

## Structure Description Ambiguity Depending Upon Which Edition of *International Tables for (X-ray) Crystallography* is Used

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### Abstract

The editorial policy of certain scientific journals where crystal structure data are published does not expressly specify that all three fractional coordinates of the atoms in the asymmetric unit have to be given for all Wyckoff sites. Owing to the differences between the 1952 edition and the 1983 edition of *International Tables for (X-ray) Crystallography* – in the way the *xyz* triplets of certain Wyckoff sites are formulated and also the interchange of Wyckoff letters assigned to the sites – failure to give all three atom coordinates may lead to ambiguities. It is shown that for seven monoclinic space groups (setting with unique axis *c*), three tetragonal and one cubic space groups (all with origin choice 2, *i.e.* symmetry centre at the origin) the shortened description may lead to different atom arrangements depending upon which edition of the *International Tables* is used.

### Structure description ambiguity due to a different expression for the *xyz* triplets

For certain special Wyckoff sites, two (or even all three) unspecialized fractional coordinates of an *xyz* triplet are linearly related to one other and can be expressed in terms of only one fractional coordinate. The algebraic expressions relating fractional coordinates given in the new *International Tables for Crystallography* (1983) [denoted as *IT*(1983)] are different in a few cases from the ones given in the old *International Tables for X-ray Crystallography* (1952) [*IT*(1952)]. These differences have their origin in the particular choice of the symmetry generators in *IT*(1983) and in the particular way the triplets of special point positions are derived by fusion from two (or more) triplets of the general point position.\* These differences are without any consequence if numerical values are specified for each of the fractional coordinates of an atom. If, however, only one (or only two) numerical values are given, as is unfortunately the custom with some journals, an ambiguity may arise.

\* Professors Theo Hahn and Hans Wondratschek are preparing a publication where the reasons for these differences will be discussed in detail.

A comparison of all Wyckoff sites in all space groups in the two editions of *International Tables* shows that ambiguities due to different representations of the *xyz* triplets can occur in seven space groups: *B*112 (no. 5) and *B*112/*m* (no. 12) in the setting with unique axis *c* and cell choice 2, *P*112/*b* (no. 13) in the setting with unique axis *c* and cell choice 3, *P*4/*nbm* (no. 125), *P*4/*ncc* (no. 130), *P*4<sub>2</sub>/*nmc* (no. 137) and *Pn* $\bar{3}$ *m* (no. 224) – the last four with origin choice 2 having the symmetry centre at the origin – and altogether with eight Wyckoff sites. In Table 1 are listed the seven space groups and their Wyckoff sites which are expressed differently in *IT*(1952) and in *IT*(1983). One notes that the unspecialized coordinates are defined in a different way. Atoms on any of these Wyckoff sites, for which instead of all three fractional coordinates only the values of *z* (*B*112, *B*112/*m* and *P*112/*b*) or *x* (*P*4/*ncc*, *P*4<sub>2</sub>/*nmc* and *Pn* $\bar{3}$ *m*) or *x* and *z* (*P*4/*nbm*) are specified, may not be sufficiently determined if it is not stated which edition of *International Tables* is used.\*

To obtain unambiguously the same sites within the unit cell upon passing from one edition of *International Tables* to the other the coordinate changes given in the third column of Table 2 have to be made. If one neglects to make these coordinate changes one will in certain cases obtain a different (*i.e.* wrong) atom arrangement. For six space groups this depends, as will be demonstrated by means of the right-hand side of Table 2, on what other Wyckoff sites are occupied in the structure.

For the first six space groups the change of the coordinate is equivalent to a translation of the *xyz* triplets by an amount given in the fourth column. A study of the other Wyckoff sites in these space groups reveals that some Wyckoff sites are not affected by this translation. The Wyckoff letters of those sites are listed in the last but one column. Finally, in the last

\* In the case of the cubic space group *Pn* $\bar{3}$ *m* the unspecialized coordinate is labelled *x* in *IT*(1952) but *y* in *IT*(1983); however, this is of no help to distinguish between the two editions. There is only one unspecialized coordinate, which may be called *x*, *y* or even *z* depending upon which *xyz* triplet of the list is considered as representative.

