Rigaku VariMax Dual Part 2b Analysis Manual with OLEX²

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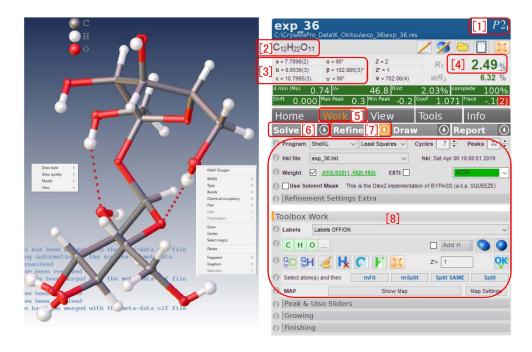


Figure 0: Whole window of OLEX². Molecular structure of sucrose.

The molecular structure of sucrose has been solved with the OLEX² based on 'exp_36.ins' made by the CrysAlis^{Pro}. This was refined by clicking 'Refine [7]' after determination of the initial phases by clicking 'Solve [6]'. '[1] $P2_1$ ' (refer to §B.4.2) [p.41] is the space group, '[2] $C_{12}H_{22}O_{11}$ ' is the molecular formula, '[3] $a, b, c, \alpha, \beta, \gamma$ ' are the lattice constants, and '[4] 2.49' is the R-factor. 'Solve [6]', 'Refine [7]', 'Draw' and 'Report' have been displayed by clicking 'Work [5]'. ' \Downarrow ' on the right of them can be clicked to open their option menus. ' \Uparrow ' on the right of 'Refine [7]' has been clicked to open the option menus shown in the red frame [8].

The molecular model can be 3D-rotated by left click&dragging, be scaled by right click&dragging and be moved parallel by both click&dragging the mouse. Display options can be opened by right-clicking the background. Options of an atom can be opened by right-clicking the atom. Red dashed lines are hydrogen bonds.

Chapter 1 [p.1] describes how to download and install 'OLEX²', 'Shelx' and 'PLATON'. Chapter 2 [p.7] and Chapter 3 [p.20] describes how to solve the molecular structure with the OLEX².

Appendix A [p.30] describes the reasonability of defining the reciprocal lattice. This is strongly recommended to read. The understanding of the reciprocal lattice is necessary for crystallography.

Appendix B [p.34] describes how to determine the space group based on the extinction rule.

Appendix C [p.48] describes the definition of coordinate system and the extinction rule for the trigonal and hexagonal crystal systems.

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Chapter 1

Download and installation of 'OLEX²', 'SHELX' and 'PLATON'



Figure 1.1: Registration at the URL of OlexSys

Username	Password	
к_окітsu [1]	[•••••• [2]]	
First Name	Last Name	
Kouhei	OKITSU	
Company or Organisation	Position	
Tokyo Univ.	Researcher	
Email	Country	
yrt01404yrt@yahoo.co.jp [3]	Japan	~

Figure 1.2: Registration of the user information

1.1 Download and installation of 'OLEX²'

The user information is asked when clicking '[2] register' after entering the URL whose address is shown at '[1]' of Fig. 1.1: http:// www.olexsys.org/software. By clicking 'register [4]' in Fig. 1.2, you can receive an e-mail as shown in Fig. 1.3. You can copy the sign in URL to paste the browser to login it.

In Fig. 1.4, 'User name [1]' and 'Password 1.6 [p.2] should be clicked.

OlexSys
 Sys
 Second Sys

Now hurry up and get started with Olex²

Figure 1.3: Copy of the sign-in URL.

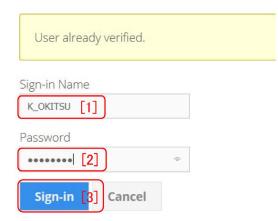


Figure 1.4: Sign in.

[2]' that have been inputted in Fig. 1.2 should be typed to 'Sign-in [3]' in Fig. 1.4.

By scrolling down the URL of OlexSys, click '[1] Download' in Fig. 1.5 [p.2], please. '[2] Execute' should be clicked to download and execute '[3] olex2-installer.exe'. Then, 'Install' in Fig. 1.6 [p.2] should be clicked.



Figure 1.5: Download of 'OLEX²'.

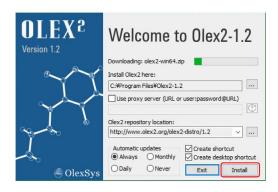


Figure 1.6: Installation of 'OLEX²'.

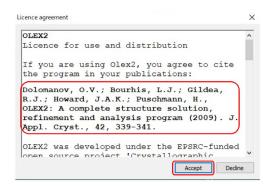


Figure 1.7: License Agreement.

After finishing the installation, 'License Agreement' is shown in Fig. 1.7. It should be read to click 'Accept'. When publishing a paper that reports the results obtained with OLEX², the literature shown in the red frame in Fig. 1.7 should be cited.

For messages about 'Help' and automatic update as shown in Fig. 1.8, 'YES' is recommended to click.

elp needed!			
The program usage statistics can provide very hel contribute into the Olex2 development by provid use?			
		はい(Y) いいえ(M	N) キャンセル
Automatic Upd	ates		×
Update	re new updates available s will be downloaded in t e effect with the next res	the background during t	his session and
		Do not show this i	nessage again
		Yes	

Figure 1.8: Settings of 'Help' and 'Auto Update'.



Figure 1.9: Download of SHELX-2013.

🖻 🕫 🗖 The SHELX h	omepage × + ^			0	×
\leftrightarrow \rightarrow \circlearrowright \textcircled{a}	③ shelx.uni-goettingen.de/index.php	h	ß	~	
Registration Downloads Tutorials & talks Wikis & manuals Open access papers SM GUIs etc. MM GUIs etc. SHELX workshops	Academic use Percarboti use SHELX is a set of programs for crystal structures by single or executables require NO libraries, with all modern versions of Linux, profit users are expected to pay users. SHELXT - New small molecule (SM) Q	lex2,	Osca	<u>il</u>	~

Figure 1.10: No charge for Academic Use.

1.2 Download and installation of 'SHELX'

In Fig. 1.9, to the URL of SHELX 'http://shelx.uni-ac.gwdg.de/ [1]' should be accessed to click '[2] SHELX-2013' to display Fig. 1.10. 'Registration' and then 'Academic use' should be clicked.

In Fig. 1.11, necessary items should be typed to click 'Submit'. Then, an e-mail in which 'user name' and 'password' are written as shown in Fig. 1.12, is sent to the e-mail address that has been typed in Fig. 1.11. To the URL as shown in Fig. 1.13, should be accessed again to

SHELX registration for academic use only "Xtal question" should be the name of space group number 19 First name(s) Kouhei Last name OKITSU Affiliation Tokyo Univ City Tokyo Post/zipcode 113-8656 Country Japan Email yrt01404yrt@yahoo.co.jp **Xtal question** P212121 Submit Congratulations, your registration was successful The downloading instructions have been emailed to the above address.

Figure 1.11: Registration of the user information.

SHEL	x
From:	no-reply@shelx.uni-goettingen.de +
To:	okitu vahoo

Figure 1.12: Username and password in the email.

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$\leftarrow \ \ \rightarrow \ \ \mho$	shelx.uni-goettingen.de/download.php
	Registration
	Downloads
	Tutorials & talks
	Wikis & manuals
	Open access papers

Figure 1.13: Click 'Downloads'.

Windows セキュリティ	×
Microsoft Edge	
サーバー shelx.uni-goettingen.de がユーザー名とパスワードを要 す。	要求していま
サーバーからの報告: "Enter username and password"。	
警告: ユーザー名とパスワードは、セキュリティで保護されていない 認証を使用して送信されます。	接続で基本
shelx	
ОК キャンセル	

Figure 1.14: Input the user name and password.

click 'Downloads'. In Fig. 1.14, 'User name' and

\leftrightarrow \rightarrow \circlearrowright \bigstar	(i) she	lx.uni-goettingen.de/bin/
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Parent Directory		新しい InPrivate ウィンドウで開く
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mac/	2018-	印刷
test data/	2018-	リーディングリストに追加
win32/	2016- 2018-	このリンクについて Cortana に質問する
Apache/2.4.18 (Ubun	tu) Server at .	音声で読み上げる

Figure 1.15: Download of the installer.



Figure 1.16: Execution of the installer.

'Password' written in Fig. 1.12 should be typed to click 'OK'.

In Fig. 1.15, 'install-shelx-win32.exe' or 'install-shelx-win64.exe' depending on the system of the computer should be right-clicked. It should be saved in a newly made folder 'C:\Shelx' and double-clicked.

In Fig. 1.16 (b), 'Detailed information' should be clicked to open Fig. 1.16 (c). Here, 'Execute' should be clicked to install the SHELX. In Fig. 1.17 [p.4], all programs should be checked to click 'Next'.

In Fig. 1.18 [p.4], installed files are shown.

4CHAPTER 1. DOWNLOAD AND INSTALLATION OF 'OLEX2', 'SHELX' AND 'PLATON'

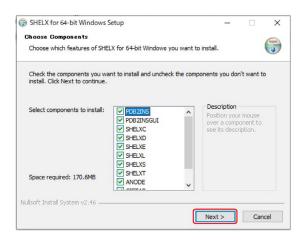


Figure 1.17: Choice of files to be installed.

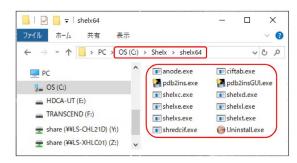


Figure 1.18: Choice of files to be installed.

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D Read at Last		100				
Bond r: Set		100	Colour:	elements		
Bond r: Set Debug Mode: S		100 pug Mode (Res	Colour:	elements		

Figure 1.19: Registration of 'SHELX' to 'OLEX 2 '.

1.3 Registration of 'SHELX' to 'OLEX²'

In Fig. 1.19, a part of menus is shown just after starting the OLEX². 'Settings' bellow 'Start' should be clicked to display many items. In the text box of 'PATH', the folder name 'C:\Shelx\shelx64' should be typed such that

Q すべて 🖬 画像 🗏 ニュース 🥥 ショッピング 🕨 🛚	PLATON	nomepage	•		
	२ इर्र	🖬 画像	■ ニュース	⊘ ショッピング	▶ 動画
約4,570,000件(0.46秒)	匀 <mark>4,570,000</mark>)件(0.46利	砂)		

Figure 1.20: How to search 'PLATON' home-page.

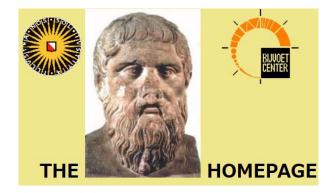


Figure 1.21: 'PLATON' homepage.

The Program PLATON is designed as a Multipurpose
Crystallographic Tool.
(C) 1980-2019 A.L.Spek, Utrecht University, Padualaan 8, 3584
CH Utrecht, The Netherlands.
Reference: A.L.Spek, Acta Cryst. 2009, D65, 148-155.
The PLATON Homepage gives pointers to all information available on the program PLATON.
Download Sites:
http://www.platonsoft.nl/spek/xraysoft/
http://www.cryst.chem.uu.nl/spek/xraysoft/

Figure 1.22: Reference and the download sites.

the SHELX can be used on the $OLEX^2$.

1.4 Download and installation of 'PLATON'

'PLATON' can be downloaded and installed without charge for academic use.

On the Google homepage, 'PLATON homepage' can be typed to find the 'PLATON' home-

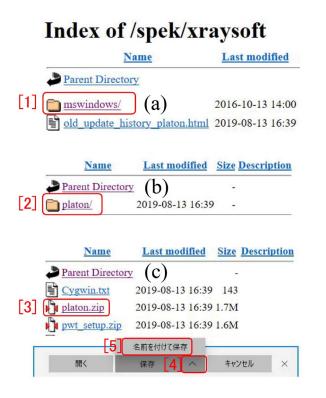


Figure 1.23: Downloading the PLATON.

名前を付けて保存				×
← ↑ 📙 > PC > C	DS (C:)	> PLATO	SN √ Č	Q
整理 ▼ 新しいフォリ	ルダー	-		0
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🛀 OS (C:)				
🔰 HD-LXU3 (F:)				
	~	<		>
ファイル名(N): p	laton.	zip		~
ファイルの種類(T): B	E縮 (zi	ip 形式) フォ	tルダー (*.zip)	~
▲ フォルダーの非表示		保存(S)	++>>セ	JL

Figure 1.24: Saving 'platon.zip'.

page as shown in Fig. 1.21.

By scrolling down the URL, the reference that should be cited and the sites from which the 'PLATON' can be downloaded, are found.

One of the download sites can be clicked to show Fig. 1.23. '[1] mswindows/' in Fig. 1.23 (a) can be clicked to show Fig. 1.23 (b). '[2] platon' in it can be clicked to show Fig. 1.23 (c). '[3]

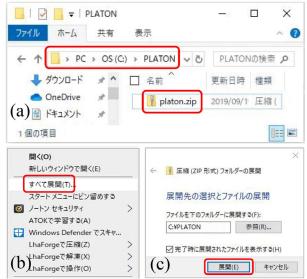


Figure 1.25: Expansion of 'platon.zip'.

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Program Files	
Program Files (x8t	
□ ProgramData V K 2個の項目)

Figure 1.26: Extracted 'platon.exe'.

platon.zip', '[4] \wedge ' and then '[5] Save as' should be clicked to display Fig. 1.24. 'platon.zip' should be saved in the folder of 'C:\PLATON'.

In Fig. 1.25 (a), 'platon.zip' should be rightclicked to show Fig. 1.25 (b). Here, 'Expand All (T)...' should be clicked to show Fig. 1.25 (c). In Fig. 1.25 (c), 'Expand (E)' should be clicked to expand the file in 'C:\PLATON'. 'platon.exe' can be decompressed as shown in Fig. 1.26.

1.5 Registration of 'PLATON' to 'OLEX²'

'Home' on the upper left of the window of the $OLEX^2$ in Fig. 1.27 [p.6] has been clicked to open. Then, 'Settings' can be clicked to let the text box of 'PATH' be shown.

6CHAPTER 1. DOWNLOAD AND INSTALLATION OF 'OLEX2', 'SHELX' AND 'PLATON'

Home	/ork	View	Tools	s Ir	ifo
Start					
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	uules				
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-	-				1
Debug Mode:	Start Olex2 in	Debug Mode (Res	tart required))	
O PATH:	C:\Shebx\shel	k64;C:\PLATON			
Various:	Diagnostics				

Figure 1.27: Registration of 'PLATON' to 'OLEX 2 '.



Figure 1.28: The icon of 'PLATON' on 'OLEX²'.

Here, 'C:\PLATON' should be typed after 'C:\Shelx\shelx64' by separating them with a semicolon (;) without space. After closing the $OLEX^2$, it can be opened again such that the icon of the PLATON is found as shown in Fig. 1.28 and it can be used.

1.6 Registration of the parameter file to the 'OLEX²'

'[2] Rigaku_XtaLAB_P200_007.cif' in the folder of '[1] Program Files\Olex2-

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< → < 1 <mark>[1]</mark> •	Program Files > Olex2-1.3 > etc >	site	√ Č	siteの検索	Q
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🔰 HD-LXU3 (Rigaku AFC12K 724P 007HE.	2019	/03/29 13:59	CIF ファイル	
share (¥¥1!	Rigaku_XtaLAB_P200_007.cif	2019	/10/03 16:30	CIF ファイル	
HD-LXU3 (F	template.cif	2019	/03/29 13:59	CIF ファイル	>

Figure 1.29: The parameter file.

Home	Work	1 V	iew	Toc	ls	Info
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Definition F	ile. [5]	6 C:\Pro	gram Files\Ole:	x2-1.3\etc	:\site\Rigaku	_XtaLAB_P200_0

Figure 1.30: Registration of the parameter file.

1.3\etc\site' in Fig. 1.29 is the parameter file of the apparatus. This file should be placed in the same folder as '[1]'. It is available from the same folder in the computer placed near the entrance of the room #333 of the 9th building of the school of engineering.

