

Comments on the Problem of Obtaining Magnetic Structures from Nuclear Magnetic Resonance Data

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The general systematic procedure is described for determining the magnetic space group (Shubnikov group) of a crystal from the magnetic point symmetry found from nuclear magnetic resonance data (Heesch, standard representation) and the crystallographic structure. The aspect group, which is the observed n.m.r. symmetry, is therefore defined and the Heesch groups which are related by the time inversion operation for magnetic moments to each aspect group are derived. The proposed method is demonstrated with a few specific examples. The difference between the concept of a magnetic point group and the concept of a Heesch group is clarified.

In a magnetically ordered crystal the three axial vector fields \mathbf{B} , \mathbf{H} and \mathbf{M} , which are related by $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ all exhibit repetition patterns given by the magnetic space group (Shubnikov group) of the crystal (Opechowski & Guccione, 1965; Koptsik, 1966). Each symmetry element of such a group is specified by giving two rotation matrices φ_i and θ_i , and a translation τ_i . Through the relation

$$\mathbf{r}_i = \varphi_i \cdot \mathbf{r}_0 + \tau_i, \quad (1)$$

the quantities φ_i and τ_i specify the position vectors \mathbf{r}_i of a set of points at which \mathbf{B} , \mathbf{H} and \mathbf{M} have the same magnitudes as at the point whose position vector is \mathbf{r}_0 . The orientation of the axial vectors at \mathbf{r}_i and \mathbf{r}_0 is related by

$$\mathbf{B}(\mathbf{r}_i) = \theta_i \cdot \mathbf{B}(\mathbf{r}_0), \quad (2)$$

with similar equations for \mathbf{H} and \mathbf{M} . The matrices φ_i and θ_i are connected by (Opechowski & Guccione, 1965)

$$\theta_i = \varepsilon_i \delta_i \varphi_i, \quad (3)$$

where δ_i is the value of the determinant of φ_i and the signature ε_i equals +1 for the so-called unprimed, uncoloured, or ordinary elements and equals -1 for the so-called primed, coloured or anti-elements. The quantities φ_i and τ_i constitute the elements ($\varphi_i|\tau_i$) of an ordinary space group which is often the chemical space group of the crystal or one of its subgroups. The matrix φ_i induces a proper or improper rotation and the translation τ_i is the vector sum of translations inherent in the elements (as in glide planes or screw axes), displacements which locate the elements in the unit cell, and translations which are formed from the basis vectors of the unit cell of the space group to which ($\varphi_i|\tau_i$) belongs.

Consider a nuclear magnetic resonance (n.m.r.) experiment carried out on a nucleus located at a site whose position vector is \mathbf{r}_0 . If the elements ($\varphi_i|\tau_i$) constitute the elements of the chemical space group of the crystal, or one of its subgroups, then the sites whose position vectors \mathbf{r}_i are related to \mathbf{r}_0 by equation (1) will be occupied by similar nuclei. The fields $\mathbf{B}(\mathbf{r}_i)$ at these sites can be directly measured by the n.m.r. experiment and will be found to differ only in direction but not in magnitude. Consider the array of axial vectors \mathbf{B}_i formed by translating each $\mathbf{B}(\mathbf{r}_i)$ to a common origin. The symmetry of the array may be represented by one of the 122 Heesch groups (Heesch, 1930). The concept of Heesch group used here and first introduced by Riedel & Spence (1960) corresponds to the 'standard representation' of Opechowski & Guccione (1965). The elements of this group will be represented by the matrices θ_i . The representation is, however, an *unfaithful* one (Lomont, 1959) and thus the experimental determination of the θ_i by n.m.r. does not uniquely determine the Heesch group G_h . In fact, there are only 32 distinguishable sets of θ_i corresponding to the 122 Heesch groups. The 32 sets are isomorphous with the 32 ordinary point groups. Thus Neumann's principle remains intact (Nye, 1957). Let us call each of the 32 observable sets of θ_i an *aspect* group G_a . We may think of the aspect group of a given magnetically ordered crystal as being the point group under which the \mathbf{B}_i would transform if they were polar vectors rather than axial vectors as they actually are. The aspect group is easily determined from n.m.r. data.

We prefer to consider the fundamental internal magnetic field as \mathbf{B} . \mathbf{B} is in turn generated by the distribution of magnetization \mathbf{M} which arises from the spin and orbital angular momentum. The alternate point of view which considers the internal field as \mathbf{H} (see e.g. Abragam, 1961) is more conventional but in this case it is most convenient to consider the field as arising from a set of currents which can be related to the spin and orbital angular momentum. Our prefer-

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ence for the first point of view stems from the fact that in the neutron diffraction experiment it is easy to conceive of measuring the distribution of magnetization.