Table 1. Comparison of the way the symmetry-related xyz triplets of particular Wyckoff sites of seven space groups are listed in *IT*(1952) and in *IT*(1983)

This is a shortened and rearranged list of symmetry-related xyz triplets. The *IT*(1983) data are reordered to correspond to the order of the triplets in *IT*(1952); however, triplets which are related to given ones by the centre of symmetry at the origin and/or a Bravais-lattice translation have been omitted. For each Wyckoff site in the tetragonal and cubic space groups only four triplets are given instead of 8 and 24, respectively.

	<i>IT</i> (1952)	<i>IT</i> (1983)
<i>B</i> 112 (no. 5) Wyckoff site 2( <i>b</i> )	Setting with unique axis <i>c</i> , cell choice 2 $0\frac{1}{2}z$	$0\frac{1}{2}\frac{1}{2}+z$
<i>B</i> 112/ <i>m</i> (no. 12) Wyckoff site 4( <i>h</i> )	Setting with unique axis <i>c</i> , cell choice 2 $0\frac{1}{2}z$	$0\frac{1}{2}\frac{1}{2}+z$
<i>P</i> 112/ <i>b</i> (no. 13) Wyckoff site 2( <i>f</i> )	Setting with unique axis <i>c</i> , cell choice 3 $\frac{1}{2}\frac{1}{4}z$	$\frac{1}{2}\frac{1}{4}z$
<i>P</i> 4/ <i>n</i> <i>b</i> <i>m</i> (no. 125) Wyckoff site 8( <i>m</i> )	Origin choice 2 with symmetry centre at origin $\bar{x}xz \frac{1}{2}+x\frac{1}{2}-xz \quad x\frac{1}{2}+xz \quad \frac{1}{2}-x\bar{x}z$	$x\bar{x}z \quad \frac{1}{2}-x\frac{1}{2}+xz \quad \bar{x}\frac{1}{2}-xz \quad \frac{1}{2}+xxz$
<i>P</i> 4/ <i>n</i> <i>c</i> (no. 130) Wyckoff site 8( <i>f</i> )	Origin choice 2 with symmetry centre at origin $\bar{x}x\frac{1}{4} \quad \frac{1}{2}-x\bar{x}\frac{1}{4} \quad x\frac{1}{2}+x\frac{1}{4} \quad \frac{1}{2}+x\frac{1}{2}-x\frac{1}{4}$	$x\bar{x}\frac{1}{4} \quad \frac{1}{2}+xx\frac{1}{4} \quad \bar{x}\frac{1}{2}-x\frac{1}{4} \quad \frac{1}{2}-x\frac{1}{2}+x\frac{1}{4}$
<i>P</i> 4 <sub>2</sub> / <i>n</i> <i>m</i> <i>c</i> (no. 137) Wyckoff site 8( <i>f</i> )	Origin choice 2 with symmetry centre at origin $\bar{x}x\frac{1}{4} \quad \frac{1}{2}+xx\frac{1}{4} \quad \bar{x}\frac{1}{2}-x\frac{1}{4} \quad \frac{1}{2}+x\frac{1}{2}-x\frac{1}{4}$	$x\bar{x}\frac{1}{4} \quad \frac{1}{2}-x\bar{x}\frac{1}{4} \quad x\frac{1}{2}+x\frac{1}{4} \quad \frac{1}{2}-x\frac{1}{2}+x\frac{1}{4}$
<i>P</i> $\bar{3}$ <i>m</i> (no. 224) Wyckoff site 24( <i>j</i> )	Origin choice 2 with symmetry centre at origin $\frac{1}{2}\frac{1}{4}+x\frac{3}{4}+x \quad \frac{1}{2}\frac{1}{4}-x\frac{3}{4}-x \quad 0\frac{1}{4}+x\frac{3}{4}-x \quad 0\frac{1}{4}-x\frac{3}{4}+x$	$\frac{1}{2}y\frac{1}{2}+y \quad \frac{1}{2}\frac{1}{2}-y\bar{y} \quad 0y\bar{y} \quad 0\frac{1}{2}-y\frac{1}{2}+y$
Wyckoff site 24( <i>i</i> )	$\frac{1}{2}\frac{1}{4}+x\frac{3}{4}-x \quad \frac{1}{2}\frac{1}{4}-x\frac{3}{4}+x \quad 0\frac{1}{4}+x\frac{3}{4}+x \quad 0\frac{1}{4}-x\frac{3}{4}-x$	$\frac{1}{2}y\bar{y} \quad \frac{1}{2}\frac{1}{2}-y\frac{1}{2}+y \quad 0y\frac{1}{2}+y \quad 0\frac{1}{2}-y\bar{y}$

