spacing, normal reflections were observed only when *l* is even. According to formula (7), odd-*l* reflections should not be present at all. However, the odd-*l* reflections did not disappear completely. Some diffuse scattering was seen at positions of the odd-*l* reflections. This might be because the crystal has limited dimensions and/or the distribution of the displacement errors is not truly binomial. The crystals might be constructed by stacking of ordered microcrystals consisting of several *ab* planes along **c**, instead of randomly distributed single *ab* planes. Nevertheless, the statistical analysis demonstrated that the random distribution of a small error in the spacing of the *ab* planes in the **c** direction will cause such an unusual diffraction pattern in which the odd-*l* reflections would be missing.

Amino acid substitutions in the loops

The crystals of B/mem/89 (form II) have the same space group as the other three crystalline forms, but they do not exhibit the disorder along **c**. The conditions used for crystallizing B/mem/89 NA did not produce crystals for the other three strains. Amino acid sequence analysis of the NAs indicated that there are five residues in the B/mem/89 NA head which are different from all the other strains (Air, Laver, Luo, Stray, Legrone & Webster, 1990). These differences are Glu148 → Lys148, Glu250 → Lys250, Asp340 → Asn340, Arg345 → Leu345 and Lys436 → Glu436. These residues are all located on the upper surface of the NA in comparison with the NA structure of the type A influenza virus and the substitutions all involved charge changes. It will be interesting to see what structural changes cause the unusual disorder when the atomic structure of the type B NA is determined.

We are grateful to Pat Bossart, Y. Babu and Craig D. Smith for their help on diffraction data collection. We also thank Michael G. Rossmann for pointing out the similarity of the disorder with that of the catalase crystals. The work is supported by grants from NIH (AI-27518) and NCI (AI-13148) to ML and a NIH grant (AI-26718) to GMA.

References

Air, G. M., Laver, W. G., Luo, M., Stray, S. J., Legrone, G. & Webster, R. G. (1990). *Virology*, **177**, 578-587.

Bossart, P. J., Babu, Y. S., Cook, W. J., Air, G. M. & Laver, W. G. (1988). *J. Biol. Chem.* **263**, 6421-6423.

Bragg, W. L. & Howells, E. R. (1954). *Acta Cryst.* **7**, 409-411.

Burnet, F. M. & Stone, J. D. (1947). *Aust. J. Exp. Biol. Med. Sci.* **25**, 227-233.

Cochran, W. & Howells, E. R. (1954). *Acta Cryst.* **7**, 412-415.

Glauser, S. & Rossmann, M. G. (1966). *Acta Cryst.* **21**, 175-177.

Howells, E. R. & Perutz, M. F. (1954). *Proc. R. Soc. London Ser. A*, **225**, 308.

Laver, W. G., Luo, M., Bossart, P. J., Babu, Y. S., Smith, C. D., Accavitti, M. A., Tulloch, P. A. & Air, G. M. (1989). *Virology*, **167**, 621-624.

Lin, Y., Luo, M., Laver, W. G., Air, G. M., Smith, C. D. & Webster, R. G. (1990). *J. Mol. Biol.* **214**, 639-640.

Varghese, J. N., Laver, W. G. & Colman, P. M. (1983). *Nature (London)*, **303**, 35-40.

Acta Cryst. (1992). **A48**, 266-271

The Piezomagnetoelectric Effect

By Hans Grimmer

Laboratorium für Materialwissenschaften, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

(*Received* 22 *July* 1991; *accepted* 23 *October* 1991)

Abstract

Taking time reversal into account there are 122 crystallographic Shubnikov point groups and 21 limiting Shubnikov point groups containing ∞-fold rotation axes. The restrictions on the form of the tensor describing the piezomagnetoelectric effect are given for all these groups and compared with results of other authors. Antiferromagnetic materials with non-centrosymmetric point groups containing space-time inversion are suitable candidates for measuring the piezomagnetoelectric effect.