The possible Heesch groups corresponding to each aspect group can be found in the following straightforward but rather tedious way. The set of elements in a given G_h is enumerated. In the set each element arising from a rotation or rotatory inversion axis of order n is replaced with a corresponding element arising from a rotation axis of order n . Thus, for example, both the elements arising from 2 and $m=\bar{2}$ are to be replaced with the elements arising from 2 (Riedel & Spence, 1960). Elements arising from anti-rotation and anti-rotatory inversion axes of order n are replaced with corresponding elements arising from ordinary rotatory inversion axes of order n . Thus, the elements generated by $2'$ and $m'=\bar{2}'$ are to be replaced by corresponding elements of $\bar{2}=m$. The collection of distinct elements which remains after all the replacements have been made constitute the elements of G_a . Consider, for example, $G_h=2'/m'$, whose elements are 1, $2'$, m' , $\bar{1}$. The corresponding set of elements after replacements are 1, $\bar{2}$, $\bar{2}$, 1, and G_a is therefore just $\bar{2}=m$. In Table 1 we give the Heesch groups corresponding to each aspect group.

Table 1. Heesch groups and corresponding local field symmetries

Aspect group	Heesch group	N_h	N_a
Triclinic system			
1	1	1	1
2	$\bar{1}$	2	1
3	$\bar{1}$	2	2
4	$\bar{1}\bar{1}'$	4	2
5	$1'$	2	2
Monoclinic system			
6	m	2	2
7	m'	2	2
8	$2'/m'$	4	2
9	2	2	2
10	m	2	2
11	$2/m$	4	2
12	$2/m$	4	4
13	$m1'$	4	4
14	$2/m1'$	8	4
15	$2/m'$	4	4
16	$2'/m$	4	4
Orthorhombic system			
17	$mm2$	4	4
18	$m'm'2'$	4	4
19	$22'2'$	4	4
20	$mm'm'$	8	4
21	222	4	4
22	$mm2$	4	4
23	mmm	8	4
24	mmm	8	8
25	$mm21'$	8	8
26	$mmm1'$	16	8
27	$m'm'm'$	8	8
28	$m'mm$	8	8

Aspect group	Heesch group	N_h	N_a
Tetragonal system			
29	4	4	4
30	$\bar{4}$	4	4
31	$4/m$	8	4
32	$\bar{4}$	4	4
33	$\bar{4}'$	4	4
34	$4'/m$	8	4
35	$4/m$	8	8
36	$\bar{4}1'$	8	8
37	$4/m1'$	16	8
38	$4/m'$	8	8
39	$4'/m'$	8	8
40	$\bar{4}2u$	8	8
41	$4'mm'$	8	8
42	$\bar{4}'2m'$	8	8
43	$\bar{4}2'm$	8	8
44	$4/mmm'$	16	8
45	$4mm$	8	8
46	$4m'm'$	8	8
47	$42'm'$	8	8
48	$4/mm'm'$	16	8
49	422	8	8
50	$4mm$	8	8
51	$\bar{4}2m$	8	8
52	$4/mmm$	16	8
53	$4/mmm$	16	16
54	$4mm1'$	16	16
55	$\bar{4}2m1'$	16	16
56	$4/mmm1'$	32	16
57	$4/mmm$	16	16
58	$4/m'mm$	16	16
59	$4'/m'mm$	16	16
Trigonal system			
60	3	3	3
61	$\bar{3}$	6	3
62	$\bar{3}$	6	6
63	$\bar{3}1'$	12	6
64	$3'$	6	6
65	$3m$	6	6
66	$3m'$	6	6
67	$\bar{3}m'$	12	6
68	32	6	6
69	$3m$	6	6
70	$\bar{3}m$	12	6
71	$\bar{3}m$	12	12
72	$3m1'$	12	12
73	$\bar{3}m1'$	24	12
74	$\bar{3}'m$	12	12
75	$\bar{3}'m'$	12	12
Hexagonal system			
76	6	6	6
77	$\bar{6}$	6	6
78	$6/m$	12	6
79	$\bar{6}$	6	6
80	$\bar{6}'$	6	6
81	$6/m$	12	6
82	$6/m$	12	12
83	$\bar{6}1'$	12	12
84	$6/m1'$	24	12
85	$6/m$	12	12
86	$6/m$	12	12
87	622	12	12
88	$6mm$	12	12
89	$\bar{6}m2$	12	12
90	$6/mmm$	24	12
91	$\bar{6}2m$	12	12
92	$\bar{6}'m2'$	12	12

Table 1 (cont.)