On the window of the OLEX², 'Work [1]' in Fig. 1.30 and then '[2] \Downarrow ' on the right of 'Report' can be clicked to let the options of 'Report' be shown. Here, 'Diffraction [3]' and then 'Definition File [5]' should be clicked to open the file explorer as shown in Fig. 1.29. In Fig. 1.29, '[2] Rigaku_XtaLAB_P200_007.cif' should be clicked to load it. In Fig. 1.30, 'XtaLAB AFC10 (RCD): quarter-chi single' can be selected from the pull-down menu of 'Diffractometer [4]'.

Chapter 2

Example of structure determination with the $OLEX^2$ (Sucrose)

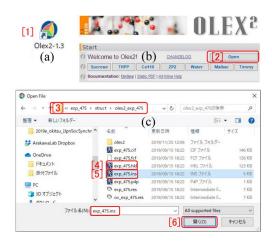


Figure 2.1: Startup of $OLEX^2$ and opening files

2.1 Startup of the $OLEX^2$ and opening the project

By double-clicking '[1]' icon in 2.1 (a), CrysAlis^{Pro} can be started as shown in Fig. 2.1 (b). Fig. 2.1 (c) where the file explorer is displayed, can be opened by clicking '[2] Open' in Fig. 2.1 (b). Here, the folder of '[3]' in which '[4] *.hkl' and '[5] *.ins' exist, should be opened by clicking '[6] Open(O)' with '[5] *.ins' clicked to select it. With this procedure, the files can be loaded.

2.2 Determination of the initial phases with the direct method

In Fig. 2.2, options to determine the initial phases with the direct method have been set.

exp 3	6[1] o_Data\K_Okitsu\e	exp 36\exp 36.p	4p	[2] <i>P</i> 1
C24H28O22			/ 🎽 🗧) 🗍 🔀
a = 7.7098(2) b = 8.6536(3) c = 10.7995(3)	$\alpha = 90^{\circ}$ $\beta = 102.995(3)^{\circ}$ $\gamma = 90^{\circ}$	Z = 1 Z' = 1 V = 702.06(4)		n/a
d min (Mo) (Shift	0.74 ^{I/o} n/a ^{Max Peak}	41.5 Rint n/a Min Peak	1./970	^{iplete} 81%
Home	Work [5]	View	Tools	Info
Solve Program Reflections Composition	C24 H28 O2] ~ 8] 2[9]	Method Intrinsic	eport Phasing ✓ 27 16:44:40 2019 1 Z'= 1 10
Space Grou	p <u>[Rigaku XPlain]</u> XPlain GU	[Olex2]	P1 P21/n P21	· [12]

Figure 2.2: Setting of options for Solve

'exp_36 [1]' is the name of the project. '[2] P1' is the default space group that has the lowest symmetry that is the triclinic system without symmetric center. 'C₂₄H₂₈O₂₂ [3]' is the formula of molecule in a single unit cell, where the number of hydrogen is wrong. '[4]' are lattice constants that are almost correct.

After clicking 'Work [5]', options '[7]-[12]' for 'Solve' can be opened by clicking ' \Downarrow [6]' on the right of 'Solve'. The most recommended program 'ShelXT [7]' for phase determination has been selected from the pull-down menu. 'exp_36.hkl [8]' is the file that has the X-ray diffraction intensities. 'C₂₄H₂₈O₂₂ [9]' is the molecular formula that is the same as '[3]'. Since there is no symmetric element in the case of '[2] P1', the number of molecule in a symmetric element Z' is the same as the number of molecule in a unit cell Z. By clicking 'Olex2 [11]', 'P21/m' and 'P21' are added as candidates

Home	Work	View	Tools	i Info	
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O Program	ShelXT	~	Method	Intrinsic Phasing	~
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🕜 <u>Run Rigaku XF</u>	Plain <u>GU</u>	(a		P21	v A
			N (P21 Report Intrinsic Phasing	~ ~
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) <u>Run Rigaku XF</u> Solve [3]) Program	Refine	(a)	Method	Report Intrinsic Phasing Wed Mar 27 16:44:4	€ √ 0 2019

Figure 2.3: Change of the molecular formula

of the space group to the pull-down menu of 'Space Group [12]'.

With regard to the space groups, refer to Appendix B [p.34], please.

In Fig. 2.3 (a), the molecular formula is ${}^{\circ}C_{24}H_{28}O_{22}$ [1]'. In Fig. 2.3 (b), however, the molecular formula and Z' have been changed to be ${}^{\circ}C_{12}H_{14}O_{11}$ [4]' and 'Z' = 1', respectively, by typing such that 'Z = 2'. Here, in Fig. 2.3 (b), 'Solve [3]' can be clicked for obtaining the initial phases to display the molecular model as shown in Fig. 2.4 (b). When a too large molecular model is displayed, click '[1]' on the upper right of Fig. 2.5 (a), please to display the model with a proper size.

The molecular structure in Fig. 2.4 (b) has been obtained by determining the initial phases with '[1] ShelXT' in Fig. 2.4 (a). The number of hydrogen in 'C12 H14 O11 [2]' is not correct, yet.

2.3 Concerning the direct method and 'SHELX'

There is a difficulty in the crystal structure analysis that the phase angles of the crystal structure factor cannot be directly measured while their absolute values can be measured. This difficulty is called the phase problem. The direct method was developed by Hauptman (Herbert Aaron Hauptman; 1917/2/14-2011/10/23) and Karle (Jerome Karle; 1918/6/18-2013/6/6) from 1950's. The

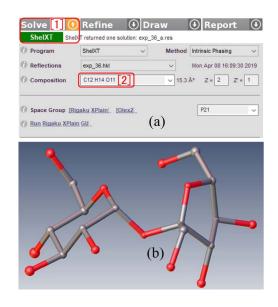


Figure 2.4: Molecular structure with the initial phases determined.

direct method is a purely mathematical method to determine the phases of the crystal structure factors based on the evident fact the electron density in the unit cell is a positive real function. It was rapidly wide-spread after Karle's wife (Isabella Karle; 1921/12/2-2017/10/3) developed a computer program to solve the phase problem on the computer.

Hauptman and Karle were awarded the Nobel prize for chemistry in 1985 for this work.

SHELX is a series of programs to determine the initial phases with the direct method and refine the molecular structure that has been developed by Sheldrick of the University of Göttingen (George Michael Sheldrick; 1942/11/17-) from 1976. A feature article by Sheldrick titled 'A short history of SHELX' was published in *Acta Cryst.* A64 (2008) 112-122. Due to the large number of citations of this article, IF (Impact Factor) of *Acta Cryst.* A64 during 2009-2011 reached around 50, which gave a shock to the scientific community. This reveals the excellence of SHELX and also the important role of crystallography in the current chemistry and science.

Sheldrick was awarded the Ewald prize for this work in 2011.



Figure 2.5: Molecular structure with initial phases determined



Figure 2.6: Result after clicking 'Refine' twice

2.4 Refinement of the structure by least-square fitting

Fig. 2.5 (b) shows the initial setting of the refinement of structure when starting it. Options '[4]-[7]' when clicking 'Refine [2]' have been opened by clicking ' \Downarrow [3]' on the right of 'Refine [2]'. 'ShelXL [4]' has been set (recommended) as the refinement program. Number of fitting done when clicking 'Refine [2]' has been set to be 7 in '[5]'. Number of peaks of electron density that are not assigned to atoms (Q peaks), has been set to be '22 [6]' (number of hydrogen). From the pull-down menu of '[7]', 'ACTA' has been selected (recommended).

The refinement should be done, first with isotropic temperature factors without hydrogens, secondly with anisotropic temperature factors without hydrogens, and finally with anisotropic temperature factors with hydrogens.

2.4.1 Refinement with isotropic temperature factors

Fig. 2.6 shows the result after clicking 'Refine [2]' twice with the settings of Fig. 2.5 (b). The R-factor has been estimated to be '[1] 5.70%'. 'Shift [2]' is 0.000 and green. However, 'GooF



Figure 2.7: Result after further twice refinement with the weight optimized

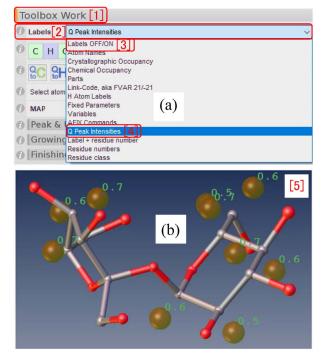


Figure 2.8: Electron density peaks not assigned to any atom (Q peak) and their intensity

[3]' (Goodness of fit) is 1.680 and red. These values estimate the soundness of least-square fitting. The ideal values of 'Shift [2]' and 'GooF
[3]' are zero (0) and unity (1), respectively.

Fig. 2.7 (a) shows the result of refinement by typing [Ctrl]+[R] or clicking 'Refine [2]' in Fig. 2.5 (b) with 'Weight [4]' checked in Fig. 2.7 (b). The R-factor has decreased slightly to '[1] 5.51%'. Both 'Shift [2]' and 'GooF [3]' are green which shows that the structure has been refined soundly.

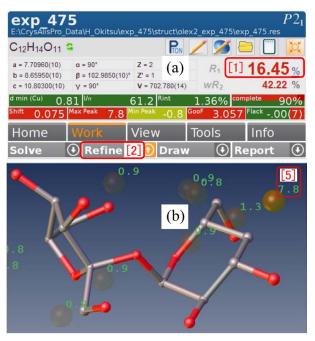
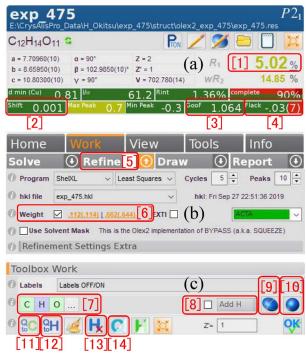


Figure 2.9: Refinement result with an oxygen atom deleted.



2.4.2 Displaying peaks of electron density that have not been assigned to atoms (Q peaks)

In Fig. 2.8 (b) [p.9], peaks of electron density that have not been assigned to any atom (Q peaks) have shown as brown spheres. In Fig. 2.8 (a) [p.9], the pull-down menu of 'Labels [2]' bellow 'Toolbox Work [1]' has been opened. 'Q Peak Intensities [4]' in Fig. 2.8 (a) [p.9] can be clicked to let the Q peak intensities be shown with green characters. The unit is [electrons/Å³]. 'Q [14]' in Fig. 2.10 (c) can be clicked to let the Q peaks be displayed, be displayed with bonds or not be displayed (as shown in Fig. 2.11).

After typing [Delete] key to delete the oxygen at '[5]' on the upper right of Fig. 2.8 (b) [p.9], the structure can be reined by clicking 'Refine [2]' in Fig. 2.9 (a) or typing [Ctrl]+[R] to display a brown sphere (Q peak) at '[5]' on the upper right of Fig. 2.9 (b). The Q peak intensity '7.8' [electrons/Å³] is also displayed with green characters near here. The peak intensities of the Q peaks in Fig. 2.8 (b) [p.9] are $0.5 \sim 0.7$. All of these correspond to hydrogens. After refining the structure with an atom deleted, what it was can be expected from the Q peak intensity.

Figure 2.10: Result after further twice refinement with anisotropic temperature factors

The Q peak can be returned to be oxygen by clicking it after clicking 'O' of 'C H O ... [7]' in Fig. 2.10 (c) or by clicking 'O' of 'C H O ... [7]' after clicking the Q peak.

2.4.3 Refinement with anisotropic temperature factors

The blue elliptical mark of '[9]' in Fig. 2.10 (c) can be clicked to refine the structure with anisotropic temperature factors. Fig. 2.12 should be displayed by right-clicking the background of the molecular model to click 'Ellipses & sticks' in it. By clicking'Refine [5]' in Fig. 2.10 (b) or typing [Ctrl]+[R], the molecular model can be displayed as shown in Fig. 2.13.

In Fig. 2.10 (a), the R-factor has further decreased to '[1] 5.02%' and both 'Shift [2]' and 'GooF [3]' are green, which means that the structure has soundly been refined. The Flack parameter is approximately 0.0 when the chirality is right but approximately 1.0 when the chirality is wrong. 'Flack [4] -.03(7)' on the right lower of Fig. 2.10 (b) means that it has been estimated to be -0.03 ± 0.07 and then the chirality is right. However, 'Weight .112(.114)

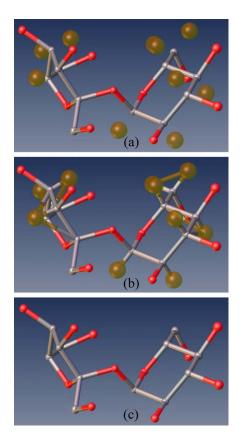


Figure 2.11: Switching the display mode of Q peaks

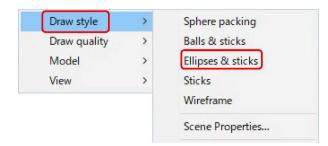


Figure 2.12: Setting of the 'Thermal ellipsoid' mode.

.662(.644) [6]' is displayed with yellow characters. Then, it should be further optimized such that it is displayed with green characters.

2.4.4 Refinement with hydrogens assigned

2.4.4.1 Automatical assignment of hydrogens

Fig. 2.14 shows the molecular model refined with hydrogens automatically assigned by click-

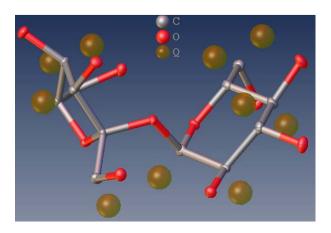


Figure 2.13: The molecular structure displayed with the 'Thermal ellipsoid' mode.

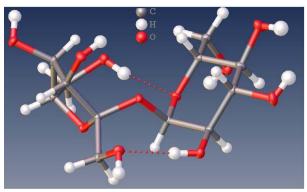


Figure 2.14: Molecular model with hydrogens automatically assigned.

ing '[8] Add H' in Fig. 2.10 (c). When checked between '[8]' and 'Add H' in Fig. 2.10 (c), the molecular structure is automatically refined only by clicking '[8] Add H'. This is also applied when '[9]' or '[10]' on the right of '[8] Add H' is clicked. 'H_× [13]' in Fig. 2.10 (c) can be clicked to cancel the all assignments of hydrogens.

2.4.4.2 Assignment by replacing Q peaks with hydrogens

One molecule of sucrose has 22 hydrogen atoms. By setting '[9]' in Fig. 2.16 (d) [p.12] such that 22 Q peaks are displayed after the refinement, the molecular structure is refined as shown in Fig. 2.15 (a) [p.12]. 'Q to H [12]' in Fig. 2.16 (e) [p.12] can be clicked to replace all Q peaks with hydrogens as shown in Fig. 2.15 (b) [p.12]. If 'Weight · · · [10]' in Fig. 2.16 (d) [p.12] is

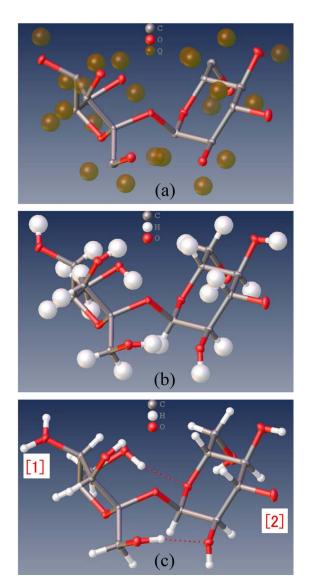


Figure 2.15: Q peaks have been replaced with hydrogens.

displayed with orange or red characters, the structure should be refined with 'Weight [10]' checked such that it is displayed with green characters as shown in Fig. 2.6 (d). The refinement can be repeated to show Fig. 2.15 (c). While hydroxy groups are considered to exist at positions of '[1]' and '[2]', there are two and no hydrogens at '[1]' and '[2]'. After deleting two hydrogens at '[1]' by typing [Delete] key, the molecular structure can be refined as shown in Fig. 2.16 (a).

After clicking Q peaks of '[1]' and '[2]' to select them, they can be changed to hydrogens by clicking 'H' of 'C H O ... [11]' in Fig. 2.16 (e). The structure can be refined as shown in Fig.