1. Introduction

The piezomagnetoelectric effect was first considered by Rado (1962) who derived its form for materials

0108-7673/92/030266-06$03.00

with magnetic point group $\bar{3}'m'$ in view of the possible existence of this effect in Cr_2O_3. One way in which this effect will manifest itself is the appearance of an electric polarization P in a material subject to stress σ and to a magnetic field H, even if the material is neither piezoelectric nor magnetoelectric. Restricting attention to terms linear in H and σ, one can write the polarization as

$$P_i = \pi_{ijkl} H_j \sigma_{kl}, \qquad (1)$$

where π denotes the piezomagnetoelectric tensor.

Lyubimov (1965) showed that π may be different from zero in 69 of the 122 crystallographic Shubnikov point groups and he determined the number of independent components of π for the 69 groups. Stefanakos, Tinder & Thapliyal (1979) tried to determine the form of π for these 69 groups and claimed that some of the results of Rado (1962) and Lyubimov (1965) were incorrect. It is the aim of the present paper to show that the form of π can be obtained easily by making use of the general results of Grimmer (1991*a*)* and that the criticized results of Rado and Lyubimov are correct in contrast to several forms given by Stefanakos *et al.* (1979). The form of π will also be given for the limiting point groups, which are relevant, for example to textured polycrystals.

To our knowledge, the piezomagnetoelectric effect has not been observed so far. Point-group symmetries are, therefore, pointed out for which this effect cannot be masked by other effects of lower or equal order in the applied fields.

2. The form of the piezomagnetoelectric tensor

A tensor is either invariant or changes sign under space inversion $\bar{1}$, time inversion $1'$ and space-time inversion $\bar{1}'$. Four combinations are possible: *i* tensors are *i*nvariant under all three inversions, *s* tensors only under *s*pace inversion, *t* tensors only under *t*ime inversion, and *u* tensors only under space-time inversion. Equation (1) shows that π is a *u* tensor because P is a *t* tensor, H an *s* tensor and σ an *i* tensor. π_{ijkl} is a tensor of rank 4, symmetric in its last two indices. Using a Cartesian coordinate system, Sirotine & Chaskolskaïa (1984) give on p. 648 the form of an *i* tensor, *h*, of rank 4 and symmetric in its first two indices. Interchanging the first and second pairs of indices in *h* we obtain the form of π for the pure-rotation groups since, for materials with such point groups, the restrictions imposed on property tensors by Neumann's principle obviously do not depend on the type of the tensor (*s*, *t*, *u* or *i*).

It is usual to represent π by a 9×6 matrix $\pi_{\mu\nu}$ with the nine rows corresponding to the following values of the first two indices of π_{ijkl}:

row	1	2	3	4	5	6	7	8	9
indices	11	22	33	23	31	12	32	13	21 ;

and the six columns corresponding to the following values of the last two indices:

column	1	2	3	4	5	6
indices	11	22	33	23	31	12 .

The stress σ is then described by a column vector with elements $(\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{31}, \sigma_{12})$. If the convention of summation over repeated tensor indices is replaced by matrix multiplication, a factor of 2 must be introduced in $\pi_{\mu\nu}$ if $\nu = 4$, 5 or 6, *e.g.* $\pi_{74} = 2\pi_{3223}$.

A property tensor of type *u* must vanish if the point group of the material contains $\bar{1}$ or $1'$. The form of $\pi_{\mu\nu}$ for the remaining 69 crystallographic Shubnikov point groups has been obtained using the general result by Grimmer (1991*a*) and is given in Tables 1-3. These tables give the form of $\pi_{\mu\nu}$ for the point groups in all orientations in which they appear in the holohedry of the crystal system to which the point group belongs. They give the form for the holohedries in their conventional orientation with respect to the Cartesian coordinate system; the monoclinic holohedry is presented in the first and second setting. The different orientations are distinguished by the order of the entries in the Hermann–Mauguin symbol. A symbol in parentheses refers to a point group that has been met before in a different orientation when the nine fields in each table are read in the usual sequence from left to right and downwards.

