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**Some advantages of a complete data set.** By JAMES A. IBERS, *Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.*

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Some of the many practical advantages of collecting a complete data set are discussed. These include the detection of errors in the measurement of intensities, assignment of meaningful standard deviations to the intensities, and, if anomalous scattering is important, the determination of the point group.

With the advent of multi-circle diffractometers it has become easy to collect *all* intensity data within a given range of scattering angle. In this note we point out some of the important advantages of such a procedure.

Consider first a light-atom structure in which anomalous scattering may be neglected. It is a matter of experience that even from a non-absorbing, centrosymmetric crystal  $I(hkl)$  will generally differ systematically from  $I(\bar{h}\bar{k}\bar{l})$  regardless of counting times\*. Therefore, under sensible experimental conditions a better average data set is apt to result if one collects all  $N$  of the equivalent forms and then averages these (after corrections for absorption and other effects, if appropriate) rather than if one spends  $N$  times as long counting each of the  $1/N$  independent reflections. Particularly if one collects these equivalent forms at widely varying times during the experiment, then comparison of the individual estimates of  $\sigma(I)$  with those obtained from the spread among the equivalent forms provides a very useful means of detecting electronic and crystal instabilities, as well as gross errors in setting and accidental events, such as occasional scattering from a secondary crystallite. In addition, such a comparison enables one to assess the inherent uncertainties in the particular data set and to assign standard deviations that apply meaningfully to the particular crystal at hand (Corfield, Doedens & Ibers, 1967).

Consider now the case where anomalous dispersion is important. Before the comparisons indicated above can be made, it is necessary to know the point group. To take a trivial example, if the point group is 1, and if the effects of anomalous dispersion are detectable, then  $F^2(hkl)$  may not be averaged with  $F^2(\bar{h}\bar{k}\bar{l})$ ; if the point group is  $\bar{1}$ , then these two forms may be averaged. In principle† the point group can be determined from the data set by noting the manner in which the  $N$  equivalent reflections of a given Laue class separate into two subsets of  $N/2$  equivalent reflections if Friedel's Law breaks down. Reflections that are equivalent to a given one by the operations of the point group remain equivalent. The  $N/2$  members of a subset are readily derived by inspection of the relations among the phase angles, or since these are not given explicitly in all cases in *International Tables* (1965), by noting that the sign of the  $B$  term must remain the same for the equivalent reflections in the subset in the space group formed by putting a  $P$  in front of the point group symbol. (This latter criterion holds for the standard settings of the space

groups in question. It would not necessarily hold on shift of origin.) In the accompanying table we present the sets of reciprocal lattice points that remain equivalent under the operations of the various point groups. In some cases alternate settings of the symmetry elements with respect to the cell are possible in the Laue group; the table includes information which enables one to distinguish one setting from the other.

If the effects of anomalous dispersion are greater than the errors of measurement in the intensity data, then after correction for absorption effects the entire data set may be scanned with the aid of a computer and the point group determined. After the point group has been determined, then the appropriate reflections may be averaged together and the same checks made on crystal and electronic stability, as noted above. Obviously if the effects of anomalous

Table 1. *Reciprocal lattice points equivalent under the operations of a given non-centrosymmetric point group*

Point group	Equivalent reflections
1	$hkl^*$
2 } second	$hkl = \bar{h}\bar{k}\bar{l}$
$m$ } setting	$hkl = h\bar{k}\bar{l}$
222	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l}$
$mm2$	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l}$
4	$hkl = \bar{h}\bar{k}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
$\bar{4}$	$hkl = \bar{h}\bar{k}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
422	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
$4mm$	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
$42m$ } $42m$	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
} $4m2$	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l} = k\bar{h}\bar{l}$
In all of the following cases, cyclic rotation of the first three indices ( $hki$ or $hkl$ ) yields additional equivalent reflections.	
3	$hkil^\ddagger$
32 } 321	$hkil = h\bar{k}\bar{l}$
} 312	$hkil = \bar{h}\bar{k}\bar{l}^\ddagger$
$3m$ } 3m1	$hkil = \bar{h}\bar{k}\bar{l}$
} 31m	$hkil = h\bar{k}\bar{l}^\ddagger$
6	$hkil = \bar{h}\bar{k}\bar{l}$
$\bar{6}$	$hkil = \bar{h}\bar{k}\bar{l}$
622	$hkil = \bar{h}\bar{k}\bar{l} = h\bar{k}\bar{l} = \bar{h}\bar{k}\bar{l}$
$6mm$	$hkil = \bar{h}\bar{k}\bar{l} = h\bar{k}\bar{l} = \bar{h}\bar{k}\bar{l}$
$\bar{6}m2$ } $\bar{6}m2$	$hkil = \bar{h}\bar{k}\bar{l} = h\bar{k}\bar{l} = \bar{h}\bar{k}\bar{l}$
} $\bar{6}2m$	$hkil = \bar{h}\bar{k}\bar{l} = h\bar{k}\bar{l} = \bar{h}\bar{k}\bar{l}$
23	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l}$
432	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l}$
43m	$hkl = \bar{h}\bar{k}\bar{l} = \bar{h}k\bar{l} = \bar{h}k\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l} = h\bar{k}\bar{l}$

\* The second subset of reflections is obtained by changing the signs of all indices.