Aspect group	Heesch group	N_h	N_a
Hexagonal system			
93	6'2'2	12	12
94	6mm	12	12
95	6'/mmm'	24	12
96	62'2'	12	12
97	6mm	12	12
98	6m'2'	12	12
99	6/mmm'm'	24	12
100	6'/mm'm'	24	24
101	6'/mmm	24	24
102	6'/mm'm'	24	24
103	6221'	24	24
104	6mm1'	24	24
105	6m21'	24	24
106	6/mmm1'	48	24
Cubic system			
107	23	12	12
108	m3	24	12
109	m3	24	24
110	m31'	48	24
111	m3	24	24
112	432	24	24
113	43m	24	24
114	m3m	48	24
115	43m	24	24
116	432	24	24
117	m3m	48	24
118	m3m	48	48
119	m3m	48	48
120	m3m1'	96	48
121	m3m	48	48
122	m3m	48	48

Let N_a be the number of elements in a given G_a and N_h the number of elements in a G_h belonging to the given G_a . N_a is either equal to $N_h/2$ or equal to N_h , depending on whether G_h does or does not contain the inversion $\bar{1}$. The number N_a is experimentally just the number of local fields having the same field magnitude, provided the fields have general orientations. Let N_n be the number of equivalent nuclei in the chemical unit cell and let N_f be the number of observed distinct local field magnitudes. The ratio N_n/N_f is equal to $N_h/2$ or N_h depending on whether G_h does or does not contain the anti-identity $1'$. Combining the previous ideas we have three cases:

- (1) $N_a = \frac{1}{2}N_n/N_f \dots G_h$ contains $\bar{1}$ but not $1'$,
- (2) $N_a = 2N_n/N_f \dots G_h$ contains $1'$ but not $\bar{1}$,
- (3) $N_a = N_n/N_f \dots G_h$ contains both $\bar{1}$ and $1'$,
or does not contain
either $\bar{1}$ or $1'$.

For example, consider the mineral azurite (Riedel & Spence, 1960), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, which becomes anti-ferromagnetically ordered below 1.86°K . One finds experimentally $G_a = 2/m$ (hence $N_a = 4$) and $N_f = 2$. There are two molecular units in the chemical unit cell (hence $N_n = 4$). Thus, $N_a = 2N_n/N_f$, and G_h must contain $1'$ but not $\bar{1}$. Referring to Table 1, one finds that of the five G_h permitted by $G_a = 2/m$, only $G_h = 21'$ and $G_h = m1'$ are allowed. As a second example, consider

$\text{CoCl}_2[\text{CS}(\text{NH}_2)_2]_4$ whose Néel temperature is $\sim 1^\circ\text{K}$ (Au, Cowen, Spence & Van Till, 1965). There are four molecular units in the chemical unit cell and therefore $N_n = 64$. Experimentally, one finds $G_a = 4/m$ (hence $N_a = 8$) and $N_f = 8$. Hence, $N_a = N_n/N_f$ and the permitted G_h must either contain both $\bar{1}$ and $1'$, or it must contain neither $\bar{1}$ nor $1'$. From Table 1, one finds that the first possibility allows $G_h = 4/m1'$ and the second allows $4/m'$ and $4'/m'$.

After finding a set of permitted G_h one must restore the translations to obtain the permitted magnetic space groups. If the G_h does not contain $1'$, one has only to consider possible non-primitive translations which convert axes into screw axes and mirror planes into glide planes. If G_h contains $1'$, the magnetic unit cell is a multiple of the chemical unit cell. In either case, the translations which are restored must be selected so that they in no way modify the positions of nuclei as given by the chemical space group. Opechowski & Guccione (1965) have given a convenient listing of the magnetic space groups in which all magnetic space groups compatible with a given chemical space group are listed together. Starting with such a list, one has only to eliminate those magnetic space groups which do not reduce to the experimentally permitted Heesch groups when the non-primitive translations are removed or the extended magnetic cell is indicated by $1'$ in the Heesch group symbol. Finally, when this process is completed, there will generally remain a small set of magnetic space groups which satisfy all the criteria for acceptability we have mentioned. The final decision as to the correct magnetic space group must be made by computing the *magnitudes* of the internal fields at the sites of the probe for each of the permitted groups and comparing them with the experimental values. This process also involves the knowledge of the direction of magnetization which can be obtained from magnetic susceptibility measurements. An example of the results of such computations can be found in the article by Spence & Nagarajan (1966).