The orientation of the axes **x**, **y** and **z** of the right-handed Cartesian coordinate system with respect to the symmetry elements in the Hermann–Mauguin symbol follow the usual conventions. For cubic crystals **x**, **y** and **z** have directions corresponding to the first entry in the Hermann–Mauguin symbol; for tetragonal, trigonal and hexagonal crystals **z** has direction corresponding to the first entry and **x** has direction corresponding to the second entry. (If there is no second entry then **x** may be any direction perpendicular to **z**.) For orthorhombic crystals **x** has the direction of the first entry, **y** the second and **z** the third. The monoclinic axis has direction **z** in the first setting and **y** in the second setting. For anorthic (=triclinic) crystals any right-handed orthonormal system may be chosen.

The Hermann–Mauguin symbols are given in the heading of the matrix together with the crystal system, the number of independent components (between square brackets) and a letter *A* to *F* used by Grimmer (1991*a*) to name the matrix. The number preceding the letter refers to the column in Tables 1 and 2 of that paper. The form of the tensor is shown similarly to that in Stefanakos *et al.* (1979). For the anorthic,

---

* *Note added in proof*: General results similar to those of Grimmer (1991*a*) were also given by Kopský (1979).

Table 1. *The form of $\pi_{\mu\nu}$ for anorthic, monoclinic and orthorhombic point groups*

Anorthic, 4*A*, [54] 1, $\bar{1}'$						Monoclinic, 4*B*, [28] (2nd setting) 2, *m*′, 2/*m*′						Monoclinic, 4*C*, [26] (2nd setting) *m*, 2′, 2′/*m*					
11	12	13	14	15	16	11	12	13	-	15	-	-	-	-	14	-	16
21	22	23	24	25	26	21	22	23	-	25	-	-	-	-	24	-	26
31	32	33	34	35	36	31	32	33	-	35	-	-	-	-	34	-	36
41	42	43	44	45	46	-	-	-	44	-	46	41	42	43	-	45	-
51	52	53	54	55	56	51	52	53	-	55	-	-	-	-	54	-	56
61	62	63	64	65	66	-	-	-	64	-	66	61	62	63	-	65	-
71	72	73	74	75	76	-	-	-	74	-	76	71	72	73	-	75	-
81	82	83	84	85	86	81	82	83	-	85	-	-	-	-	84	-	86
91	92	93	94	95	96	-	-	-	94	-	96	91	92	93	-	95	-

Monoclinic, 5*A*, [28] (1st setting) (2, *m*′, 2/*m*′)						Orthorhombic, 5*B*, [15] 222, *m*′*m*′2, (*m*′2*m*′, 2*m*′*m*′) *m*′*m*′*m*′						Orthorhombic, 5*C*, [13] *mm*2, 2′2′2, 2′*mm*′, (*m*2′*m*′) *mmm*′					
11	12	13	-	-	16	11	12	13	-	-	-	-	-	-	-	-	16
21	22	23	-	-	26	21	22	23	-	-	-	-	-	-	-	-	26
31	32	33	-	-	36	31	32	33	-	-	-	-	-	-	-	-	36
-	-	-	44	45	-	-	-	-	44	-	-	-	-	-	-	45	-
-	-	-	54	55	-	-	-	-	-	55	-	-	-	-	54	-	-
61	62	63	-	-	66	-	-	-	-	-	66	61	62	63	-	-	-
-	-	-	74	75	-	-	-	-	74	-	-	-	-	-	-	75	-
-	-	-	84	85	-	-	-	-	-	85	-	-	-	-	84	-	-
91	92	93	-	-	96	-	-	-	-	-	96	91	92	93	-	-	-

Monoclinic, 5*D*, [26] (1st setting) (*m*, 2′, 2′/*m*)						Orthorhombic, 5*E*, [13] (*m*2*m*, 2′22′, 2′*m*′*m*, *mm*′2′ *mm*′*m*)						Orthorhombic, 5*F*, [13] (2*mm*, 22′2′, *m*′2′*m*, *m*′*m*2′ *m*′*mm*)					
-	-	-	14	15	-	-	-	-	-	15	-	-	-	-	14	-	-
-	-	-	24	25	-	-	-	-	-	25	-	-	-	-	24	-	-
-	-	-	34	35	-	-	-	-	-	35	-	-	-	-	34	-	-
41	42	43	-	-	46	-	-	-	-	-	46	41	42	43	-	-	-
51	52	53	-	-	56	51	52	53	-	-	-	-	-	-	-	-	56
-	-	-	64	65	-	-	-	-	64	-	-	-	-	-		65	-
71	72	73	-	-	76	-	-	-	-	-	76	71	72	73	-	-	-
81	82	83	-	-	86	81	82	83	-	-	-	-	-	-	-	-	86
-	-	-	94	95	-	-	-	-	94	-	-	-	-	-	-	95	-