Table 2. Coordinate changes to be made to obtain a correspondence between the xyz triplets listed in *IT*(1952) and *IT*(1983) and the influence of these changes on the coordinates of atoms in the other Wyckoff sites

Space group	Wyckoff site	Change of coordinate to be made if other edition of <i>IT</i> is used	Translation of the xyz triplets which is equivalent to the change of coordinate	Other Wyckoff sites of the space group which are not affected by the translation	Wyckoff sites of the space group which are affected by the translation
<i>B</i> 112 (no. 5) Setting with unique axis <i>c</i> , cell choice 2	2( <i>b</i> )	$z_{IT(1983)} = \frac{1}{2} + z_{IT(1952)}$	$00\frac{1}{2}$ or $\frac{1}{2}00$		2( <i>a</i> ), 4( <i>c</i> )
<i>B</i> 112/ <i>m</i> (no. 12) Setting with unique axis <i>c</i> , cell choice 2	4( <i>h</i> )	$z_{IT(1983)} = \frac{1}{2} + z_{IT(1952)}$	$00\frac{1}{2}$ or $\frac{1}{2}00$	4( <i>e</i> ), 4( <i>f</i> )	2( <i>a</i> ), 2( <i>b</i> ), 2( <i>c</i> ), 2( <i>d</i> ), 4( <i>g</i> ), 4( <i>i</i> ), 8( <i>j</i> )
<i>P</i> 112/ <i>b</i> (no. 13) Setting with unique axis <i>c</i> , cell choice 3	2( <i>f</i> )	$z_{IT(1983)} = -z_{IT(1952)}$	$0\frac{1}{2}0$	2( <i>a</i> ), 2( <i>b</i> ), 2( <i>c</i> ), 2( <i>d</i> )	2( <i>e</i> ), 4( <i>g</i> )
<i>P</i> 4/ <i>n</i> <i>b</i> <i>m</i> (no. 125) Origin choice 2	8( <i>m</i> )	$x_{IT(1983)} = -x_{IT(1952)}$	$\frac{1}{2}\frac{1}{2}0$	2( <i>a</i> ), 2( <i>b</i> ), 2( <i>c</i> ), 2( <i>d</i> ), 4( <i>e</i> ), 4( <i>f</i> ), 4( <i>g</i> ), 4( <i>h</i> ), 8( <i>i</i> ), 8( <i>j</i> ), 8( <i>k</i> ), 8( <i>l</i> )	16( <i>n</i> )
<i>P</i> 4/ <i>n</i> <i>c</i> (no. 130) Origin choice 2	8( <i>f</i> )	$x_{IT(1983)} = -x_{IT(1952)}$	$00\frac{1}{2}$ or $\frac{1}{2}\frac{1}{2}0$	4( <i>a</i> ), 4( <i>b</i> ), 4( <i>c</i> ), 8( <i>d</i> ), 8( <i>e</i> )	16( <i>g</i> )
<i>P</i> 4 <sub>2</sub> / <i>n</i> <i>m</i> <i>c</i> (no. 137) Origin choice 2	8( <i>f</i> )	$x_{IT(1983)} = -x_{IT(1952)}$	$00\frac{1}{2}$ or $\frac{1}{2}\frac{1}{2}0$	4( <i>d</i> ), 4( <i>e</i> )	2( <i>a</i> ), 2( <i>b</i> ), 4( <i>c</i> ), 8( <i>g</i> ), 16( <i>h</i> )
<i>P</i> $\bar{3}$ <i>m</i> (no. 224) Origin choice 2	24( <i>j</i> )	$y_{IT(1983)} = \frac{1}{4} + y_{IT(1952)}$			
Origin choice 2	24( <i>i</i> )	$y_{IT(1983)} = \frac{1}{4} + y_{IT(1952)}$			

column are given the letters of the Wyckoff sites where the translation leads to new xyz triplets.