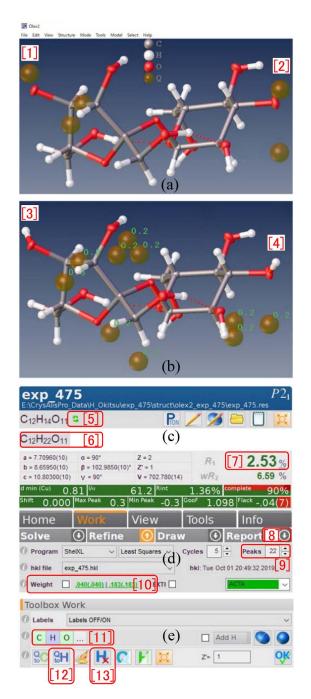


Figure 2.16: The refined structure with hydrogens of hydroxy groups assigned.

2.16 (b). In Fig. 2.16 (c), the R-factor has decreased to '[7] 2.53%'. Here, '[5]' can be clicked to such as to display the correct molecular formula as 'C₁₂H₂₂O₁₁[6]'. Fig. 2.16 (b) shows the final molecular structure of sucrose since all intensities of Q peaks are extremely small values around 0.2 [electrons/Å³].

2.5. CREATION OF THE REPORT

There is conflicting information!

Some of your files contain conflicting information regarding information that should go into your cif file.

	exp_475.cif Use all	exp_475.p4p Use all	exp_475.cif_od Use all	User value
_diffrn_radiation_type <u>Unapplicable (.) _Unknown (?</u>)	<u>CuK¥a</u>		<u>Cu K¥a[1]</u>	? Use
_diffrn_measured_fraction_theta_max <u>Unapplicable (.)_Unknown (?</u>)	<u>0.975</u>		<u>0.8636</u> [2]	? Use
_diffrn_measured_fraction_theta_full <u>Unapplicable (.) _Unknown (?</u>)	<u>0.999</u>		1.0000 [3]	? Use

Figure 2.17: The window displayed just after clicking $\binom{8}{4}$ in Fig. 2.16 (d).

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Style default.css V B Table label style: As in CIF	egin with def	ault.htm	~	End with	templates/foc 、
Collection Crystal Crystal Image Diffraction Absorption Correction Publication Citations Reference Source Files	[1] [2] [3] [4] [6] [6] [7] [8] [9]	[3]			
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Figure 2.18: Setting window of report.

2.4.4.3 Manual assignment of hydrogens

Hydrogens can also be manually assigned. Refer to the description in §3.8 [p.25], please.

2.5 Creation of the report

'[8] \Downarrow ' on the right of 'Report' in Fig. 2.16 (d) can be clicked to show the window of Fig. 2.17. 'CuKa [1]', '0.8636 [2]' and '1.0000 [3]' displayed with green characters, can be clicked to display Fig. 2.18. 'Make Report [1]' on the upper right of Fig. 2.18 can be clicked to create the report of html, later. The items in the red frames of '[2]' and '[4]' in Fig. 2.18 should be set as this. In the red frame of 'Absolute structure determination

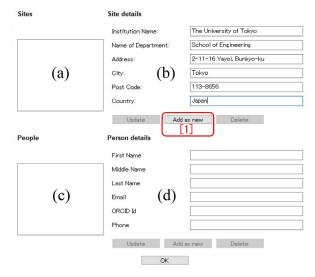


Figure 2.19: Setting window of 'Report'

Collection [1]		
Sample ID			H
Submitter	?	Operator	?
Submitted 2019	/10/05 V Collec	ted 2019/10/05 ~	Completed 2019/10/05 ~

Figure 2.20: Setting window of 'Report'

[5]', the Flack parameter has been estimated to be $-0.04(\pm 0.07)$, which means that the chirality of the molecular structure is right.

'Collection [1]'-'Source Files [9]' can be clicked to set parameters of them, which is described in the following subsections.

2.5.1 Settings of 'Collection'

Fig. 2.20 has been displayed by clicking 'Collection [1]' on the upper left of this figure. The text box of 'Submitter' in Fig. 2.20 can be clicked to

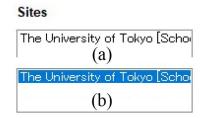


Figure 2.21: Choice of the first author's affiliation

details

First Name	\frown	Kouhei
Middle Name		
Last Name	547	Okitsu
Email	[1]	yrt01404yrt@yahoo.co.jp
ORCIDId		
Phone		+81-3-5841-7470
Update	2 Add a:	s new Delete
[3	ОК)

Figure 2.22: Typing the first author's name and address



Figure 2.23: The first author's name

display Fig. 2.19 [p.13].

After typing the first author's affiliation in Fig. 2.19 (b) [p.13], 'Add as new [1]' can be clicked to type his (her) name and address in Fig. 2.19 (d) [p.13] as shown in '[1]' of Fig. 2.22. His (her) name as in Fig. 2.23 is displayed in the field of (c) in Fig. 2.19 [p.13]. When the number of the author is one, '[2] Add as new' and then '[3] OK' should be clicked in Fig. 2.22 to finish.

To add the second author whose affiliation is the same as the first author, at first, the affiliation of the first author should be clicked as shown in Fig. 2.21 (b) in the field of (a) in Fig. 2.19 [p.13]. Here, the second author's name and address should be typed as shown in Fig. 2.24 '[1]'. Then, '[2] Add as new' should be clicked such that Fig. 2.25 is displayed in (c) of Fig.

Person details		
First Name	\bigcap	Jiro
Middle Name		
Last Name	[1]	Todai
Email	L1J	jiro-todai@yahoo.co.jp
ORCID Id		
Phone		+81-3-5840-7472
Update	[2]Add a	s new Delete
[3	ОК	<u>ן</u>

Figure 2.24: Typing the second author's name and address

People	
Okitsu, K. Todai, J.	

Figure 2.25: The first and second authors' name

Site details	_		_
Institution Name:	(Nakasu Bussiness University	
Name of Department:		School of Business	
Address:	[1]	880-22-5 Nakasu	
City:	1.1.1	Hakata	
Post Code:		810-0880	
Country:		Japan	
Update [2	Add as	: new Delete	

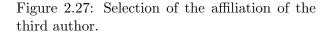
Figure 2.26: Addition of the third author's affiliation

2.19 [p.13]. When the number of author is two, '[3] OK' in Fig. 2.24 should be clicked to finish.

To add the third author whose affiliation is different, at first, his (her) affiliation should be typed in (b) of Fig. 2.19 [p.13] as shown in Fig. 2.26 '[1]'. Then, '[2] Add as new' should be clicked such as to display it in (a) of Fig. 2.19 (a) [p.13]. It can be clicked to display Fig. 2.27 (b) such that the third author's name and address can be typed as shown in Fig. 2.28 '[1]'. Here, '[2] Add as new' can be clicked such as to display Fig. 2.29 in (c) of Fig. 2.19 [p.13]. Then, '[3] OK' in Fig. 2.28 can be clicked to finish the

2.5. CREATION OF THE REPORT





Person details		
First Name	\bigcap	Kenta
Middle Name		
Last Name	[1]	Sugakura
Email		kenta.sugakura@yahoo.co.jp
ORCID Id		
Phone		+81-42-8880-8888
Update	[2]Add a	s new Delete
[3]	ОК	

Figure 2.28: Typing the third author's name and address.

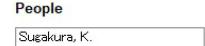


Figure 2.29: The third author's name

creation of the authors list.

^{(1]} Submitter' in Fig. 2.30 (a) can be clicked to open the authors list as shown in Fig. 2.19 [p.13]. In (a) of Fig. 2.19 [p.13], at first, the affiliation should be clicked as shown in Fig. 2.30 (b). Then, the submitting author can be clicked as shown in Fig. 2.30 (c).

After clicking 'Operator [2]', the operator can also be set with a similar procedure as above.

From the pull-down menus of 'Submitted [3]', 'Collected [4]' and 'Completed [5]' on the bottom of Fig. 2.30 (f), the dates can be selected. Now, all items of 'Collection [1]' on the upper left of Fig. 2.20 [p.13] have been set.

Collectio	n				
Sample ID		(a))		
Submitter	[1] ?		Operator	2])	?
Submitted	2019/10/06 🗸	Collected 20	19/10/06 ~	Complete	ed 2019/10/06
Sites			Sites		
Nakasu Buss The Univers	siness University ity of Tokyo [So	/ [S hou			University [S Tokyo [Scho
	(b)			(d)	
People			People		
Okitsu, K. Todai, J.	(c) -		Okitsu, Todai, J		
Collectio	'n				
Sample ID	Sucrose as-grow	n (f)			
Submitter	Okitsu	, К.	Operator	То	odai, J.
Submitted	2019/10/10 3	Collected 20	19/08/19 4	Complete	ed 2019/09/17

Figure 2.30: Selections of 'Submitter' and 'Operator'.

clear	~	light	~	colourless	~
0.20	0.22	0.24	pris	m	~
As-grow	/n				0
Batch ne	ethod				0
	0.20 As-grow		0.20 0.22 0.24 As-grown	0.20 0.22 0.24 pris	0.20 0.22 0.24 prism As-grown

Figure 2.31: Selection or typing of crystal information.

2.5.2 Settings of 'Crystal'

Fig. 2.31 has been opened by clicking 'Crystal [2]' on the upper left of it. Here information concerning the crystal can be selected or typed. If inputted on the CrysAlis^{Pro}, it has already been set. Even if not, at least, 'Colour [1]' and 'Size & Shape [2]' shouled be selected or typed.

2.5.3 Settings of 'Crystal Image'

Fig. 2.32 [p.16] has been opened by clicking 'Crystal Image [3]' on the upper left of it. Here, '>' can be clicked to reproduce the optical images of the crystal continuously.

16CHAPTER 2. EXAMPLE OF STRUCTURE DETERMINATION WITH THE OLEX² (SUCROSE)

0	44 🕨 🖪 22

Figure 2.32: Selection or typing of crystal information.

Diffractometer	XtaLAB AFC10 (RCD	3): quarter-chi sin	igle 1	~
Definition File [2]	C:\Program Files\Olex	2-1.3\etc\site\Rig	aku_XtaLAB_F	200_0
Diffraction T (K)	93(1)			
Cell Measurement T (K)	93(1)			
Special Details	?			¢
	(a)			_
Refine Special Details	? (u)			0
	? (**)			~
Refine Special Details			- 0) × × ©
■ ☑ = = site ファイル ホーム 共有 表示		site v ð	ー ロ siteの検索	~
■ ☑ = = site ファイル ホーム 共有 表示		site 更新日時		~ × ~
ファイル ホーム 共有 表示 ← → ∨ ([4] ≪ Program Fi ♪ ミュージック へ 二 名前			siteの検索	ب ب م
	iles > Olex2-1.3 > etc >	更新日時	siteの検索 種類	ې م
	iles > Olex2-1.3 > etc >	更新日時 2019/03/29 13:59	siteの検索 種類 CIF ファイル	ب ب م
	iles → Olex2-1.3 → etc →	更新日時 2019/03/29 13:59 2019/03/29 13:59	siteの検索 種類 CIF ファイル CIF ファイル	ب ب م

Figure 2.33: Setting of the parameter file

Abs Type	multi-scan	~
Abs Details	CrysAlisPro 1.171.40.54a (Rigaku Oxford Diffraction,	\$
Abs T max	1.00000	
Abs T min	0.91921	

Figure 2.34: Information about the absorption correction.

2.5.4 Settings of 'Diffraction'

Fig. 2.33 has been displayed by clicking 'Diffraction [4]' on the upper left of it. Here, 'Definition file [2]' can be clicked to display the file explorer as shown in Fig. 2.33 (b). In Fig. 2.33 (b), '[5] Rigaku_XtaLAB_P200_007.cif' in the folder of '[4] Program Files\Olex2-1.3\etc\site', should be clicked to load it as shown in Fig. 2.33 (a)

CCDC Number	?	
Contact Author	Okitsu, K.	~
Authors 🔶 🗙	Okitsu, K.	
[2] + • ×	Todai, J.	
•×	Sugakura, K.	
Add Author [3		
] Add	~
Add Author 3	Add Acta Crystallogr.,Sect.B:Struct.Sci.	~

Figure 2.35: List of the authors and title of the journal

	\times
	^
	- D

Figure 2.36: Cover letter to the editor.

0	Citations [7]	
	Current Citations: Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341. Sheldrick, GM, (2015). Acta Cryst. A71, 3-8.	
	Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.	

Figure 2.37: Articles that should be cited.

Reference [8]		
CSD Refcode		
Authors [1]	K. Okitsu, J. Todai and K. Sugakura	
Journal [2]	Acta Crystallogr.,Sect.B:Struct.Sci.	~
Volume		
Pages		
Year		
Comment		0

Figure 2.38: Information concerning the submitted article

'[3]'. Then, the pull-down menu of '[1]' can be found as shown in Fig. 2.33 (a).

CIF OD	.\exp_47	5.cif_od			
All conflicts are reso	olved Reset Previo	usly Resolved Con	flicts		Н
Edit CIF Info	N	Merge CIF	HKL/RES Leave as	is 🗸	So
0 IUCr CheckCh	pdf 🗸	CCDC	Request CCDC Nu	umber	e
Image: OF: Merge CIF: met Image: OF: Image: OF: Merge			Add local de	efault CIF	Sty

Home	Work	< V	iew	Тос	bls	Info	
Solve	🕑 Re	fine	🕑 Drav	N	🕑 Re	port	0
exp_475		Image	No Image	~	Make Re	eport [1]	1
Style default	CSS 🗸	Begin with	default.htm	~	End with	templates/fo	c 🗸
Table label style	: As in CIF						~

Figure 2.39: Information concerning the the source file

Figure 2.40:	Creation	of the report	

	exp_475.cif Use All	exp_475.p4p Use All	Rigaku_XtaLAB_P200_007.cif	exp_475_acta.cif Use All	exp_475.cif_od Use All	New User Value
_computing_structure_solution Unapplicable (.) <u>Unknown (?</u>)	SHELXT 2018/2 (Sheldrick, 2018)			Sheldrick, 2015		Use
_diffrn_detector_area_resol_mean Jnapplicable (,) _Unknown (?)	<u>5.8140</u>		<u>5811</u>		<u>5.8140</u>	Use
diffrn_radiation_monochromator Jnapplicable (.) _Unknown (?)	<u>mirrar</u>		multi-laver mirror optics		mirror	Use
_diffrn_detector Jnapplicable (.) _Unknown (?)	CCD plate		PLATUS 200K area detector		CCD plate	Use
_diffrn_measurement_device_type Unapplicable (.) <u>Unknown (?)</u>	XtaLAB AFC10 (RCD3): guarter-chi single		Rigaku XtaLAB P200		XtaLAB AFC10 (RCD3) guarter-chi single	Use
_diffrn_source_type Jnapplicable_(,)Unknown_(?)	Rigaku (Cu) X-ray DW. Source		micromax007		Rigaku (Cu) X-ray DW Source	Use
_diffrn_source <u>Unapplicable (.) _Unknown (?)</u>	Rotating-anode X-ray tube (dual wavelength)		rotating anode X-ray generator		Rotating-anode X-ray tube (dual wavelength)	Use
_computing_publication_material Jnapplicable (.) _Unknown (?)	Olex2.1.3 (Dolomanov.et. al., 2009)			Olex2 1.3 (Dolomanov et al., 2009)		Use
_publ_section_references Unapplicable [.jUnknown (?)	Oolomanov, O.V., Bourhis, I. J., Gildes, R.J., Howerd, J.A.K. & Puschmann, H. (2009), J. Appl. Crvst. 42, 339–341 Sheldrick, GM. (2015), Acta Crvst. 671, 3–8, Acta Crvst. C71, 3–8,			Sheldrick, 2015. Sheldrick, G.M. (2015). Acta Crivet, A71, 3-8. Sheldrick, 2015. Sheldrick, GM (2015). Acta Crivet, C71, 3-8. Olex2: Dolomanov, O. V. Bourhis, L. J., Gildes, R. J., Houred, J. A. K. S. andfin . Puschmann, H. (2005). J. Appl. Crivet, 42, 389341.	[1]	Usc
_computing_molecular_graphics Jnapplicable (.) _Unknown (?)	Olex2.1.3 (Dolomanov.et. al., 2009)			Olex2 1.3 (Dolomanov et al., 2009)		Use
computing_structure_refinement Unapplicable (.) Unknown (?)	SheiXL 2018/3 (Sheidrick, 2015)			Sheldrick, 2015		Use

Figure 2.41: Conflicting information

2.5.5 Settings of 'Absorption Correction'

Fig. 2.34 has been opened by clicking 'Absorption Correction [5]' on the upper left of it. In the CrysAlis^{Pro}, empirical correction is necessarily applied to taking into account the absorption effect based on the expected crystal shape from the comparison of X-ray intensities of equivalent reflections. Information concerning the absorption correction has been performed based on the measured crystal shape, information concerning this method is also described.