monoclinic and orthorhombic point groups considered in Table 1 a matrix element either vanishes (marked -) or may have an arbitrary value (marked by the indices of the matrix element). For the tetragonal and cubic point groups given in Table 2, two matrix elements may be equal (marked by the same integer) or opposite (marked by integers with the same modulus but opposite sign). For the trigonal and hexagonal point groups given in Table 3, more complicated connections between matrix elements appear, as explained in the caption. The heading of the forms $8A-8C$ in Table 3 shows that these forms are valid not only for certain hexagonal point groups but also for circular point groups, *i.e.* point groups with an ∞-fold rotation axis (see Grimmer 1991*b*). The form of $\pi_{\mu\nu}$ for the spherical point groups $\infty\infty$ and $\infty\infty m'$ is given by 9*B* in Table 2 with the additional restriction $44 = 11-12$, which reduces the number of independent components to two.

It follows from Grimmer (1991*a*, *b*) that the same forms of the matrices also appear for *s*, *t* and *i* tensors of rank 4 that are symmetric in two indices. Only the groups that appear in the heading have to be changed. For the crystallographic groups this is done according to Table 2 in Grimmer (1991*a*) and for the limiting groups according to the table at the end of Grimmer (1991*b*).

An example is the *t* tensor Γ describing induced gyrotropic birefringence according to

$$\varepsilon_{ij} = \Gamma_{ijkl} H_k k_l,$$

where ε denotes the dielectric tensor, *H* the magnetic field and *k* the wave vector of the light wave. The tensor Γ is symmetric in its first two indices so that the matrices given in Tables 1-3 must be transposed. Induced gyrotropic birefringence has been observed in $LiIO_3$ (Markelov, Novikov & Turkin, 1977).

3. Comparison with earlier results

Comparing the numbers of independent components for the various point groups in Tables 1-3 with the results in Table 2 of Lyubimov (1965) one finds that they agree; only a few underlines, which correspond to our primes, are missing in the point-group symbols.

Rado (1962) defined the tensor π in his equation (*A*18) to be symmetric in its first two indices; he did not change from tensor components to matrix elements. Taking these differences into account one finds that his restrictions (*A*19) of the form of π for Cr_2O_3 (Shubnikov point group $\bar{3}'m'$) agree with our result 7*B* for $\bar{3}'m'$.

The critical remarks of Stefanakos *et al.* (1979) concerning the papers by Rado and Lyubimov are