If a structure contains as other Wyckoff sites only those from the penultimate column of Table 2 it is not crucial if one forgets to make the coordinate change upon passing from one edition of *International Tables* to the other. One obtains either way a correct structure (except for a translation). However, if at least one of the other Wyckoff sites is from the last column, a different and wrong atom arrangement is

obtained if the coordinate change for the Wyckoff site in column 2 has been omitted upon passing from one edition of *International Tables* to the other.

In the case of space group *P* $\bar{3}$ *m*, no matter whether or not other Wyckoff sites are occupied, neglecting to add or subtract  $\frac{1}{4}$  from the unspecialized coordinate in 24(*j*) or 24(*i*) when passing from one edition of *International Tables* to the other will always lead to a different atom arrangement.

## Examples

BaAl<sub>2</sub>Te<sub>4</sub> (II): Eisenmann, Jakowski & Schäfer (1982)*P4/nbm*,  $a = 8.516$ ,  $c = 6.713$  Å.2Ba in 2(*a*)  $\frac{1}{4} \frac{1}{4} 0$ 2Al in 2(*c*)  $\frac{3}{4} \frac{1}{4} 0^*$ 2Al in 2(*d*)  $\frac{3}{4} \frac{1}{4} \frac{1}{2}$ 8Te in 8(*m*)  $x = 0.9180$ ,  $z = 0.7484$ .

In the publication only the numerical values of  $x = 0.9180$  and  $z = 0.7484$  were given to characterize the 8(*m*) site. Thus the first *xyz* triplet of the 8(*m*) site appears to anyone who uses *IT*(1952) to be at 0.0820 0.9180 0.7484, but for users of *IT*(1983) it is at 0.9180 0.0820 0.7484. Fortunately this is without significance here since the 16(*n*) site is not occupied. The same atom arrangement and the same interatomic distances are obtained with either of the two *xyz* triplets, so that one can use *IT*(1983) without changing the sign of the original *x* coordinate given in the 1982 publication.

Pu<sub>5</sub>Rh<sub>3</sub>: Beznosikova, Chebotarev, Luk'yanov, Chernyi & Smirnova (1975)*P4/ncc*,  $a = 10.941$ ,  $c = 6.0203$  Å.16 Pu in 16(*g*)  $x = 0.034$ ,  $y = 0.339$ ,  $z = 0.889$ 4Pu in 4(*b*)8Rh in 8(*f*)  $x = 0.593$ 4Rh in 4(*c*)  $z = 0.071$ .

It was not stated in the publication whether or not the centre of symmetry is at the origin, but it can be concluded from the accompanying drawing that the data refer to the space group setting with origin choice 2, having the symmetry centre at the origin. Since only the numerical value of  $x = 0.593$  was given for the 8(*f*) site the first *xyz* triplet for those using *IT*(1952) is at 0.407 0.593  $\frac{1}{4}$ , but for those who use *IT*(1983) it is at 0.593 0.407  $\frac{1}{4}$ . Here this difference is significant. In the Pu<sub>5</sub>Rh<sub>3</sub> structure the Wyckoff site 16(*g*) is occupied. Thus if *IT*(1983) is used without changing the sign of the *x* (and *y*) coordinate in 8(*f*) (i.e. fractional coordinates 0.593 0.407  $\frac{1}{4}$ ) a different and wrong atom arrangement is obtained which is characterized by different Rh[8(*f*)]-Pu[16(*g*)] distances, all other distances being unchanged.

An isotypic structure was reported four years later with Nd<sub>5</sub>Ir<sub>3</sub> (Paccard, LeRoy & Moreau, 1979).