2.5.6 Settings of 'Publication'

Fig. 2.35 has been displayed by clicking 'Publication [6]' on the upper left of it. In '[2]' of Fig. 2.35, three author's names are listed. They have been inputted in Figs. 2.19 [p.13]-2.29 [p.15]. The 'Contact Author [1]' can be selected from the pull-down menu in Fig. 2.35. The order of the authors can be changed by clicking the arrow of '[2]' in Fig. 2.35. 'Add Author [3]' can be clicked to add another author into the list. 'Requested Journal [4]' can be selected from the pull-down menu. 'Journal Style [5]' can also be selected from the pull-down menu. 'Contact Letter [6]' in Fig. 2.35 can be clicked to show Fig. 2.36 in which a contact letter to the editor can be typed. 'OK' on the lower left of it can be clicked to finish.

2.5.7 Settings of 'Citations'

Fig. 2.37 has been opened by clicking 'Citations [7]' on the upper left of it. These three articles should necessarily be cited when the $OLEX^2$ and the ShelX have been used.

2.5.8 Setting of 'Reference'

Fig. 2.38 [p.16] has been displayed by clicking 'Reference [8]' on the upper left of it. In 'Authors [1]', the authors that have been set in Fig. 2.35 [p.16] are listed. 'Journal [2]' can be selected from the pull-down menu.

2.5.9 Settings of 'Source Files'

Fig. 2.39 [p.17] has been opened by clicking 'Source Files [9]' on the upper left of it. Here, information concerning the source files is described.

2.5.10 Creation of the final report

'Make Report [1]' on the right of Fig. 2.40 [p.17] can be clicked to let Fig. 2.41 [p.17] be displayed. 'Use' on the right of Fig. 2.41 [p.17] can be clicked to open the browser on which Fig. 2.42 is opened. In this file, the space group, the lattice parameters, the crystal size and all other information concerning the crystal are described.

exp_475

Table 1 Crystal data and structure refinement for exp	475.
-------------------------------------------------------	------

	and of decide remement for exp
Identification code	exp_475
Empirical formula	C ₁₂ H ₁₄ O ₁₁
Formula weight	334.23
Temperature/K	93(1)
Crystal system	monoclinic
Space group	P21
a/Å	7.70960(10)
b/Å	8.65950(10)
c/Å	10.80300(10)
a/°	90
β/°	102.9850(10)
Y/°	90
Volume/Å ³	702.780(14)
Z	2
p _{calc} g/cm ³	1.579
µ/mm ⁻¹	1.261
F(000)	348.0
Crystal size/mm ³	$0.24 \times 0.22 \times 0.2$
Radiation	Cu Ka ($\lambda = 1.54184$)
20 range for data of	collection/°8.4 to 144.526

Figure 2.42: Final information concerning the crystal

2.5. CREATION OF THE REPORT

To be continued

Chapter 3

Example of structure detemination with the OLEX² (α -cyclodextrin)

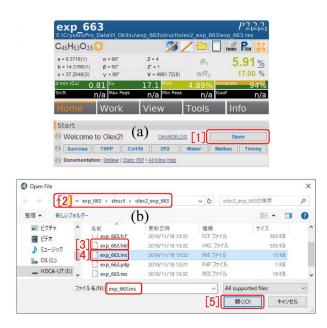


Figure 3.1: Loading the file

3.1 Opening the project

[1] Open' on the lower right of Fig. 3.1 (a) can be clicked to let Fig. 3.1 (b) be shown. In the folder of project '[2] ... exp_663\struct\olex2_exp_663', in Fig. 3.1 (b), '[3] exp_663.hkl' and '[4] exp_663.ins' are found. After selecting '[4] exp_663.ins', '[5] Open(O)' on the lower right should be clicked. Fig. 3.2 shows the molecular structure automatically determined by 'AutoChem' in the OLEX². By typing [Ctrl]+[T], this window can be changed such as to display only the text as shown in Fig. 3.3 (a). By typing [Ctrl]+[T] again, Fig. 3.3 (a) can be changed such as to display only the molecular model as shown in Fig. 3.3 (b). By

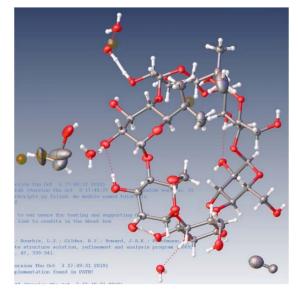


Figure 3.2: Molecular structure automatically determined by the AutoChem.

typing [Ctrl]+[T] once more, both the molecular model and the text can be displayed as shown in Fig. 3.2, which is recommended.

3.2 Determination of the initial phases

In Fig. 3.4 (b), 'Work [1]' and then ' \Downarrow [2]' on the right of 'Solve [3]' can be clicked to display 'Solve' options. 'ShelXT [4]' is recommended to select from the pull-down menu since this is recognized to be the most excellent as the phase determination program. 'Solve [3]' can be clicked to start the initial phase determination. It is time consuming due to the large size of the

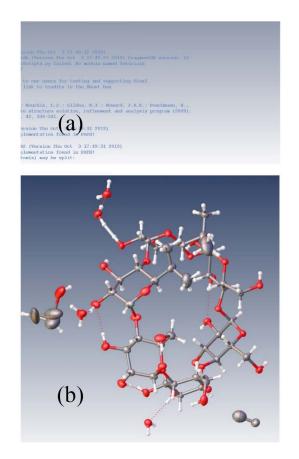


Figure 3.3: [Ctrl]+[T] can be typed to display these windows.

exp_663 E:\CrysAllisPro_Da	 ta\H_Okitsu\exp_663\struct	\olex2_exp_663\e	P212121 exp_663.res
C45H53O33 😂	(a) 🎽	/ 🖻 🗍	TWINS PON
			[6]
Home 🚺	Nork [1] View	Tools	Info
Solve 3	Refine 🕑 Dra	aw 🕑 R	eport 🕑
ShelXT 2	returned one solution: exp_66	3_a.res	
O Program	SheIXT 4	Method Intrinsio	Phasing 🗸 🗸
Reflections	exp_663.hkl	V Sun [Dec 1 15:12:43 2019
Composition	C45 H53 O33	✓ 16.0 Å ³ Z	= 4 Z' = 1
Space Group Su	iggest SG (b)	P2'	12121 ~
Solution Set	ttings Extra		
	(c) Solv	ing <mark>[5]</mark>	

Figure 3.4: Settings for determination of the initial phases.

molecule to determine the initial phases. Then, 'Solving [5]' as shown in Fig. 3.4 (c) is displayed for one minute or so on the upper right corner of the molecular model display region.

At first, the initial structure model of the

0. e394 0. e364 0. 1342 0. 1342 2. 0.00 5. 11. 4.6 0. 5188 0. 0.667 0. 1345 0. 1312 2. 340 360 13. 107 0. 5028 0. 0.667 0. 1345 0. 1412 2. 348 360 13. 107 0. 5028 0. 0.467 0. 1345 0. 1412 2. 425 367 13. 60 0. 677 0. 3060 0. 1150 0. 1412 1. 579 371 13. 21 0. 5028 0. 1370 0. 1300 0. 1412 1. 579 371 13. 21 0. 695 0. 677 0. 1346 0. 0.142 1. 257 371 13. 21 0. 695 0. 677 0. 1346 0. 0.142 1. 257 371 13. 21 0. 695 0. 677 0. 1346 0. 0.142 1. 257 371 13. 21 0. 695 0. 677 0. 1348 0. 1312 0. 67 382 1 0. 695 0. 677 0. 1348 0. 1312 0. 67 382 1 0. 695 0. 6319 0. 1319 0. 1412 0. 67 382 1 0. 695 0. 6319 0. 1319 0. 1412 0. 67 382 1 0. 695 0. 6310 0. 1380 0. 1412 0. 67 382 1 0. 695 0. 6310 0. 1380 0. 1412 0. 67 382 1 0. 695 0. 6310 0. 1360 0. 1560 2.36 5 10 1. 0 0. 596 0. 6310 0. 1380 0. 1560 2.36 5 10 1. 0 0. 598 0. 4202 0. 1381 0. 0.156 2. 36 5 10 1. 0 0. 598 0. 4202 0. 1381 0. 0.156 2. 36 5 10 1. 0 0. 677 0. 0.887 3. 0.887 9. 0.879 1. 123 1. 0 1 0. 598 0. 0.100 0. 368 0. 0.569 2. 2. 57 371 1. 45 0. 0744 0.000 0.887 9. 0.897 9. 0.153 13. 15. 5 0. 074 0. 0.087 9. 0.897 9. 0.897 9. 1.723 132 11. 0 0 0. 140 0.000 0.887 0.087 9. 0.153 13. 15. 5 0.074 0.000 0.887 0.087 9. 0.153 13. 15. 5 0.074 0.000 0.887 0.087 9. 0.153 13. 15. 5 0.074 0.000 0.887 0.087 9. 0.153 13. 15. 5 0.074 0.000 0.887 0.087 9.07 5.07 311 1. 26 0.075 0.082 0.422 0.158 0. 687 9.2. 471 13. 318 0.014 0.000 0.887 0.087 9.087 5.03 13. 10. 6 0.075 0.082 0.422 0.158 0. 68 2.471 1. 13.38 1. solution 25 selected with best Cl - 0.8879, had - 0 1. 43.032 secs 2. and 56 non-centrosymetric space groups taluated Indica: 9. 382 secs 3. solution 25 selected with best Cl - 0.8879, had - 0 1. 43.032 secs 3. and 56 non-centrosymetric space groups taluated Indica: 9. 382 secs 3. solution 3. Secs 5. solution 3. Secs

Figure 3.5: Initial structure obtained by the phase determination

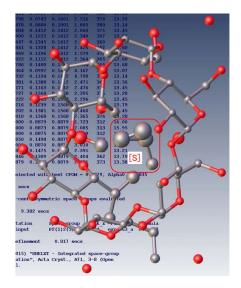


Figure 3.6: solvent molecule moved by symmetrical operation

molecule is displayed as shown in Fig. 3.5. By clicking '[6]' on the right of Fig. 3.4 (a), 'Solvent molecule [S]' on the left of Fig. 3.5 can be moved to inside the ring as shown in Fig. 3.6. While only one molecule of the solvent is displayed following the rule that just one symmetric unit is displayed, the solvent molecules exist both inside and outside of the ring.

Home	Work	View	Tools	Info
Solve	Refine	3 🕦 Dra	w 🕑 R	eport 🕑
O Program Sh	eKL [2] ~ L.	.s. [1] 🗸	Cycles 7	Peaks 10 +
() hkl file ex	p_663.hkl	~	hkl : Sun Dec 1	20:07:37 2019
🛈 Weight 🔲	.100 .197 .000	14.884 EXTI		ICTA V
🕜 🗌 Use Solve	nt Mask This is t	he Olex2 implemen	tation of BYPASS (a	.k.a. SQUEEZE)
Refineme	ent Settings Ex	ktra		
Toolbox W	ork[4]			
O Labels	abels OFF/ON			~
ОСНО			Add H	
0 8C 8H	🤞 🕂 🕻	F 💢	Z'= 1	Ok

Figure 3.7: Starting the optimization of the molecular structure

Home Work Vie	ew Tools	Info [1]
Recent Files		
Electron Density Peaks		
Refinement Indicators		
Bad Reflections		
Reflection Statistics [2]		
● hkl File exp_663.hkl ∨ Use pk	otly? Write file?	Pin Summary
0	[3]	~
Please Select Wilson Plot Cumulative Intensity Systematic Ausences Fobs-Fcalc Vsigma vs resolution		

Figure 3.8: Checking the existence of symmetric center

3.3 The optimization of the molecular structure

Fig. 3.7 shows the initial window to start the optimization of the molecular structure.

At first, ' \Downarrow [1]' can be clicked to set the options for optimization.

After selecting 'ShelXL [2]' which is recommended, the optimization can be repeated by clicking 'Refine [3]' or typing [Ctrl]+[R]. Here, tools in 'Toolbox Work [4]' can be used.

As described in chapter 2 [p.7], the optimization of the molecular structure should be done in the order of optimization with isotropic temperature factors without hydrogen, that with anisotropic temperature factors without hydrogen and that with anisotropic temperature factors and hydrogen atoms.

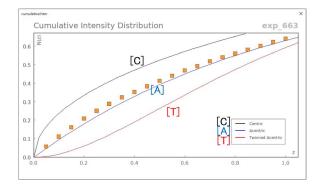


Figure 3.9: Checking the existence of symmetric center

d min (Cu) ^{Shift} 0.01	0.01	l∕σ Peak	2.2	17.1 ^R	int -0.9	-		Flack 1	94% 1(11)
Home	VV	ork		View	8	Тос	ols	Info	
Solve	٢	Refi	ne	0	Dra	w	€ Re	eport	٢
1 Program	ShelXL		~ L.S	i.	~	Cycles	7 🔹	Peaks	20 🛓
🛈 hkl file	exp_663	.hkl			~	hkl :	Mon Dec 2	00:37:36 2	2019
🕐 Weight	.187	187	13.2	13.2 EX	ті 🗆			CTA	~

Figure 3.10: Anomalous intensity of Maximum Peak

In the following sections, items that have not been described in chapter 2 are described.

3.4 Checking the existence of symmetric center

After finishing the optimization of the molecular structure, 'Info [1]' on the upper right of Fig. 3.8 should be clicked. After opening 'Reflection Statistics [2]' in Fig. 3.8, 'Cumulative Intensity [4]' should be selected from the pull-down menu of '[3]' to display Fig. 3.9. Here, three curves '[C] Centric', '[A] Acentric' and '[T] Twinned Acentric' correspond to crystals with symmetric center, those without symmetric center and twinned crystals without symmetric center, respectively. It can be found that the crystal whose structure to be solved does not have symmetric center since square marks are plotted in the vicinity of '[A] Acentric'. This is reasonable since the space group $P2_12_12_1$ (orthorhombic #19) displayed on the upper right of Fig. 3.4 (a) [p.21] does not have symmetric center and α -cyclodextrin has a chiral molecular structure.



Figure 3.11: Anomalous intensity of Maximum Peak

3.5 Consideration on the intensities of Q peaks

'MaxPeaks 2.2 [1]' in Fig. 3.10 is a warning that the maximum intensity of Q peak 2.2 [electrons/Å³] which is a peak of electron density not assigned to any atom, is too large. In Fig. 3.11, 'Info [1]' and then 'Electron Density Peaks [2]' have been clicked to open. The intensities of Q peaks are displayed on a bar chart. 'Q1 2.240 [3]' on the left of the yellow bar is also a warning that the maximum intensity (2.240 [electrons/Å³]) of Q peak is too large.

In Fig. 3.12 showing the molecular model, number of Q peaks displayed can be decreased by scrolling the mouse wheal to the near direction as shown in Figs. 3.12 (a), 3.12 (b) and 3.12 (c). In Fig. 3.12 (c), only one Q peak is found which is nothing but the largest electron density peak as shown in Figs. 3.10 and 3.11.

The molecule of α -cyclodextrin is a molecule of cyclic oligosaccharide that consists of glucoses linked with glycosidic bonds. Therefore, Q peaks labelled with C, C, Q and C in Fig. 3.12 (c) are actually disordered oxygen atoms. When attention is focused on Q and C on the rightmost of Fig. 3.12 (c), oxygen atoms exist at either of these sites with an occupancy ratio of approximately 1 : 1. The situation is similar to the above case also for the first and second leftmost C. In the following section, the procedure to separate these disordered oxygens is described.