Finally, we wish to clarify the difference between the concept of a magnetic point group as defined by Opechowski & Guccione (1965) and the Heesch groups used here. Formally, this difference amounts to the fact that the magnetic point group as defined by Opechowski & Guccione is obtained by removing *all* translations from the magnetic space group while in the Heesch groups employed here the anti-translations are carried into the symbol as the anti-identity $1'$. The point groups of two magnetic space groups one of which contains anti-translations, and the other of which does not, may be the same, but the Heesch group symbol will clearly indicate the fact that they stem from different unit cells. There are only 90 magnetic point groups. In the language of color groups, these would be called black-white groups. The remaining 32 groups added to this set to make the 122 Heesch groups would be called grey groups. Their use in the present type

of discussion seems first to have been introduced by Donnay & Donnay (1959). Their use in the same connexion was also suggested by Landau & Lifshitz (1958).

References

- ABRAGAM, A. (1961). *The Principles of Nuclear Magnetism*. London: Oxford Univ. Press.
- AU, R., COWEN, J. A., SPENCE, R. D. & VAN TILL, H. (1965). *Low Temperature Physics* p. 877. New York: Plenum Press.
- DONNAY, J. D. H. & DONNAY, G. (1959). *C.r. Acad. Sci. Paris*, **248**, 3317.
- HEESCH, H. (1930). *Z. Kristallogr.* **73**, 325.
- KOPTSIK, V. A. (1966). *Shubnikov Groups*. Moscow Univ. Press.
- LANDAU, L. & LIFSHITZ, E. (1958). *Statistical Physics*. London: Pergamon Press.
- LOMONT, J. S. (1959). *Applications of Finite Groups*. New York: Academic Press.
- NYE, J. F. (1957). *Physical Properties of Crystals*. Oxford: Clarendon Press.
- OPECHOWSKI, W. & GUCCIONE, R. (1965). *Magnetism*. Vol. II A. Edited by G. T. RADO & H. SUHL. p. 105. New York: Academic Press.
- RIEDEL, E. P. & SPENCE, R. D. (1960). *Physica*, **26**, 1174.
- SPENCE, R. D. & NAGARAJAN, V. (1966). *Phys. Rev.* **149**, 191

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The Influence of Thermal Parameters on Electron Density Maps

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Accurate formulae for the convolution of atomic one-electron density functions onto anisotropic Gaussian distribution functions are presented. Theoretical time average electron density functions for some first row atoms at various degrees of resolution are analyzed by variation of Debye-Waller factors. The calculations show that for present day precision in thermal parameters Fourier difference maps suffer an unmanageable bias near the time-average nuclear positions. Residual densities at distances greater than 0.4 Å from time-average nuclear positions are affected only marginally by errors in atomic thermal parameters. The upper limit in $\sin \theta/\lambda$ for proper reconstruction of valence densities is also studied. For the room temperature case, 0.8 Å⁻¹ in $\sin \theta/\lambda$ is adequate; for low temperature work ($\sim -180^\circ\text{C}$) 1.2 Å⁻¹ is more appropriate.

Introduction

Electron density maps evaluated by Fourier syntheses using X-ray diffraction structure factors, F_o 's, can present a variety of distortions as a result of experimental limitations. In the difference Fourier technique, parametric errors in the calculated structure factors, F_c 's, must also be considered. A recent study on bonded electron distributions in organic molecular crystals (O'Connell, Rae & Maslen, 1966) has prompted the author to investigate some errors inherent in the difference Fourier syntheses of X-ray diffraction data. It is important that these effects be reviewed and studied in quantitative detail, so that one can make meaningful interpretations of electron density maps. In the present paper we shall assume that there is an adequate macroscopic theory for the determination of structure factors from X-ray diffraction intensities of real crystals (*cf.* Zachariasen, 1967). We shall also assume that the observed structure factors can be phased by conventional structure factor calculations (this restricts us primarily to centric structures). We will thus confine ourselves to the problems of series termination error

and parametric errors in the difference Fourier synthesis technique.

If, in a Fourier difference synthesis, only the $(1s)^2$ density is subtracted out, we shall call the residual density a valence electron density map. For a molecular crystal, comprised of first row atoms, such a density map should be of interest to chemists and is hopefully interpretable in terms of $2s$ and $2p$ orbital product density functions. The influence of thermal motion on electron densities is an important effect to be considered.

In an analysis of the valence electron density ρ_v , however, the error must be assessed from the corresponding errors in $\bar{\rho}_o$ and $\bar{\rho}_c$, the respective incomplete Fourier series of the observed and calculated structure factors. Thus

$$\Delta F_v = F_o - F_c$$

implies

$$\rho_v = \bar{\rho}_o - \bar{\rho}_c$$

and any variation in ρ_v is

$$\delta \rho_v = \delta \bar{\rho}_o - \delta \bar{\rho}_c.$$