Table 2. *The form of $\pi_{\mu\nu}$ for tetragonal and cubic point groups*

Tetragonal, $6A$, [14] 4, $\bar{4}'$ $4/m'$						Tetragonal, $6B$, [8] 422, $4m'm'$, $\bar{4}'2m'$, $(\bar{4}'m'2)$ $4/m'm'm'$						Tetragonal, $6C$, [6] $4mm$, $42'2'$, $\bar{4}'m2'$, $(\bar{4}'2'm)$ $4/m'mm$					
11	12	13	-	-	16	11	12	13	-	-	-	-	-	-	-	-	16
12	11	13	-	-	-16	12	11	13	-	-	-	-	-	-	-	-	-16
31	31	33	-	-	-	31	31	33	-	-	-	-	-	-	-	-	-
-	-	-	44	45	-	-	-	-	44	-	-	-	-	-	-	45	-
-	-	-	54	55	-	-	-	-	-	55	-	-	-	-	54	-	-
61	62	63	-	-	66	-	-	-	-	-	66	61	62	63	-	-	-
-	-	-	55	-54	-	-	-	-	55	-	-	-	-	-	-	-54	-
-	-	-	-45	44	-	-	-	-	-	44	-	-	-	-	-45	-	-
-62	-61	-63	-	-	66	-	-	-	-	-	66	-62	-61	-63	-	-	-
Tetragonal, $6D$, [14] $\bar{4}$, $4'$ $4'/m'$						Tetragonal, $6E$, [7] $\bar{4}2m$, $4'22'$, $\bar{4}m'2'$, $4'm'm$ $4'/m'm'm$						Tetragonal, $6F$, [7] $(\bar{4}m2$, $4'2'2$, $\bar{4}2'm'$, $4'mm'$ $4'/m'mm')$					
11	12	13	-	-	16	11	12	13	-	-	-	-	-	-	-	-	16
-12	-11	-13	-	-	16	-12	-11	-13	-	-	-	-	-	-	-	-	16
31	-31	-	-	-	36	31	-31	-	-	-	-	-	-	-	-	-	36
-	-	-	44	45	-	-	-	-	44	-	-	-	-	-	-	45	-
-	-	-	54	55	-	-	-	-	-	55	-	-	-	-	54	-	-
61	62	63	-	-	66	-	-	-	-	-	66	61	62	63	-	-	-
-	-	-	-55	54	-	-	-	-	-55	-	-	-	-	-	-	54	-
-	-	-	45	-44	-	-	-	-	-	-44	-	-	-	-	45	-	-
62	61	63	-	-	-66	-	-	-	-	-	-66	62	61	63	-	-	-
Cubic, $9A$, [5] 23, $m'\bar{3}'$						Cubic, $9B$, [3] 432, $\bar{4}'3m'$, $m'\bar{3}'m'$						Cubic, $9C$, [2] $\bar{4}3m$, $4'32'$, $m'\bar{3}'m$					
11	12	13	-	-	-	11	12	12	-	-	-	-	12	-12	-	-	-
13	11	12	-	-	-	12	11	12	-	-	-	-12		12	-	-	-
12	13	11	-	-	-	12	12	11	-	-	-	12	-12	-	-	-	-
-	-	-	44	-	-	-	-	-	44	-	-	-	-	-	44	-	-
-	-	-	-	44	-	-	-	-	-	44	-	-	-	-	-	44	-
-	-	-	-	-	44	-	-	-	-	-	44	-	-	-	-	-	44
-	-	-	74	-	-	-	-	-	44	-	-	-	-	-	-44	-	-
-	-	-	-	74	-	-	-	-	-	44	-	-	-	-	-	-44	-
-	-	-	-	-	74	-	-	-	-	-	44	-	-	-	-	-	-44

therefore not justified. The results of Stefanakos *et al.* (1979) are given in their Table 1. It contains each of the six tetragonal forms twice. The result for the point group 3 is erroneous, which also affects most of the other trigonal and hexagonal forms because they are obtained by combining the restrictions for 3 with restrictions for other generators of the point group in question. Their result for 32 has been obtained by combining the restrictions for 3 and 2‖y instead of 2‖x as usual. Also the result for the cubic group $\bar{4}3m$ is not correct.

4. Possibilities for measuring the effect

Instead of measuring the electric polarization P in a material subject to σ and H it is also possible to measure the magnetic polarization M in a material subject to σ and an electric field E or the strain ε in a material subject to E and H. Up to second order in the applied fields, the three experimental situations can be described by the relations

$$P_i = \kappa_i^0 + \alpha_{ij}H_j + d_{ikl}\sigma_{kl} + A_{ijk}H_jH_k + \pi_{ijkl}H_j\sigma_{kl} + D_{iklmn}\sigma_{kl}\sigma_{mn}, \qquad (2)$$

$$M_j = \chi_j^0 + \alpha_{ij}E_i + q_{jkl}\sigma_{kl} + A'_{jkl}E_kE_l + \pi_{ijkl}E_i\sigma_{kl} + Q_{jklmn}\sigma_{kl}\sigma_{mn}, \qquad (3)$$

$$\varepsilon_{kl} = s_{kl}^0 + d_{ikl}E_i + q_{jkl}H_j + e_{ijkl}E_iE_j + \pi_{ijkl}E_iH_j + m_{ijkl}H_iH_j, \qquad (4)$$

where κ^0 and χ^0 denote the spontaneous electric and magnetic polarizations, s^0 the spontaneous strain (*cf.* Aizu, 1970, or Schmid, 1973), α the magnetoelectric tensor, A and A' second-order magnetoelectric tensors, d and q the piezoelectric and piezomagnetic tensors, D and e second-order piezoelectric tensors and Q and m second-order piezomagnetic tensors (e and m describe electrostriction and magnetostriction).