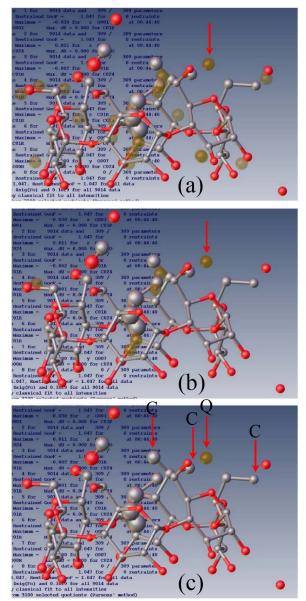


Figure 3.12: Changing the number of displayed Q peaks.

3.6 Separation of disordered atoms

After three carbons indicated with red arrows in Fig. 3.12 (c) are deleted or replaced to oxygens, the molecular structure can be refined by typing [Ctrl]+[R] or clicking 'Refine [3]' in Fig. 3.7 as shown in Fig. 3.13 [p.24].

The procedure to separate a pair of Q peak and oxygen on the right of Fig. 3.13 [p.24] into oxygens disordered at two cites, is described referring Figs. 3.14-3.16 [p.24] as follows. At

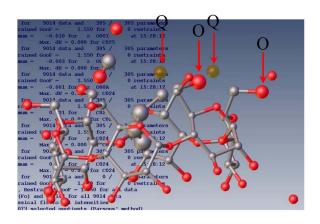


Figure 3.13: Refined with oxygen replaced from carbon.

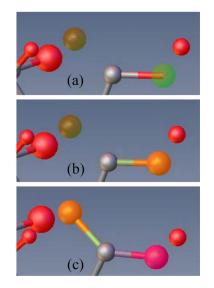


Figure 3.14: The oxygen is dragged to Q peak with [Shift] key pressed.

first, the oxygen atom should be clicked to let it be displayed as a green sphere as shown in Fig. 3.14 (a). Next, in Fig. 3.15, 'Tools [1]', 'Disorder [2]' and then '[3] mSprit' should be clicked such that an orange band is displayed on the bottom of Fig. 3.15. Further, the orange sphere as shown in Fig. 3.14 (b) should be click&dragged to the position of Q peak with [Shift] key pressed as shown in Fig. 3.14 (c). The positions of the orange sphere and the Q peak should three-dimensionally coincide with each other. The molecular model should be rotated by click&dragging it without [Shift] key pressed such that the positions of the orange sphere and the Q peak can be adjusted also in

Home	Work	Vie	w T	ools [1] li	nfo
HARt					
JIEIA COI	прасіріє і	(estraint.	3		_
Hydroger	Atoms				
Disorder	2]				
Ilia's Fragmer	nt Library				
Link Select	ed: Occupancie	s Parts & Oco	cupancies		
Link Parts	& Occupanies +	+ EADE ISOR			
Assign sele	ection to Parl				1
Assign sele	ection to 2 part	s in order			
Show PART	01 02 0-1 0	-2 12 1 2 6	ALL		
O Split & restra	ain on click	Split	EADP	ISOR	SIMU
3 Select atom	(s) and then	mFit	3 mSplit	Split SAME	Split

Figure 3.15: Starting to separate the disordered oxygens

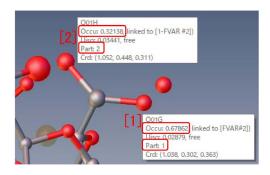


Figure 3.16: The disordered oxygen separated to two sites

the depth direction of Fig. Fig. 3.14 (c). [Esc] key can be clicked to escape from the peak separation mode.

The molecular structure with the disordered oxygen separated can be refined by typing [Ctrl]+[R] or clicking 'Refine [3]' in Fig. 3.7 [p.22] as shown in Fig. 3.16. By placing the mouse cursor on the oxygens at '[1]' and '[2]', labels can be displayed for several seconds around there. The labels show the occupancies of oxygen at cites [1] and [2] are 0.67862 and 0.32138, respectively.

The similar procedure can be applied to separating the pair of Q peak and oxygen at upper central part of Fig. 3.13

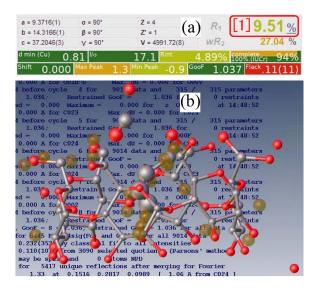


Figure 3.17: Refined result with isotropic temperature factors

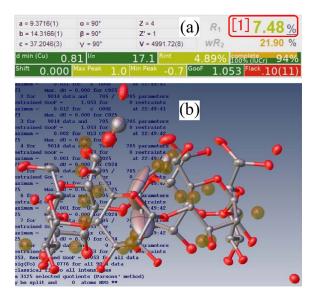


Figure 3.18: Refined result with anisotropic temperature factors

3.7 Refinement with isotropic and anisotropic temperature factor

Similarly to the case of sucrose, after refining the structure under the assumption of isotropic temperature factors such that the R-factor comes to be '[1] 9.51%' as shown in Fig. 3.17, the temperature factor should be changed to anisotropic such that the R-factor comes to be

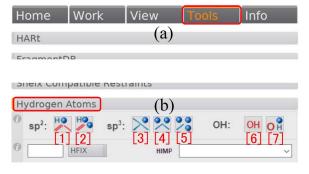


Figure 3.19: Manual addition of hydrogens to carbons

'[1] 7.48%' as shown in Fig. 3.18 (a).

The temperature factor can be changed from isotropic to anisotropic by clicking '[9]' and vice versa by clicking '[10]' on the lower left of Fig. 2.10 (c) [p.10].

3.8 Refinement with hydrogen atoms added

In the case of sucrose, the automatic assignment of hydrogen as in §2.4.4.1 [p.11] and the assignment by changing Q peaks to hydrogens as in §2.4.4.2 [p.11] have been described. However, how to manually assign hydrogen atoms is described in this section.

'Tools' in Fig. 3.19 (a) and then 'Hydrogen Atoms' in Fig. 3.19 (b) can be clicked such as to display icons indicated by [1]-[7] on the bottom. These can be clicked to display the orange bands of '[1] Carbon of benzene ring', '[2] Carbon of ethylene group', '[3] Carbon of methine group', '[4] Carbon of methylene group', '[5] Carbon of methyl group', '[6] Oxygen of hydroxy ion' and '[7] Oxygen of hydroxy group' as shown in Fig. 3.20 [p.26] to assign them. [Esc] key can be clicked to escape from these modes.

In the next subsection, how to assign carbon of methine group, carbon of methylene group and oxygen of hydroxy group, are described.

3.8.1 Assignment of methine groups

Peaks of electron density due to hydrogens of methine groups have relatively large values since the parent atoms are supported by three atomic bonds like a tripod.

26 CHAPTER 3. EXAMPLE OF STRUCTURE DETEMINATION WITH THE OLEX² (α -CYCLODEXTER DETEMINATION WITH THE DETEMINAT

You are in <i>mode</i> MODE_DISP 43 Press the <u>ESC</u> key to exit.	[1]
You are in <i>mode</i> MODE_DISP 93 Press the <u>ESC</u> key to exit.	[2]
You are in <i>mode</i> MODE_DISP 13 Press the <u>ESC</u> key to exit.	[3]
You are in <i>mode</i> MODE_DISP 28 Press the <u>ESC</u> key to exit.	[4]
You are in <i>mode</i> MODE_DISP 137 Press the <u>ESC</u> key to exit.	[5]
You are in <i>mode</i> MODE_DISP 147 Press the <u>ESC</u> key to exit.	[6]
You are in <i>mode</i> MODE_DISP 83 Press the <u>ESC</u> key to exit.	[7]

Figure 3.20: [1]-[7] correspond to Fig. 3.19 [1]-[7].

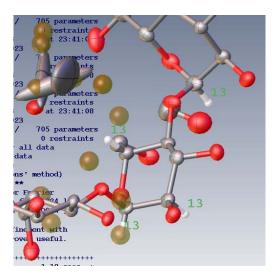


Figure 3.21: Methine groups have been assigned.

⁽³⁾ in Fig. 3.19 (b) [p.25] can be clicked to let the orange band of Fig. 3.20 [3] be displayed. Here, carbons of methine groups can be clicked to assign them such that green labels of '13' are displayed as shown in Fig. 3.21.

After clicking carbons of all methine groups to assign them, [Ctrl]+[R] can be typed about ten times to refine the structure to display Fig. 3.22. As shown on the upper right of Fig. 3.22 (a), the R-factor has decreased to 6.54%. On the lower right of Fig. 3.22 (b), Q peaks due to hydrogens of methylene groups are found.

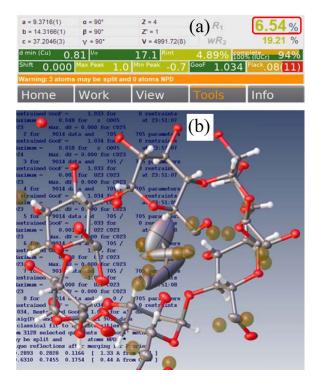


Figure 3.22: Refined result after methine groups assigned

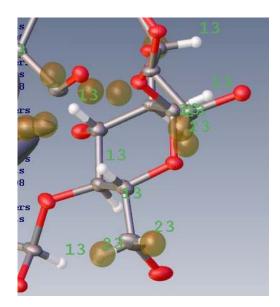


Figure 3.23: Methylene groups have been assigned.

3.8.2 Assignment of methylene groups

Methylene group has two hydrogens and two atomic bonds linked to non-hydrogen atoms.

In Fig. 3.23, the orange band of Fig. 3.20 [4] has been displayed by clicking Fig. 3.19 (b)

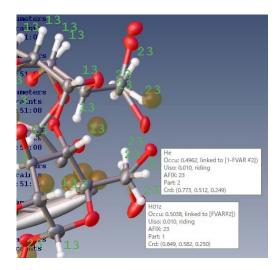


Figure 3.24: Hydrogens of disordered methylene group have been assigned.

[p.25] [4]. Here, carbons of methylene group have been clicked to assign them such that green labels '23' are displayed.

In Fig. 3.24, hydrogen atoms have been added to the disordered oxygens of methylene groups by clicking the parent atoms. Therefore, the carbons of the methylene groups have four hydrogens due to the disordered oxygens. By placing the mouse cursor on these hydrogens, labels can be shown as shown in Fig. 3.24 for several seconds. The same values of occupancy as the disordered oxygen have also been applied to these hydrogens.

After adding hydrogens to all methylene groups, the molecular structure can be refined about ten times by typing [Ctrl]+[R] or clicking 'Refine [3]' in Fig. 3.26 to show Fig. 3.25. As displayed on the upper right of Fig. 3.25 (a), the R-factor decreased to 6.08%. In Fig. 3.25 (b), hydrogens of hydroxy group and H₂O are found as Q peaks.

3.8.3 Assignment of hydroxy groups and H_2O

Hydrogens can be added to hydroxy groups (and H_2O) by replacing Q peaks with hydrogens more correctly than by clicking the icon of '[7]' in Fig. 3.19 (b) [p.25] to assign hydroxy groups since hydroxy groups and H_2O have high flexibility of rotation.

In Fig. 3.26, the refinement options have been

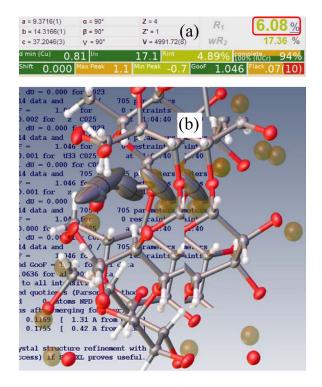


Figure 3.25: Refined with hydrogens of methine groups added

a = 9.3716(1)	a	= 90°		Z = 4			<u>п</u>	115 7	4 ~
b = 14.3166(1	l) β	= 90°		Z' = 1			R_1	1]5.7	%
c = 37.2046(3) V	= 90°		V = 49	91.72(8)	И	VR ₂	16.	37 %
d min (Cu)	0.81	I/σ	1	.7.1	Rint	4.8	9% 18	nplete 0% (IUCr)	94%
Shift 0.00	00 Max	Peak	1.0 ^M	in Peak	-0.7	GooF	1.043	Flack.0	8(11)
Warning: 3 at	oms ma	y be sp	lit and 0 ;	atoms	NPD				
Home	W		[2] \	liew	/	Тос	ols	Info	
Solve	\bullet	Ref	ine <mark>[3</mark>		Drav	N	• R	eport	\odot
O Program	ShelXL		✓ L.S.	[4]	~	Cycles	7 🔺	Peaks	20
🛈 hkl file	exp_663	.hkl			~	hkl :	Sun Dec 1	5 13:39:12	2019
🕜 Weight	.109	.110	2.24 2	.23 E	ті 🗆			ACTA	~
1 Use So	lvent Ma	sk T	his is the	Olex2 in	plement	ation of B	YPASS (a	.k.a. SQUEE	ZE)
Refine	ment S	Settin	gs Extr	а					
Toolbox	Work	[5]							
0 Lab [6]	Labels	OFF/ON							~
ОСН	0						Add H		9

Figure 3.26: Refinement with hydrogens of hydroxy groups and H₂O added

displayed by clicking 'Work [2]' and then ' \Downarrow [4]' on the right of 'Refine [3]'. The Q peaks that are considered to be hydrogens can be clicked to assign them to hydrogen after clicking 'Toolbox Work [5]' and then '[6] H' in Fig. 3.26.

After assigning all hydrogens to hydroxy groups or H_2O , the molecular structure can be

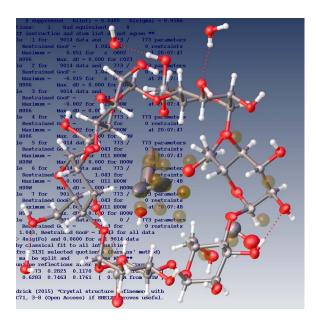


Figure 3.27: Refined with hydrogens of hydroxy groups and H_2O added

Home	Work	Ń	/iew	Tools	Info [1]
Recent Fi	les				
Electron [Density Pe	aks			
Refineme	nt Indicato	ors			
Bad Refle	ctions [2]				
6[3]оміт	all reflection	s where	Error/esd >	than 10	ClearOMITs
() Unsigned so	rting by Error/esd	l (refine t	o update)		
П Н	к	E		Error/esd	d/A
[5] 0	0	2		12.60	18.60 omitEdit
0	2	0	(a)	8.17	4.69 <u>omittai</u>
1	0	2 2	(a)	-6.51	8.37 <u>omitEdit</u>
1	4 0	2 5		6.28 -6.15	3.29 <u>omitEdit</u> 5.83 <u>omitEdit</u>
1	-	-		-0.15	5.65 <u>Unitedit</u>
Он	к	1		Error/esd	d/A
6	0	2		12.60	18.60 Omitted Edit
0	2	6	(1.)	8.17	4.69 <u>omit</u> Edit
1	0	2 2	(b)	-6.51	8.37 omit Edit
1	4	2	. /	6.28	3.29 <u>omit</u> <u>Edit</u>
1	0	5		-6.15	5.83 omit Edit

Figure 3.28: Omitting bad reflections

refined about ten times by typing [Ctrl]+[R] or clicking 'Refine [3]' in Fig. 3.26 [p.27] to show Fig. 3.27. The R-factor has decreased to '[1] 5.71%' as shown on the upper right of Fig. 3.26 [p.27]. This is the final molecular structure of α -cyclodextrin since further unfounded refinement should not be done.