\* In the published list of the atom coordinates Ba in 2(*a*) is given twice, but Al in 2(*c*) is not mentioned. It is obvious from the drawing that there are Al atoms on Wyckoff site 2(*c*).

Table 3. Differences between *IT*(1952) and *IT*(1983) in the letters assigned to Wyckoff sites in monoclinic space groups with settings having unique axis *c*

	<i>IT</i> (1952)	<i>IT</i> (1983)
<i>P</i> 112 (no. 3)	1( <i>c</i> ) $\frac{1}{2} 0 z$ 1( <i>b</i> ) $0 \frac{1}{2} z$	1( <i>c</i> ) $0 \frac{1}{2} z$ 1( <i>b</i> ) $\frac{1}{2} 0 z$
<i>B</i> 11 <i>b</i> (no. 9)	Data for this setting only given in <i>IT</i> (1952).	
<i>P</i> 112/ <i>m</i> (no. 10)	2( <i>k</i> ) $0 \frac{1}{2} z$ $0 \frac{1}{2} \bar{z}$ 2( <i>j</i> ) $\frac{1}{2} 0 z$ $\frac{1}{2} 0 \bar{z}$ 1( <i>f</i> ) $0 \frac{1}{2} \frac{1}{2}$ 1( <i>e</i> ) $\frac{1}{2} 0 \frac{1}{2}$ 1( <i>d</i> ) $\frac{1}{2} 0 0$ 1( <i>c</i> ) $0 \frac{1}{2} 0$	2( <i>k</i> ) $\frac{1}{2} 0 z$ $\frac{1}{2} 0 \bar{z}$ 2( <i>j</i> ) $0 \frac{1}{2} z$ $0 \frac{1}{2} \bar{z}$ 1( <i>f</i> ) $\frac{1}{2} 0 \frac{1}{2}$ 1( <i>e</i> ) $0 \frac{1}{2} \frac{1}{2}$ 1( <i>d</i> ) $0 \frac{1}{2} 0$ 1( <i>c</i> ) $\frac{1}{2} 0 0$
<i>P</i> 112 <sub>1</sub> / <i>m</i> (no. 11)	2( <i>c</i> ) $0 \frac{1}{2} 0$ $0 \frac{1}{2} \frac{1}{2}$ 2( <i>b</i> ) $\frac{1}{2} 0 0$ $\frac{1}{2} 0 \frac{1}{2}$	2( <i>c</i> ) $\frac{1}{2} 0 0$ $\frac{1}{2} 0 \frac{1}{2}$ 2( <i>b</i> ) $0 \frac{1}{2} 0$ $0 \frac{1}{2} \frac{1}{2}$
<i>B</i> 112/ <i>m</i> (no. 12) Cell choice 2	2( <i>d</i> ) $0 \frac{1}{2} \frac{1}{2}$ 2( <i>c</i> ) $0 \frac{1}{2} 0$	2( <i>d</i> ) $0 \frac{1}{2} 0$ 2( <i>c</i> ) $0 \frac{1}{2} \frac{1}{2}$
<i>P</i> 112 <sub>1</sub> / <i>b</i> (no. 14) Cell choice 3	2( <i>d</i> ) $\frac{1}{2} \frac{1}{2} 0$ $\frac{1}{2} 0 \frac{1}{2}$ 2( <i>b</i> ) $\frac{1}{2} 0 0$ $\frac{1}{2} \frac{1}{2} \frac{1}{2}$	2( <i>d</i> ) $\frac{1}{2} 0 0$ $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ 2( <i>b</i> ) $\frac{1}{2} \frac{1}{2} 0$ $\frac{1}{2} 0 \frac{1}{2}$
<i>B</i> 112/ <i>b</i> (no. 15)	Data for this setting only given in <i>IT</i> (1952).	

However, there is no danger here of obtaining the wrong atom arrangement. The structure of Nd<sub>5</sub>Ir<sub>3</sub> was published in *Acta Crystallographica* where all three fractional atom coordinates are customarily printed.