The tensor π can be measured most conveniently if all other terms on the right-hand sides of (2)-(4) vanish. The Neumann principle requires property tensors to be invariant under the point group of the material. Property tensors of type u must vanish for all point groups containing $\bar{1}$ or $1'$, those of type t if the group contains $\bar{1}$ or $\bar{1}'$ and those of type s if the group contains $1'$ or $\bar{1}'$. Tensors of low rank may vanish for additional point groups. The property tensors appearing in (2)-(4) have the following types:

Type	Property tensor
u	α, π
t	κ^0, A, d, D
s	χ^0, A', q, Q
i	s^0, e, m.

Table 3. *The form of $\pi_{\mu\nu}$ for trigonal and hexagonal point groups*

$$\mathit{66} = 11 - 12, \quad \mathit{16} = 62 - 61$$

Boldface numbers designate elements that are twice the element with the same number in normal type style.

Trigonal, 7*A*, [18] 3, $\bar{3}'$						Trigonal, 7*B*, [10] 32, $3m'$, $\bar{3}'m'$						Trigonal, 7*C*, [8] $3m$, $32'$, $\bar{3}'m$					
11	12	13	14	-25	*16*	11	12	13	14	-	-	-	-	-	-	-25	*16*
12	11	13	-14	25	*-16*	12	11	13	-14	-	-	-	-	-	-	25	*-16*
31	31	33	-	-	-	31	31	33	-	-	-	-	-	-	-	-	-
41	-41	-	44	45	**82**	41	-41	-	44	-	-	-	-	-	-	45	**82**
-52	52	-	54	55	**71**	-	-	-	-	55	**71**	-52	52	-	54	-	-
61	62	63	25	14	*66*	-	-	-	-	14	*66*	61	62	63	25	-	-
71	-71	-	55	-54	**52**	71	-71	-	55	-	-	-	-	-	-	-54	**52**
-82	82	-	-45	44	**41**	-	-	-	-	44	**41**	-82	82	-	-45	-	-
-62	-61	-63	25	14	*66*	-	-	-	-	14	*66*	-62	-61	-63	25	-	-
Hexagonal, 8*A*, [12] 6, $\bar{6}'$ $6/m'$ ∞, ∞/m'						Hexagonal, 8*B*, [7] 622, $6m'm'$, $\bar{6}'2m'$, ($\bar{6}'m'2$) $6/m'm'm'$ $\infty 2$, $\infty m'$, $\infty/m'm'$						Hexagonal, 8*C*, [5] $6mm$, $62'2'$, $\bar{6}'m2'$, ($\bar{6}'2'm$) $6/m'mm$ ∞m, $\infty 2'$, $\infty/m'm$					
11	12	13	-	-	*16*	11	12	13	-	-	-	-	-	-	-	-	*16*
12	11	13	-	-	*-16*	12	11	13	-	-	-	-	-	-	-	-	*-16*
31	31	33	-	-	-	31	31	33	-	-	-	-	-	-	-	-	-
-	-	-	44	45	-	-	-	-	44	-	-	-	-	-	-	45	-
-	-	-	54	55	-	-	-	-	-	55	-	-	-	-	54	-	-
61	62	63	-	-	*66*	-	-	-	-	-	*66*	61	62	63	-	-	-
-	-	-	55	-54	-	-	-	-	55	-	-	-	-	-	-	-54	-
-	-	-	-45	44	-	-	-	-	-	44	-	-	-	-	-45	-	-
-62	-61	-63	-	-	*66*	-	-	-	-	-	*66*	-62	-61	-63	-	-	-
Hexagonal, 8*D*, [6] $\bar{6}$, $6'$ $6'/m$						Hexagonal, 8*E*, [3] $\bar{6}2m$, $6'22'$, $\bar{6}m'2'$, $6'm'm$ $6'/mm'm$						Hexagonal, 8*F*, [3] ($\bar{6}m2$, $6'2'2$, $\bar{6}2'm'$, $6'mm'$ $6'/mmm'$)					
-	-	-	14	-25	-	-	-	-	14	-	-	-	-	-	-	-25	-
-	-	-	-14	25	-	-	-	-	-14	-	-	-	-	-	-	25	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
41	-41	-	-	-	**82**	41	-41	-	-	-	-	-	-	-	-	-	**82**
-52	52	-	-	-	**71**	-	-	-	-	-	**71**	-52	52	-	-	-	-
-	-	-	25	14	-	-	-	-	-	14	-	-	-	-	25	-	-
71	-71	-	-	-	**52**	71	-71	-	-	-	-	-	-	-	-	-	**52**
-82	82	-	-	-	**41**	-	-	-	-	-	**41**	-82	82	-	-	-	-
-	-	-	25	14	-	-	-	-	-	14	-	-	-	-	25	-	-