Shift 0.000	Max Peak	1.0 Min Peak -0.7	Goof 1.0	52 Flack.08(11)
d min (Cu) 0.	81 ^{I/σ}	17.1 Rint	4.89%	180% (IUcr) 94%
c = 37.2046(3)	V = 90°	V = 4991.72(8)	WR ₂	16.00 %
b = 14.3166(1)	β = 90°	Z' = 1	741	
a = 9.3716(1)	α = 90°	Z = 4	R.	[1]5 71 o/

Figure 3.29: Result of refinement

a = 9.3716(1) b = 14.3166(1		Z = 4 Z' = 1		R ₁	[1]5.71	%
c = 37.2046(3		V = 49	91.72(8)	wR ₂	16.00	%
d min (Cu)	0.81 ^{1/σ}	17.1	Rint	4.89%	complete 100% (IUCr) 94	1%
Shift 0.00	00 Max Peak	1.0 Min Peak	-0.7	^{300F} 1.04	19 ^{Flack} .08(1	0)
Warning: 3 at	oms may be s	split and 0 atoms	NPD			
Home	Work	< [2] Viev	v	Tools	Info	
Solve	🕑 Re	fine[3] 💽	Draw	\odot	Report	٩
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🛈 hkl file	exp_663.hkl		~	hkl : Sun De	c 15 13:39:12 2019	

Figure 3.30: Result of refinement with the extinction effect taken into account

3.9 Omitting bad reflections

By clicking 'Info [1]' in Fig. 3.28 and then 'Bad Reflections [2]', reflection indices whose discrepancy in structure factor by calculation and observation can be summarized. In Figs. 3.28 (a), it is shown that reflection indices whose values of [Error/esd] is larger than '10 [4]' is '[5] 0 0 2 12.60'. '[3] OMIT' can be clicked to change 'omit' on the rightmost of '[5] 0 0 2 12.60' in Fig. 3.28 (a) to 'Omitted' on the rightmost of '[6] 0 0 2 12.60' in Fig. 3.28 (b).

Then, the structure has been refined by typing [Ctrl]+[R] about ten times to show Fig. 3.29. In this case, the R-factor '[1] 5.71%' has not been improved. However, this procedure is recommended to try since the R-factor can sometimes be improved by omitting bad reflections.

3.10 Consideration of extinction effect

In Fig. 3.30, 'Work [2]' and then ' \Downarrow [4]' on the right of 'Refine [3]' have been clicked to show the refinement options. '[5] EXTI' can be checked to do refinement with the extinction effect taken into account.

The extinction is a dynamical diffraction ef-

fect that the $h \ k \ l$ -reflected X-ray intensities do not increase linearly due to $\overline{h} \ \overline{k} \ \overline{l}$ reflection. Since the R-factor is sometimes improved by checking '[5] EXTI', it is recommended to try to refine the structure with '[5] EXTI' checked. However, '[5] EXTI' should be unchecked when the R-factor increases. In the case of Fig. 3.30 the R-factor '[1] 5.71%' has not been improved.

This is the end of refinement of the molecular

structure of α -cyclodextrin

3.11 Creation of the report

The report can be created similarly to the case of sucrose. Refer to the description in §2.5 [p.13], please.

Appendix A

Reasonability of defining the reciprocal lattice

For many students working on crystallography, the first difficulty is understanding of reciprocal lattice. In spite that the Bragg condition written by (A.1) or (A.2) can easily be understood, why such strange ideas as reciprocal lattice and reciprocal space should we use ? This chapter describes the equivalence of Bragg's reflection condition, Laue's reflection condition and Ewald construction (Reciprocal lattice node exists on the Ewald sphere), from which how reasonably the reciprocal lattice is defined can be understood.

Every space group of crystal has an extinction rule owing to its symmetry with which the crystal structure factor comes to be zero. However, it is neglected in the following description for simplicity.

A.1 Bragg's reflection condition

Figure A.1 shows Bragg's reflection condition. This figure is also found in high school text book. Bragg's reflection condition can relatively easily and intuitively referring to this figure. When atoms (or molecules) are arranged on a set of planes as shown in Fig. A.1. Optical path length of X-rays drawn as a gray line are longer than that drawn as a black line by $|\overrightarrow{ab}| + |\overrightarrow{bc}|$ (= $2d \sin \theta_B$). When this length is an integral multiplication of the wavelength, these rays interfere constructively with each other. Therefore, reflection condition can be described as follows,

$$2d\sin\theta_B = n\lambda. \tag{A.1}$$

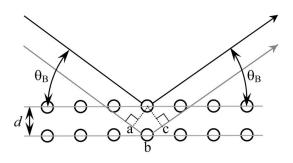


Figure A.1: Bragg's reflection condition.

By redefining lattice spacing d' to be d' = d/n, the following equation is also frequently used,

$$2d'\sin\theta_B = \lambda. \tag{A.2}$$

Now, let us consider why the angle of incidence and emergence is identical. Is it evident since the Bragg plane works as a mirror plane ? Then, why are the angles of incidence and emergence of a mirror identical ? Sometimes, even a veteran of crystallography cannot answer to this question.

A.2 Laue's reflection condition

Laue's reflection condition was used to explain the phenomenon of X-ray diffraction when it was invented by Laue (Max Theodor Felix von Laue; 1879/10/9-1960/4/24) in 1912, which is described referring to Fig. A.2 as follows,

$$R_0 B - A R_1$$

= $\overrightarrow{R_0 R_1} \cdot \mathbf{s}_1 - \overrightarrow{R_0 R_1} \cdot \mathbf{s}_0 = n_0 \lambda.$ (A.3)

Here, \mathbf{s}_0 and \mathbf{s}_1 are unit vectors in the direction of propagation of incident and reflected X-rays. When R_0 and R_1 are equivalent lattice points, difference in optical path length between black and gray paths drawn in Fig. A.2 is given by (A.3). When this difference in path length is an integral multiplication of wavelength, X-rays scattered by lattice points R_0 and R_1 interfere constructively with each other.

Incidentally, since R_0 and R_1 are equivalent lattice point, there is a restriction as follows,

$$\mathbf{R}_0 \mathbf{R}_1' = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, \qquad (\mathbf{A}.4)$$

where, n_1 , n_2 and n_3 are arbitrary integers. **a**, **b** and **c** are primitive translation vectors. That is to say the left hand side of (A.3) should be integral multiplication of wavelength for arbitrary integers n_1 , n_2 and n_3 . Lattice points R_0 and R_1 can move freely with a restriction that these are equivalent points. The value of left hand side of (A.3) is evidently positive when $\overrightarrow{R_0R_1} \cdot \mathbf{s}_1 > \overrightarrow{R_0R_1} \cdot \mathbf{s}_0$ and is negative when $\overrightarrow{R_0R_1} \cdot \mathbf{s}_1 < \overrightarrow{R_0R_1} \cdot \mathbf{s}_0$. Figure A.2 is drawn under an assumption of the latter case.

However, R_0 and R_1 can also be taken such that $\overrightarrow{R_0R_1} \cdot \mathbf{s}_1 = \overrightarrow{R_0R_1} \cdot \mathbf{s}_0$. In the following discussion in this paragraph, R_0 and R_1 are fixed such that $\overrightarrow{R_0R_1} \cdot \mathbf{s}_1 = \overrightarrow{R_0R_1} \cdot \mathbf{s}_0$. When R_0 , R_1 and optical paths drawn as black and gray lines are all on the drawing, there should be a plane perpendicular to the drawing that include those points and optical paths. When X-rays are scattered at any point on this plane under a condition that the angles of incidence and emergence are the same, the optical path length is always the same. This is also the reason for that the angle of incidence and emergence for a mirror is always identical.

In Bragg's reflection condition, under an implicit (the first and second dimensional) restriction that optical path length are always the same for a defined Bragg plane when the angle of incidence and emergence is identical, the third dimensional condition is given by (A.1) or (A.2). Behind the simple condition given by those equations, the above mentioned first and second dimensional restrictions are hidden.

Now, for description in the next section, the following equation is prepared by dividing the both sides of eq. (A.3) by the wavelength λ ,

$$\overrightarrow{\mathbf{R}_0 \mathbf{R}_1} \cdot \left(\frac{\mathbf{s}_1}{\lambda} - \frac{\mathbf{s}_0}{\lambda}\right) = n_0. \tag{A.5}$$

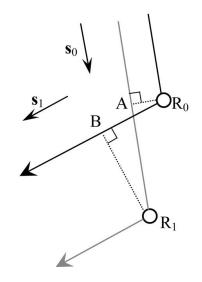


Figure A.2: Laue's reflection condition.

By substituting (A.4) into the above equation and considering that the wave vectors of incident and reflected X-rays are given by $\mathbf{K}_0 = \mathbf{s}_0 / \lambda$ and $\mathbf{K}_1 = \mathbf{s}_1 / \lambda$, the following equation can be obtained,

$$(n_1\mathbf{a} + n_1\mathbf{b} + n_1\mathbf{c}) \cdot (\mathbf{K}_1 - \mathbf{K}_0) = n_0.$$
 (A.6)

A.3 Ewald's reflection condition (Ewald construction)

A.3.1 Foundation of Ewald construction

Fig. A.3 [p.32] shows the situation that the origin O of reciprocal space and a reciprocal lattice node H_{hkl} simultaneously exist on the surface of Ewald sphere. Its center is the common initial point of wave vectors \mathbf{K}_0 and \mathbf{K}_1 .

In the description of Ewald construction, at first, reciprocal fundmental vectors \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* are defined as follows:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})},$$
 (A.7a)

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad (A.7b)$$

$$\mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}.$$
 (A.7c)

The denominator of (A.7), $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{b} \cdot (\mathbf{c} \times \mathbf{a}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$ is the volume of parallelepiped whose edges are \mathbf{a} , \mathbf{b} and \mathbf{c} . From

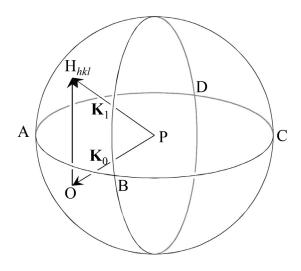


Figure A.3: Ewald sphere

the above definitions, the following equations are evident,

$$\mathbf{a} \cdot \mathbf{a}^* = 1, \qquad (A.8a)$$

$$\mathbf{b} \cdot \mathbf{b}^* = 1, \qquad (A.8b)$$

$$\mathbf{c} \cdot \mathbf{c}^* = 1. \tag{A.8c}$$

Further, $\mathbf{b} \times \mathbf{c}$ is a vector that is perpendicular to both **b** and **c** and has a length of the area of parallelogram whose sides are **b** and **c**. Here, vectors **b**, **c** and **b**×**c** construct a right-handed system. Since the above is the same for **c**×**a** and **a**×**b**, the following relations are also evident,

$$\mathbf{a} \cdot \mathbf{b}^* = \mathbf{a} \cdot \mathbf{c}^* = 0, \qquad (A.9a)$$

$$\mathbf{b} \cdot \mathbf{c}^* = \mathbf{b} \cdot \mathbf{a}^* = 0. \tag{A.9b}$$

$$\mathbf{c} \cdot \mathbf{a}^* = \mathbf{c} \cdot \mathbf{b}^* = 0. \tag{A.9c}$$

That is to say, \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* have been defined such that (A.8) and (A.9) are satisfied.

A reflection vector giving $h \ k \ l$ reflection is defined in general as follows:

$$\overrightarrow{\mathrm{OH}_{hkl}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*.$$
(A.10)

Here, O is the origin of reciprocal space. The Ewald sphere is a sphere whose center is P. The wave vector of the incident X-rays \mathbf{K}_0 is $\overrightarrow{\text{PO}}$. When a reciprocal lattice node \mathbf{H}_{hkl} exists on the surface of the Ewald sphere, reflected X-rays whose wave vector \mathbf{K}_1 is $\overrightarrow{\text{OH}_{hkl}}$ are excited. Then, the following equation is satisfied,

$$\mathbf{K}_{1} - \mathbf{K}_{0} = \overrightarrow{\mathrm{OH}_{hkl}}$$
$$= h\mathbf{a}^{*} + k\mathbf{b}^{*} + l\mathbf{c}^{*}. \qquad (A.11)$$

Let us calculate the left-hand side of (A.6) [p.31] by substituting (A.11) into the second term of the left-hand side of (A.6) [p.31] and considering (A.8) and (A.9) as follows:

$$(n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}) \cdot (\mathbf{K}_1 - \mathbf{K}_0)$$

= $(n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}) \cdot (h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*)$
(A.12)
= $n_z \mathbf{b} + n_z \mathbf{b} + n_z \mathbf{b}$

$$= n_x h + n_y k + n_z l. aga{A.13}$$

Since $n_xh + n_yk + n_zl$ is evidently an integer, Laue's reflection condition described by (A.3) [p.30], (A.5) [p.31] and (A.6) [p.31], is satisfied when the reciprocal lattice node H_{hkl} is on the surface of Ewald sphere. Therefore, Ewald's reflection condition is equivalent to Laue's reflection condition. Furthermore, Ewald's reflection condition is also equivalent to Bragg's reflection conditions, which is more clarified by the description in the next section A.3.2

Bragg's reflection condition can easily be understood by referring to Fig. A.1 [p.30]. Laue's reflection condition is more difficult than Bragg's reflection condition. However, it can also be understood by referring to Fig. A.2 [p.31]. The drawing of Fig. A.3 in reciprocal space was invented by Ewald. This way of drawing is extremely effective when considering various difficult problems in crystallography that cannot be understood by drawing figures as shown in Fig. A.1 [p.30] and /or Fig. A.2 [p.31]in real space. It is strongly recommended to use the Ewald construction by using Fig. A.3 by paying respect to Ewald (Paul Peter Ewald, $1888/1/23 \sim 1985/8/22$).

A.3.2 Relation between reciprocal lattice vector and Bragg reflection plane

Reciprocal lattice vector is a vector whose direction is perpendicular to the Bragg plane and length is 1/d', where d' is the lattice spacing of the Bragg plane. These are verified in the following paragraphs.

By considering $n_0 = n_x h + n_y k + n_z l$, (A.10) and (A.12)=(A.13), the following equation is obtained.

$$\overrightarrow{\text{OH}_{hkl}} \cdot (n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}) = n_0.$$
 (A.14)

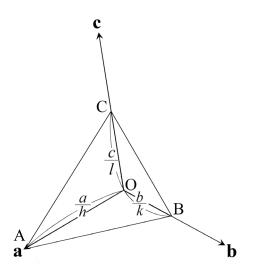


Figure A.4: Drawing of Miller and Miller indices

By multiplying $1/|\overrightarrow{OH_{hkl}}|$ to the both sides of the above equation, the following equation is obtained,

$$\frac{\overrightarrow{\mathrm{OH}_{hkl}}}{|\overrightarrow{\mathrm{OH}_{hkl}}|} \cdot (n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}) = \frac{n_0}{|\overrightarrow{\mathrm{OH}_{hkl}}|}.$$
(A.15)

A plane is described in general as follows:

Unit normal vector]
$$\cdot$$
 [Location vector]
= [Distance from the origin].
(A.16)

Therefore, $n_0 \in \{ \dots, -2, -1, 0, 1, 2, \dots \}$ in (A.15) means that location vector $n_x \mathbf{a} + n_y \mathbf{b} + n_z \mathbf{c}$ is on Bragg planes piled up with a spacing of $d'(=1/|\overrightarrow{OH_{hkl}}|)$, which reveals that the reciprocal lattice vector $\overrightarrow{OH_{hkl}}$ is the normal vector of Bragg plane whose length is 1/d'.

A.4 Drawing of Miller and Miller indices

Fig. A.4 shows the relation between the Miller indices and the Bragg plane and is found in almost all text books describing the crystallography. This way of drawing was invented by Miller (William Hallows Miller; 1801/4/6-1880/5/20). However, it should be noted that he was a mineralogist of the 19th century before X-rays and X-ray diffraction were invented. Figs. A.1[p.30] and A.4 are found in many text books. However, it cannot be recommended that the students and researchers attempt to understand the X-ray diffraction phenomena only by referring to Figs. A.1[p.30] and A.4.

Points A, B and C in Fig. A.4 exist on **a**, **b** and **c** axes, respectively. Distances of them from the origin O are a/h, b/k and c/l. Miller invented that **a**, **b** and **c** axes can be defined such that all facets of crystals are drawn as shown in Fig. A.4 with small integers h, k and l.

When h = 0, distance of A from O is inifinite and then the plane ABC is parallel to **a**. This is the case for k, B and **b** and for l, C and **c**.

h, k and l are indices of reciprocal lattice nodes, which was clarified several decades after Miller's invention. ABC is a plane whose direction is parallel to the Bragg plane and distance from O is d'. These are confirmed in the following description.