## Structure description ambiguity due to the change of the Wyckoff letters

In the case of five monoclinic space groups in the setting with unique axis *c* there are differences between *IT*(1952) and *IT*(1983) in the letters which have been assigned to particular Wyckoff sites. Fourteen differences in the Wyckoff letters have been noted; they are compiled in Table 3.\* If a structure site is described by its Wyckoff letter only, without specifying the corresponding three fractional coordinates of the first *xyz* triplet, different atom arrangements will be obtained depending upon which edition of *International Tables* is used.

## Concluding remarks

To avoid any ambiguity due to the differences between *IT*(1952) and *IT*(1983) it is strongly suggested that *all three* fractional coordinates should be published for all atoms in the asymmetric unit including those on special Wyckoff sites. This procedure would help also to solve the problem frequently encountered where centrosymmetric structures, based on one of the 24 space groups with two descriptions in *IT*(1952) and *IT*(1983), are insufficiently described

\* For space groups *B*11*b* (no. 9) and *B*112/*b* (no. 15), given in *IT*(1952), there are no corresponding entries in *IT*(1983).

because the author forgot to mention whether or not the symmetry centre is at the origin of the unit cell.

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## X-ray Analysis of Wavefunctions by the Least-Squares Method Incorporating Orthonormality. I. General Formalism

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### Abstract

The least-squares method incorporating the orthonormal relation between wavefunctions is formulated. The method fulfils the idempotency condition and allows the representation of wavefunctions to be obtained from charge-density distributions measured by the X-ray diffraction method. The present method can be applied to both the atomic-orbital (AO) and the molecular-orbital (MO) models. The scattering-factor formalisms are also described for both models. One of the most important applications of the present method to the AO models is the determination of the  $d$  wavefunctions in a general crystal field. The restrictions among the coefficients of  $d$  wavefunctions in the 32 point-group-symmetry fields are derived. The effect of expansion and contraction of electron clouds in crystal fields is highly important, since it allows the possibility of determining all the unknown  $d$  wavefunctions. Even the wavefunctions of atoms with spherical electron configuration like  $Zn^{2+}$  and high-spin  $Mn^{2+}$  ions can be determined when this effect is significant. From the scattering factors of two-center terms, the temperature factors for these terms are derived.

### Introduction

Charge-density distribution has been extensively studied with diffraction methods in the last two decades. Charge densities obtained in various molecular, ionic and metallic crystals revealed

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features of bondings. Quantitative analysis of the measured charge-density distributions was carried out with electron-population analysis (Stewart, 1969; Coppens, Willoughby & Csonka, 1971) and with the method of multipole refinement (Kurki-Suonio, 1968; Hirshfeld, 1971; Stewart, 1972; Hansen & Coppens, 1978). Multipole refinements showed remarkable success in representing charge-density distribution in crystals by analytical functions, and various electrical physical quantities such as electric moments were calculated from them. However, these methods failed to give more fundamental quantities such as first-order density matrices and the representation of wavefunctions. This is because of the lack of conditions imposed by the antisymmetric property of wavefunctions.

Assume that  $M$  electrons occupy  $M$  molecular spin orbitals (MO's)  $\psi_i$  and that each MO is represented in terms of a linear combination of  $N$  basic functions,  $\varphi_n(\mathbf{r})$ , which are normalized and orthogonalized, as follows,

$$\psi_i(\mathbf{r}) = \mathbf{c}'_i \boldsymbol{\varphi}(\mathbf{r}), \quad (i = 1, 2, \dots, M) \quad (1)$$

or

$$\boldsymbol{\Psi}(\mathbf{r}) = C \boldsymbol{\varphi}(\mathbf{r}),$$

where  $C = \{c_{in}\}$  consists of  $M$  orthonormal rows  $\mathbf{c}'_i$ .  $\boldsymbol{\Psi} = \{\psi_i\}$  and  $\boldsymbol{\varphi} = \{\varphi_n\}$  are  $M \times 1$  and  $N \times 1$  matrices, respectively. A prime means a row vector or a transposed matrix in the following discussion.  $M$  is the number of MO's to be determined and is not more