† All settings in the trigonal system are referred to hexagonal axes.

‡ Note that there is an error in the multiplicity tables of *International Tables* (1965), p.34, 'additional note'. If Friedel's Law is obeyed, then in point groups 312 and 31m,  $hkil$  is equivalent to  $h\bar{k}\bar{l}$ , but not to  $h\bar{k}\bar{l}$  as stated.

\* This systematic difference presumably arises from non-isotropic effects, such as extinction. It is handled in the usual expression for the variance of the intensity by including contributions from counting errors and from a term proportional to the square of the intensity (Busing & Levy, 1957).

† This is touched upon in *International Tables for X-ray Crystallography* (1965, p.346).

dispersion are not statistically significant and the point group cannot be determined in some other manner, then it will be necessary to choose special radiations and reflections for the point-group determination. A very important additional advantage of a complete data set when anomalous dispersion is important has been noted by Ueki, Zalkin, & Templeton (1966): particularly if the space group is polar, then it is possible to obtain a structure that differs from the correct one by many standard deviations if a partial data set is employed.

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**Crystal classes of four-dimensional space  $R_4$ .** By A. C. HURLEY, *Division of Chemical Physics, C.S.I.R.O., Chemical Research Laboratories, Melbourne, Australia*, J. NEUBÜSER, *Mathematisches Seminar der Universität Kiel, Germany*, and H. WONDRA TSCHKE, *Mineralogisches Institut der Technischen Hochschule Karlsruhe, Germany*

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There are 227 crystal classes of four-dimensional space  $R_4$ .

In 1951 one of us, (Hurley, 1951), derived a list of 222 crystallographic point groups of  $R_4$  using results of Goursat (1889). In the sequel some minor errors in this list have been detected. Therefore we have dealt again with these groups and reenumerated them by three independent methods:

- (1) A.C.H. has repeated the calculation leading to the results described in Hurley (1951).
- (2) J.N. and H.W. have used results of Hermann (1951). In this paper he dealt with the 'maximal crystallographic point symmetry groups'. In  $R_4$  there are four of them. Two of order 1152 and 240 respectively which he called *volltransitiv* are explicitly described in his paper. The other two of orders 288 and 96, belonging to types which he called *imprimitiv* and *intransitiv* respectively, are not explicitly given. Hermann only states the fact that they are easily obtained from crystallographic point groups in lower dimensions. All crystallographic point groups of  $R_4$  are contained as subgroups in these four groups. The determination of these subgroups and their equivalence relations has been done with computer programs for the investigation of finite groups described in Neubüser (1960) and Felsch & Neubüser (1963).
- (3) E. C. Dade (1965) determined the maximal finite groups of integral  $4 \times 4$  matrices up to transformation by integral unimodular matrices. There are nine of them. It is not difficult to see that under transformation by rational non-singular matrices they fall into seven crystal classes which correspond to Hermann's four groups and to some subgroups of these. We therefore used as in (2) the programs mentioned before to check the previous calculations.

The results of all these methods agree and yield the following corrections of the tables given in Hurley (1951):

- (i) In Table 1(b) two crystal classes XXXV  $\mu=2$ ,  $\nu=2$ ,  $D=1$  and XXXVII  $m=\mu=\nu=1$  of order 32 are equivalent.
- (ii) The entry for crystal class XLIV of order 96 in Table 1(b), p. 655, has to be replaced by
 
$$1I + 9E + 6F + 8K + 8N + 6R + 10T.$$

\* Mathematically formulated this means: he dealt with maximal finite groups of  $n \times n$  integral matrices classified up to transformation by rational non-singular matrices.

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- (iii) The following 6 crystal classes which are subgroups of the corrected group XLIV have to be added:

Table 2(a), p. 656,

Order 24  $1I + 9E + 8K + 6R'$ ;

Table 2(b), p. 658,

Order 8  $1I + 1E + 2F + 2R + T + T'$ ;

24  $1I + 3E + 6F + 8K + 6T'$ ;

24  $1I + 3E + 6F + 8K + 6T$ ;

48  $1I + 9E + 6F + 8K + 8N + 6R' + 3T + 7T'$ ;

48  $1I + 9E + 6F + 8K + 8N' + 6R' + 7T + 3T'$ .

- (iv) There are two misprints in Table 1(b), p. 655:

XXXIII  $\mu=1$ ,  $\nu=1$ ,  $D=6$ ,  $q=1$ ,  $l=0$

should have 1 *E* instead of 1 *F*

XLIII should have 48*C* instead of 48*A*.

- (v) There are some misprints in the values of the Goursat parameters in the first columns of Tables 1(a) and 1(b). In family XII all values of  $n$  should be doubled, and in family XIII' all values of both  $m$  and  $n$  should be doubled. In family XXXV the fifth member should have  $l=2$  instead of  $l=3$ , and the final member should have  $q=1$ ,  $l=r=0$ .

After these corrections the total number of crystal classes of  $R_4$  turns out to be 227. The complete list with further additions concerning relations to three-dimensional black-white- and grey-groups is being published by A.C.H. in the book:

*Quantum Theory of Atoms, Molecules, and the Solid State, a Tribute to John C. Slater.* Edited by P.O. Löwdin. New York: Academic Press. (To appear 1966-67.)

Other detailed information obtained in the course of the calculations described under (2) and (3) will be published later.

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