By referring to Fig. A.4, $\overrightarrow{AB} = -\mathbf{a}/h + \mathbf{b}/k$ and then $\overrightarrow{AB} \cdot \overrightarrow{OH}_{hkl}$ is calculated as follows:

$$\overrightarrow{AB} \cdot \overrightarrow{OH_{hkl}} = (-\mathbf{a}/h + \mathbf{a}/k) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$
$$= -1 + 1$$
$$= 0. \tag{A.17}$$

Therefore, line <u>AB</u> is confirmed to be perpendicular to $\overrightarrow{OH}_{hkl}$. Similarly, lines <u>BC</u> and CA are confirmed to be perpendicular to $\overrightarrow{OH}_{hkl}$. Further, from this, the distance of ABC from the origin O can be obtained from scalar product between the unit normal vector of plane ABC and vector \overrightarrow{OA} , \overrightarrow{OB} or \overrightarrow{OC} as follows:

$$\overrightarrow{OA} \cdot \overrightarrow{OH_{hkl}} / |\overrightarrow{OH_{hkl}}|$$

$$= \frac{\mathbf{a}}{h} (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) / |\overrightarrow{OH_{hkl}}|$$

$$= 1 / |\overrightarrow{OH_{hkl}}|$$

$$= d' \qquad (A.18)$$

As described above, the explanation of Fig. A.4 needs complex descriptions. It cannot be recommended to understand the phenomena of X-ray diffraction only referring to the drawing of Miller as shown in Fig. A.4.

Appendix B

Determination of space group from extinction rule

==> ge	eneral ref	lections	sorted	into	even/odd	parity	cla	asses

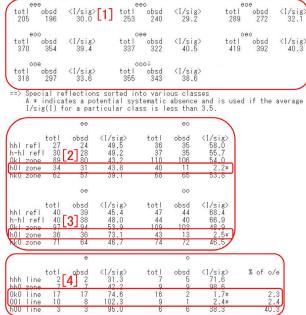


Figure B.1: Content of 'process.out' (#1). [7] [Taurine; monoclinic $P2_1/c(\#14)$].

One of the most important process in the crystal structure analysis is determination of space group. CrystalStructure 4.1 determines the space group automatically as sown in Fig. B.3.

In this chapter, how the computer determines the space group, is described. When the computer failed to determine the space group correctly, it should be determined manually referring to the description of this chapter.

Figs. B.1, B.2 and B.3 show contents of 'process.out' displayed by clicking 'View output file' button in Fig. 2.12 of Part2a manual. In this file, information about the extinction rule based

			l for iden [.] h. k. or	tifying /	in type c	ondition	5		
Okl zone hOl zone hKO zone	totl 106 37	1+b=4n obsd 102 20 66	<1/sig> 49.6 18.2 38.9	totl 299	⊦b not eq obsd 281 71 192	ual 4n <i sig=""> 50.1 30.8 48.8</i>			
0k0 line 001 zone h00 zone	totl 8 8 9 4 9 1	a=4n obsd 8 2 1	<1/sig> 77.5 60.2 91.3	tot 25 15 8	a not eq obsd 11 7 8	ual 4n <i sig=""> 28.2 54.3 41.4</i>			
htal ref	totl 34	32	<i sig=""> 47.5</i>	tot 116	⊦l not eq obsd 110	<i sig=""> 59.9</i>	J		
==> refl	h+l=3 totl		for iden (I/sig> (I/sig) 54.1] _{totl}		sig>	h+l totl	not ec obsd	qual 3n <i sig<br="">51.8</i>
h-h01	-h+l=3 totl 26	Bn;l eve obsd « 22	en (I/sig> 62.7	totl 49	-h+l=3n obsd <1/ 43 55	sig> .6	-h+l totl 102	not ec obsd 98	qual 3n <i sig<br="">56.7</i>
0001 lir	totl ne 7	l=3n obsd 2	<1/sig> 32.5	totl 12	l not eq obsd 7	ual 3n <1/sig> 67.7			
0001 lir	totl ne 2	l=6n obsd 2	<i sig=""> 185.7</i>	totl 17	l not eq obsd 7	ual 6n <i sig=""> 47.2</i>			

Figure B.2: Content of 'process.out' (#2). [Taurine; monoclinic $P2_1/c(\#14)$]

on which the space group can be determined, are summarized.

Information about extinctions of reflections whose three, two or one indices are not zero, are summarized on parts [1], [2, 3] and [4], respectively, of Fig. B.1. For example, 'eeo' found on the upper part of [1] in Fig. B.1 means that indices of hkl are even, even and odd. 'totl' and 'obsd' are numbers of total and observed reflections. $\langle I/sig \rangle$ are mean values of I/σ , where Iis observed intensity of reflected X-rays and σ is standard deviation of background. Since values of 'obsd' and $\langle I/sig \rangle$ are sufficiently large, there is no extinction for three nonzero hkl. On parts [2] and [3] in Fig. B.1, h0l reflections are

se about why '	Face-cent	ered mono	clinic' is a	added.	
Crystal system Laue group (No. of space group)	Axial distances (a, b, c) Axial angles (α, β, γ)	Primitive lattice (<i>P</i> , <i>R</i>)	Base-centered lattice (A, B, C)	Body-centered lattice (I)	Face-centered lattice (F)
Triclinic ī (#1,#2)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$				
Monoelinic 2/m (#3 ~#15)	$a \neq b \neq c$ two of α , β , γ = 90°, one \neq 90°	P A			
Orthorhombic mmm (#16~#74)	$a \neq b \neq c$ $\alpha = \beta = \gamma$ $= 90^{\circ}$	P			
Tetragonal 4/m(#75~#88), 4/mmm(#89~#142)	Two of <i>a</i> , <i>b</i> , <i>c</i> are the same. One of them is different. $\alpha = \beta = \gamma$ $= 90^{\circ}$	P P			
Trigonal $\overline{3}$ (#143 - #148), $\overline{3}m$ (#149 ~ #167)	$a = b = c$ $\alpha = \beta = \gamma$ $\neq 90^{\circ}$	P, R			
Hexagonal 6/m (#168 – #176) 6/mmm (#177 – #194)	a and b are the same. C is different. $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	P c 120° a			
Cubic $m\overline{3}$ (#195 ~# 206) $m\overline{3}m$ (# 207 ~# 230)	a = b = c, $\alpha = \beta = \gamma$ $= 90^{\circ}$				

Table B.1: 14 Bravais lattices and 'Face-centered monoclinic'. Refer to the last paragraph of §B.2 [p.37], please about why 'Face-centered monoclinic' is added.

o/e' are extremely small. In parts [5] and [6] in



Figure B.3: Content of 'process.out' (#3) [Taurine; monoclinic $P2_1/c(\#14)$]. [setting #1] corresponds to '[1] CELL CHOICE 1' in Fig. B.5.

recognized to distinguish since value of $\langle I/sig \rangle$ is extremely small when l is odd. This is indicated by an '*' mark. Similarly, in part [4] in Fig. B.1, 0k0 and 00l reflections are recognized to distinguish when k is odd and l is odd, respectively since values of $\langle I/sig \rangle$ and '% of

Reflection conditions General: h0l: l = 2n0k0: k = 2n00l: l = 2n

Figure B.4: Reflection condition of $P2_1/c(\#14)$ described in *International Tables* for Crystallography (2006) Vol.A. 0k0 reflections when k is odd and, hol and 00l reflections when l is odd, extinguish.

Fig. B.2, information about reflection indices when indices or summation of them are

nents absolute	ly.		a li li
Name of symmetric plane	Symbol	Graphic symbol (perpendicular to the space)	Graphic symbol (parallel to the space)
Mirror plane	т		
Axial glide plane	<i>a, b</i> or <i>c</i>	(Glide parallel to the space)	
Axial glide plane	<i>a, b</i> or <i>c</i>	(Glide perpendicular to the space)	
Double glide plane	е		Ţ,
Diagonal glide plane	п		r
Diamond glide plane	d	=:=:=:=	BELL

Table B.2: Symmetric elements (planes). Protein crystals do not have these symmetric elements absolutely.

divided by 4, by 3 and by 6, from which existence of four-, three- and six-fold screw axes can be discussed.

Fig. B.3 [p.35] shows that the space group of taurine crystal has been determined to be $P2_1/c(\#14)$.

Fig. B.4 shows reflection condition of $P2_1/c(\#14)$ described in *International Tables* for Crystallography (2006) Vol.A. The information described in Figs. B.1 [p.34] and B.2 [p.34] coincides with the condition in Fig. B.4 [p.35], from which the space group has been determined to be $P2_1/c(\#14)$.

In the following description, how the extinction of reflections are caused by symmetries of crystals depending on the space group, is explained.

B.1 Symmetric elements of crystal derived based on the group theory

Who showed the importance of group theory to determine the crystal structure for the first time was Shoji Nishikawa $(1884/12/5\sim1952/1/5)$. Wyckoff (R. W. G. Wyckoff; $1897/8/9\sim1994/11/3$)

		Graphic symbol	Graphic symbol
Symmetric axis or center	Symbol	(perpendicular to the	(parallel to the
		space)	space)
-	1		
Two-fold rotation axis	2	•	+
21 screw axis	21	ý	-
Three-fold rotation axis	3	A	
31 screw axis	31	À	
32 screw axis	32	A	
Four-fold rotation axis	4	*	t-
41 screw axis	41	*	F
42 screw axis	42	*	J⊢
43 screw axis	43	*	F
Six-fold rotation axis	6	٠	
61 screw axis	61	*	
62 screw axis	62	>	
63 screw axis	63	•	
64 screw axis	64	4	
65 screw axis	65	4	
Symmetry center	ī	0	
Three-fold rotatory inversion axis	3	۵	
Four-fold rotatory inversion axis	4	\$	<u>8</u> —
Six-fold rotatory inversion axis	6	۲	

Table B.3: Symmetric elements of crystal (axes and point).

who was strongly influenced by Nishikawa, systemized and established the space group theory that is widespread today and summarized in *International Tables for Crystallography* (2006) Vol.A.

As shown in Table B.1 [p.35], crystals are categorized into seven crystal systems depending on their shapes of unit cells. Further, there are several complex lattices whose backgrounds in Table B.1 [p.35] are green, other than primitive cells. Fourteen kinds of lattice except for 'bodycentered monoclinic lattice' are called Bravais lattice.

'Body-centered monoclinic lattice' was added by the present author's own judgment. The reason is that base-centered monoclinic lattice can sometimes change to body-centered lattice without changing the symmetry of monoclinic lattice or changing volume of unit cell by reselecting axes of unit cell.

In the first column of Table B.1 [p.35], Laue groups and ranges of space group number are summarized. Laue group is determined by symmetry of reciprocal lattice of crystals.

It has been clarified that crystals can be categorized into 230 space groups depending on the symmetric elements as shown in Tables. B.1 [p.35], B.2 and B.3.

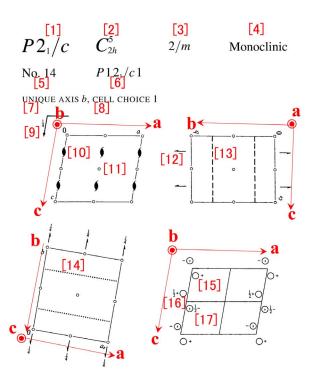
What is important to determine the space group is the extinction rule, about which the

Figure B.5: Drawings for space group $P2_1/c(\#14)$ in *International Tables for Crystal-lography* (2006) Vol.A. Protein crystals do not belong to this space group absolutely.

information can be extracted by referring to descriptions in 'process.out' as shown in Figs. B.1 [p.34] and B.2 [p.34]. It can be viewed by clicking 'View output file' button in Fig. 2.21 of Part 2a manual.

B.2 Symbols of space groups

Fig. B.5 is a diagram on the first two pages showing symmetric elements of crystal group $P12_1/c1$ in International Tables for Crystallography (2006) Vol.A, Chapter 7. Marks [1]-[17] are as follows; [1]: Hermann-Mouguin notation, [2]: Schönflies notation, [3]: Laue group, [4]: crystal system, [5]: ordinal number of space group, [6]: Hermann-Mouguin full notation, [7]: unique axis, [8]: cell choice, [9]: graphic symbol of c glide plane, [10]: graphic symbol of 2_1 screw axis, [11]: graphic symbol of symmetric center, [12]: graphic symbol of 2_1 screw axis, [13]: graphic symbol of c glide plane, [14]: graphic symbol of c glide plane, [15]: position of atom, [16]: position of atom (an image due to 2_1 screw axis), [17]: position of atom (an image



Name of lattice	Symbol	Reflection condition(not extinct)	Example
A base-centered	Α	hkl: k+l=2n	A 12/n1 (#15)
B base-centered	В	hkl: h+l=2n	B 2/n11 (#15)
C base-centered	С	hkl: h+k=2n	C 12/c1 (#15)
Body-centered	Ι	hkl: h+k+l=2n	I 2/b11 (#15)
Face-centered	F	hkl: h+k, h+l, k+l=2n	

 Table B.4:
 Extinctions owing to complex lat

Table B.5:Extinction rules owing to glideplanes.Protein crystals do not have glide planeabsolutely.

Name of glide plane	Normal	Reflection condition	Enomals
(Symbol)	to	(not extinct)	Example
Axial glide plane (a)	b	h0l: h=2n	P 12 ₁ /a1 (#14)
Axial glide plane (a)	c	hk0: h=2n	P 112 ₁ /a (#14)
Axial glide plane (b)	a	0kl: k = 2n	P21/b 11 (#14)
Axial glide plane (b)	c	hk0: k = 2n	P112 ₁ /b (#14)
Axial glide plane (c)	a	0kl: l = 2n	P21/c11 (#14)
Axial glide plane (c)	b	h0l: l = 2n	$\begin{array}{c} P \ 12_1/c1(\#14) \\ \hline C \ 12/c1 \ (\#15) \end{array}$
Double glide plane (e)	a	hkl: k+l=2n	
Double glide plane (e)	b	hkl: h+l=2n	
Double glide plane (e)	с	hkl: h+k=2n	
Diagonal glide plane (n)	a	0kl: k+l=2n	B 2/n11 (#15)
Diagonal glide plane (n)	b	h0l: h+l=2n	C 12/c1 (#15)
Diagonal glide plane (n)	c	hk0: h+k=2n	P 112 ₁ /n (#14)

due to c glide plane).

'[8] CELL CHOICE 1' corresponds to 'setting #1' in Fig. B.3 [p.35]. ' $\frac{1}{4}$ ' described near [9] is the height of c glide plane. About graphic symbols of c glide plane [9], [13] and [14], refer to Table B.2 [p.36], please. About graphic symbols of 2₁ screw axis [10] and [12], refer to Table B.3 [p.37]. Atoms at positions [16] and [17] are images of atom at [15] by symmetric operations due to 2₁ screw axis and c glide plane, respectively. ' $\frac{1}{2}$ +' near [16] and ' $\frac{1}{2}$ -' near [17] means that locations of atoms at [16] and [17] are $-x\mathbf{a} + (\frac{1}{2} + y)\mathbf{b} + (\frac{1}{2} - z)\mathbf{c}$ and $x\mathbf{a} + (\frac{1}{2} - y)\mathbf{b} + (\frac{1}{2} + z)\mathbf{c}$, respectively when that of [15] is $x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. Comma (,) in 'O' at [17] means that this atom (or molecule) is an enantiomer of those at [15] and [16].