The tensor α has the same type as π but its hexagonal forms *D*, *E*, *F* and its cubic form *C* vanish, so that α may differ from zero in only 58 instead of 69 crystallographic Shubnikov point groups (in addition to eight circular and two isotropic groups). Three among the 11 additional groups in which α vanishes contain $\bar{1}'$, *viz* $6'/m$, $6'/mm'm$ and $m'\bar{3}'m$. It follows that only the term containing π survives in (2) and (3) for these three groups. Equation (4) contains the tensors s^0, *e* and *m*, which may be different from zero in every point group.* Oleś, Kajzar, Kucab & Sikora (1976) do not list materials with point groups $6'/m$, $6'/mm'm$ or $m'\bar{3}'m$.

The 21 crystallographic and four limiting point groups containing $1'$ but neither $\bar{1}$ nor $\bar{1}'$ describe materials that are ordered antiferromagnetically and antiferrolectrically (*cf.* Schmid, 1973). Because property tensors of types *s* and *t* must vanish for these point groups, only terms with α and π can survive in (2) and (3). We have seen that α also vanishes for three of these point groups. The remaining ones are

$$\bar{1}',\ 2/m',\ m'm'm',\ 2'/m,\ mmm'$$

$$4/m',\ 4/m'm'm',\ 4/m'mm,\ 4'/m',\ 4'/m'm'm$$

$$\bar{3}',\ \bar{3}'m',\ \bar{3}'m,\ 6/m',\ 6/m'm'm',\ 6/m'mm$$

$$m'\bar{3}',\ m'\bar{3}'m',\ \infty/m',\ \infty/m'm',\ \infty/m'm,\ \infty\infty m'.$$

Some of these symmetries are also convenient for measuring the piezomagnetoelectric effect. Consider, as an example, Cr_2O_3 with point-group symmetry $\bar{3}'m'$. The non-vanishing components of α are $\alpha_{11} = \alpha_{22}$ and α_{33}. Assume that Cr_2O_3 is subject to stress and to a magnetic field $\mathbf{H} = (0, 0, H_3)$. Equation (2)

---

* The vanishing of terms in (2)-(4) may conveniently be discussed making use of Table II in Schmid (1973). The crystallographic Shubnikov point groups admitting the piezomagnetoelectric effect are exactly those that in the column 'Type of ordering' have no *D* in the subcolumn 'Magnetic' and no *O* in the subcolumn 'Electric'. The term κ^0 is permitted for the groups with an *E* in the column 'Permitted terms of stored free enthalpy', χ^0 for the groups with *H*, α for those with *EH*, *A* and *d* for those with *EHH*, *A'* and *q* for those with *HEE*.

and the form of π given in Table 3 then show that

$$P_1 = [2\pi_{2311}\sigma_{12} + 2\pi_{2323}\sigma_{31}]H_3$$

$$P_2 = [\pi_{2311}(\sigma_{11} - \sigma_{22}) + 2\pi_{2323}\sigma_{23}]H_3$$

$$P_3 = [\alpha_{33} + \pi_{3311}(\sigma_{11} + \sigma_{22}) + \pi_{3333}\sigma_{33}]H_3,$$

i.e. only the piezomagnetoelectric effect contributes to P_1 and P_2. Also $U_2N_2P_2$ U_2N_2S, $Nb_2Co_4O_9$ and $Nb_2Mn_4O_9$ have symmetry $\bar{3}'m'$ according to Oleś *et al.* (1976).

The author is indebted to Professor H. Schmid for his suggestion to investigate the form of the piezomagnetoelectric effect and for stimulating discussions.

References

Aizu, K. (1970). *Phys. Rev. B*, **2**, 754-772.
Grimmer, H. (1991*a*). *Acta Cryst.* A**47**, 226-232.
Grimmer, H. (1991*b*). *Helv. Phys. Acta*, **64**, 187-188.
Kopský, V. (1979). *Acta Cryst.* A**35**, 95-101.
Lyubimov, V. N. (1965). *Kristallografiya*, **10**, 520-524; *Sov. Phys. Crystallogr.* **10**, 433-436.
Markelov, V. A., Novikov, M. A. & Turkin, A. A. (1977). *Pis'ma Zh. Eksp. Teor. Fiz.* **25**, 404-407; *JETP Lett.* **25**, 378-380.
Oleś, A., Kajzar, F., Kucab, M. & Sikora, W. (1976). *Magnetic Structures Determined by Neutron Diffraction.* Warsaw: Państwowe Wydawnictwo Naukowe.
Rado, G. T. (1962). *Phys. Rev.* **128**, 2546-2556.
Schmid, H. (1973). *Int. J. Magn.* **4**, 337-361.
Sirotine, Y. & Chaskolskaïa, M. (1984). *Fondements de la Physique des Cristaux.* Moscow: Mir.
Stefanakos, E. K., Tinder, R. F. & Thapliyal, H. V. (1979). *J. Phys. C*, **12**, 4921-4925.

Acta Cryst. (1992). A**48**, 271-276

A Resolution-Sensitive Procedure for Comparing Protein Surfaces and its Application to the Comparison of Antigen-Combining Sites

By Mark Gerstein

MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, England,
and University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received 9 July 1991; accepted 22 October 1991*)

Abstract

Resolution is a crucial parameter to consider in making surface comparisons. A method is presented here for the rapid, objective and automatic comparison of selected parts of protein surfaces as a function of resolution using differences and correlations of Fourier coefficients. A test-case application of this procedure to the surfaces of five immunoglobulin antigen-combining sites allowed them to be partitioned into two categories.

1. Introduction

Knowledge of the topography of protein surfaces is essential to understanding molecular recognition. A solved X-ray crystal structure contains a wealth of information about these surfaces and using modern graphics technology it is relatively easy to examine and compare them in all their detail (*e.g.* Max, 1984; Connolly, 1983*a*). However, comparisons based on human observation are subjective, qualitative and time-consuming. The number of solved structures is continually increasing and so are the methods for generating new conformations and surface descriptions from these structures - *e.g.* *CONGEN* (Bruccoleri & Karplus, 1987) and the molecular surface (Richards, 1977). The time necessary to look through a comprehensive sample of surfaces can be prohibitive. Consequently, it is expedient to develop an objective and quantitative procedure for comparing protein surfaces rapidly and automatically.

An essential parameter to consider in any surface-shape comparison method is resolution. Surfaces - such as those of two human faces - that are different in medium-resolution detail may have similar low-resolution features and high-resolution texture. By comparing surfaces in terms of Fourier coefficients, one naturally obtains information ordered in terms of increasing resolution.

We are specifically interested in immunoglobulin recognition and have tested our approach by comparing the surfaces of antigen-combining sites. The problem of surface comparisons is particularly evident for these molecules, since recombination of a small number of genes can produce an estimated 10^8 different antigen-combining sites, each with distinctly different surface-recognition properties (Milstein, 1990). However, before the results of the procedure on this specific case is described, it is presented in a more general context.

0108-7673/92/030271-06$03.00