Initial character of Hermann-Mouguin notation is P (or R partially for trigonal system) for primitive lattice, A, B or C for base-centered lattice, I for body-centered lattice or F for face-centered lattice. In many cases of basecentered lattice, C is mainly used for H-M notations. However, there are four exceptions,

Table D.(· ப	vonic	uon owing	00	BULCW	anco
Name of scr axis		irection	Reflection condit (not extinct)	tion	Exan	ple
21 screw ax	is	a	h00: h = 2n		P 212121	(#19)
2 ₁ screw ax	is	b	0k0: k=2n		$ \begin{array}{c} P \ 12_1 \ 1 \ (\\ P \ 12_1 / c \ 1 \\ C \ 12 / c \ 1 \\ P \ 2_1 2_1 2_1 \end{array} $	(#14) (#15)
21 screw ax	is	c	00l: l = 2n		P 212121	(#19)
31 screw ax	is	c	00l: l = 3n			
32 screw ax	is	c	00l: l = 3n			
41 screw ax	is	c	00l: l = 4n			
42 screw ax	is	c	00l: l = 2n			
43 screw ax	is	c	00l: l = 4n			
61 screw ax	is	c	00l: l = 6n			
62 screw ax	is	c	00l: l = 3n			
63 screw ax	is	c	00l: l = 2n			
64 screw ax	is	c	00l: l = 3n			
65 screw ax	is	c	00l: l = 6n			

Table B.6: Extinction owing to screw axes.

i.e. Amm2(#38), Abm2(#39), Ama2(#40)and Aba2(#41).

There are nine H-M full notations, i.e. $P12_1/c1$, $P12_1/n1$, $P12_1/a1$, $P112_1/a$, $P112_1/n$, $P112_1/b$, $P2_1/b11$, $P2_1/n11$, $P2_1/c11$ for $P2_1/c$ due to arbitrariness to take axes. There are plural H-M full notations for an H-M notation in general. In some cases, however, there is only one H-M full notation, e.g. $P2_12_12_1$ (orthorhombic #19) since it has an identical symmetric element all in the directions of a, b and c axes.

In the case of C2/c, one of H-M full notation is I12/a1 when changing the choice of unit cell axes. This is the reason for 'body-centered monoclinic lattice' is added in Table B.1 [p.35].

B.3 How to read extinction rules

In this section, how to determine the space group by reading 'process.out' as shown in Figs. B.1 [p.34] and B.2 [p.34] and comparing them with *International Tables for Crystallography* (2006) Vol.A, Chapter 3.1, is described. When the space group were determined not correctly, it should be redetermined referring to the following description.

Table B.7 shows a part of International Ta-

Table B.7: International Tables for Crystallography (2006) Vol.A, A part of International Tables for Crystallography (2006) Vol.A, Chapter 3.1. MONOCLINIC, Laue class 2/m

Unique axis b				Laue class 1 2/m 1			
Reflection condition				Point group			
hkl 0kl hk0	h0l h00 00l	0k0	Extinction symbol	2	т	2/m	
			P1-1	P121 (3)	P1m1 (6)	P1 2/m 1 (10)	
		k	P1211	P1211 (4)		P1 21/m 1 (11)	
	h		P1a1		P1a1 (7)	P1 2/a 1 (13)	
[1]	h	k	$P1 2_1/a 1$			$P1 2_1/a 1 (14)$	
	l		P1c1		P1c1 (7)	P1 2/c 1 (13)	
[2]	l	k	$P1 \ 2_1/c \ 1$			$P1 \ 2_1/c \ 1 \ (14)$	
	h+l		P1n1		P1n1(7)	P1 2/n 1 (13)	
[3]	h+l	k	$P1 \ 2_1/n \ 1$			$P1 \ 2_1/n \ 1 \ (14)$	
h + k	h	k	C1-1	C121 (5)	C1m1 (8)	C1 2/m 1 (12)	
h + k	h, l	k	Clc1		C1c1 (9)	C1 2/c 1 (15)	
k + l	l	k	A1-1	A121 (5)	A1m1 (8)	A1 2/m 1 (12)	
k + l	h, l	k	A1n1		A1n1 (9)	A1 2/n 1 (15)	
h + k + l	h + l	k	11-1	<i>I</i> 121 (5)	I1m1 (8)	<i>I</i> 1 2/ <i>m</i> 1 (12)	
h + k + l	h, l	k	<i>I</i> 1 <i>a</i> 1		I1a1 (9)	I12/a1(15)	

bles for Crystallography (2006) Vol.A, Chapter 3.1. Here, relations between the extinction rule and space group, are summarized. You can refer to pdf version of *International Tables for Crystallography* (2006) Vol.A, Chapter 3.1 that is placed on the desktop of computers.

In part [1] of Fig. B.1 [p.34] reflection conditions for hkl all of which are not zero, is described. Since no extinction can be found, the first column of Table B.7 should be empty. h+k, k+l and h+k+l in this column means that reflection indices that satisfies h+k=2n, k+l=2n and h+k+l=2n do not distinguish. In first, second and third column in Table B.7, '= 2n' is omitted.

In the case of Fig. B.1 [p.34], 0k0 and 00l reflections distinguish when k is odd and when l is odd, respectively, which corresponds to [1], [2] and [3] rows in Table B.7. Therefore, H-M full notation of the space group of taurine is $P12_1/a1$, $P12_1/c1$ or $P12_1/n1$. These all belong to $P2_1/c(\#14)$.

For redesignating space group in Crystal-Structure 4.1, 'Space Group' Menu window as shown in Fig. B.6 [p.39] can be opened by clicking 'Space Group' from 'Parameters' menu. Since b axis is usually taken as the main axis in the case of monoclinic crystal system, $P12_1/c1$ should be selected. Then, click 'Apply' and 'OK' in this order, please.

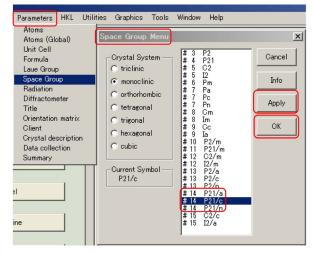


Figure B.6: Redesignation of space group in CrystalStructure 4.1. (in the case of small molecular-weight crystal).

B.4 Examples of extinction rules due to combinations of symmetric elements

In this section, several examples are described, in which the extinction rules are given by combinations of symmetric elements as summarized in Tables B.4 [p.38], B.5 [p.38] and B.6.

In cases of small molecular-weight organic crystals, frequently found space groups can be listed up in order of decreasing as follows, $P2_1/c(\#14)$, $P\overline{1}(\#2)$, C2/c(#15), $P2_12_12_1(\#19)$, $P2_1(\#4)$. As many as 80% of small molecular weight organic crystals are occupied by those with space groups that belong to the above five.

In the cases of protein crystals, however, Hermann-Morguin notations of their space group do not have symbols of $\overline{1}$ (symmetric center), m (mirror plane), a, b, c, d, e and n (glide planes) absolutely since they need both optical enantiomer molecules in spite that protein molecules consist of only L amino acids but not of D amino acids. (L and D amino acids are optical enantiomer with each other). Also in the cases of small molecularweight crystals, when they consist of chiral

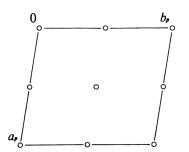


Figure B.7: Drawing for $P\overline{1}(\#2)$ in International Tables for Crystallography (2006) Vol.A. Since this space group has symmetric center, protein crystals do not belong to it. The phase problem is simple (0 or π (180°)).

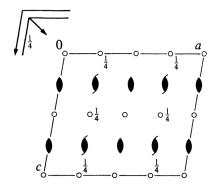


Figure B.8: Drawing for C12/c1[C2/c](#15) in International Tables for Crystallography (2006) Vol.A. Protein crystals do not belong to this space group absolutely since it has glide plane.

molecules, H-M notations of them do not have $\overline{1}$, m, a, b, c, d, e and n. In the cases of racemic crystals, these symbols are frequently included in their H-M notations.

Read the following description, please by referring Tables B.4 [p.38], B.5 [p.38] and B.6.

It can be read from Fig. B.5 [p.37] that space group $P2_1/c$ ($P12_1/c1$) has c glide plane and 2_1 screw axis in the direction of b. Reflection conditions due to these symmetric elements can be read from Tables B.5 [p.38] and B.6.

Reflection conditions are described in International Tables for Crystallography (2006) Vol.A dividing three cases in which one, two and three indices of hkl are not zero. Following this rule, the reflection conditions due to

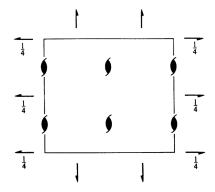


Figure B.9: International Tables for Crystallography (2006) Vol.A $P2_12_12_1(\#19)$.

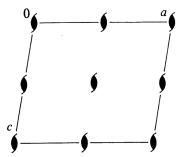


Figure B.10: International Tables for Crystallography (2006) Vol.A $P12_11[P2_1(#4)]$.

c glide plane and 2_1 screw axis are described as follows,

$$h0l:$$
 $l = 2n,$
 $0k0:$
 $k = 2n,$
 $00l:$
 $l = 2n.$

This is found as shown in Fig. B.4 [p.35] in *International Tables for Crystallography* (2006) Vol.A.

Symmetric element that space group $P\overline{1}(\#2)$ has, is only symmetric center. Therefore, there is no extinction. Protein crystals and chiral crystals do not belong to this space group, absolutely.

However, the phase problem is extremely simple (0 or π (180°)). Therefore, the molecular structure can be obtained frequently even for a crystal with low quality.

Since the initial character of C12/c1 is C, it is base-centered lattice. Since there are symmetric centers indicated by small open circles, the phase problem is very simple (0 or π (180°)). with high possibility.

Due to arbitrariness to take axes, there are three kinds of base-centered lattice, i.e. A basecentered, B base-centered and C base-centered lattice. However, let us focus the discussion on C base-centered lattice, here. The reflection condition shown in Table B.4 [p.38] can be written down dividing it into three cases in which one, two and three indices are not zero, as follows, [hkl: h+k=2n], [hk0: h+k=2n], [h0l: h = 2n], [0kl: k = 2n], [h00: h = 2n],[0k0: k=2n].

Referring to Fig. B.8[p.40], we can understand the existence of c glide plane, n glide plane and 2_1 screw axis that are perpendicular to **b** axis. The reflection condition due to c glide plane and n glide plane perpendicular to b axis can be read to be [h0l : h, l = 2n]. Further, that due to 2_1 screw axis can be read to be [0k0: k = 2n].

The logical product of the above conditions can be written down as follows,

hkl:	h+k=2n,
h0l:	h, l = 2n,
0kl:	k=2n,
hk0:	h+k=2n,
0k0:	k=2n,
h00:	h=2n,
00l:	l=2n.

B.4.1 Orthorhombic $P2_12_12_1(\#19)$

It is evident from Fig. B.9 that $P2_12_12_1(\#19)$ has 2_1 screw axes all in the directions of a, b and c axes. Therefore, referring to Table B.6 [p.38], the reflection condition is given as follows,

h00:	h = 2n,
0k0:	k=2n,
00l:	l=2n.

Monoclinic $P12_11[P2_1(#4)]$ B.4.2

There are three H-M full notations for space group $P2_1(\#4)$. Here, the description is given for $P12_11$.

Space group $P12_11$ has 2_1 screw axis as shown in Fig. B.10. Therefore, as described in Table

Then, the molecular structure can be solved B.6 [p.38], it has a reflection condition as follows.

$$0k0: \quad k=2n.$$

B.5Mathematical proofs of extinction rules

When the reader has time, refer to this chapter, please.

The extinction of reflection is caused by the existence of complex latticeC glide plane and screw axis whose background color is green in Tables B.1[p.35], B.2[p.36] and B.3[p.37]. To the contrary, only the above three symmetric elements give the extinction. However, protein crystals do not have glide plane absolutely. In this chapter, mathematical proofs of extinction due to the above symmetric elements are described.

For later description, let us note the definition of crystal structure factor, F_{hkl} for hkl reflection given as follows,

$$F_{hkl} = \int_{cell} \rho(\mathbf{r}) \exp[-i2\pi(\mathbf{h} \cdot \mathbf{r})] dv.$$

=
$$\int_{cell} \rho(\mathbf{r}) \exp[-i2\pi(hx + ky + lz)] dv.$$

(B.1)

Here, $\int_{cell} dv$ is a volume integral over a unit cell, $\rho(\mathbf{r})$ is electron density at location \mathbf{r} (= $x\mathbf{a}+y\mathbf{b}+z\mathbf{c})$, and $\mathbf{h} (= h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*)$ is a reciprocal lattice vector giving $h \ k \ l$ reflection. With regard to reciprocal lattice, refer to Appendix A [p.30], please.

Symmetry element that makes N equivalent points can be described as follows,

$$\rho[T^{(i)}(\mathbf{r})] = \rho[T^{(0)}(\mathbf{r})], \quad i \in \{0, 1, \cdots, N-1\}.$$

Since F_{hkl} is zero when the N integral elements,

$$\sum_{i=0}^{N-1} \rho[T^{(0)}(\mathbf{r})] \exp[-i2\pi \mathbf{h} \cdot T^{(i)}(\mathbf{r})] = 0$$

That is to say,

$$\sum_{i=0}^{N-1} \exp[-i2\pi \mathbf{h} \cdot T^{(i)}(\mathbf{r})] = 0$$
 (B.2)

B.5.1plex lattice

Table B.4 [p.38] summarizes the extinction rules due to complex lattice. In the following description, mathematical proofs for those due to base-centered, body-centered and face-centered lattice are given.

B.5.1.1 Extinction due to base-centered lattice

Symmetry of C base-centered lattice is described as follows,

$$\begin{split} \rho[T_C^{(i)}(\mathbf{r})] &= \rho[T_C^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}.\\ T_C^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_C^{(1)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} + (y + \frac{1}{2})\mathbf{b} + z\mathbf{c}. \end{split}$$

The extinction condition is described similarly to (B.2) as follows:

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_{C}^{(i)}(\mathbf{r})] = 0.$$
 (B.3)

Here, mathematical convenience to calculate \sum in (B.3), let us define $f_C(\mathbf{h}, \mathbf{r})$ as follows,

$$f_C(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi[h(x + \frac{1}{4}) + k(y + \frac{1}{4}) + lz]\}$$

Therefore, the extinction condition is described as follows,

$$f_C(\mathbf{h}, \mathbf{r})$$

$$\times \{ \exp[-i\frac{\pi}{2}(h+k)] + \exp[+i\frac{\pi}{2}(h+k)] \}$$

$$= 2f_C(\mathbf{h}, \mathbf{r}) \cos[\frac{\pi}{2}(h+k)] = 0.$$

Since $f_C(\mathbf{h}, \mathbf{r})$ is not zero in general, the extinction condition is given by

$$\cos[\frac{\pi}{2}(h+k)] = 0$$

Since the above equation is satisfied when h+kis odd, the reflection condition (not extinct) as shown in Table B.4 [p.38] is given by

$$hkl: @h+k=2n$$

Here, l is an arbitrary integer.

Reflection conditions for A and B basecentered lattice can be derived similarly to the above description.

Extinction rules due to com- B.5.1.2 Extinction due to body-centered lattice

Symmetry of body-centered lattice is described as follows,

$$\begin{split} \rho[T_I^{(i)}(\mathbf{r})] &= \rho[T_I^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}.\\ T_I^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_I^{(1)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} \\ &+ (y + \frac{1}{2})\mathbf{b} \\ &+ (z + \frac{1}{2})\mathbf{c}. \end{split}$$

The extinction condition is described similarly to (B.2) [p.41] as follows,

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_I^{(i)}(\mathbf{r})] = 0.$$
 (B.4)

For convenience for calculation of \sum in (B.4), let $f_I(\mathbf{h}, \mathbf{r})$ be defined as follows,

$$f_{I}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi [h(x + \frac{1}{4}) + k(y + \frac{1}{4}) + l(z + \frac{1}{4})]\}$$

Therefore, the extinction condition is given as follows.

$$f_I(\mathbf{h}, \mathbf{r}) \times \\ \{ \exp[-i\frac{\pi}{2}(h+k+l)] \\ + \exp[+i\frac{\pi}{2}(h+k+l)] \} \\ = 2f_I(\mathbf{h}, \mathbf{r}) \cos[\frac{\pi}{2}(h+k+l)] = 0.$$

Since $f_I(\mathbf{h}, \mathbf{r})$ is not zero in general, the extinction condition is given by

$$\cos\left[\frac{\pi}{2}(h+k+l)\right] = 0.$$

Since the above equation is satisfied when h +k+l is odd, the reflection condition (not extinct) as shown in Table B.4 [p.38], is given as follows,

$$hkl: \quad h+k+l=2n$$

B.5.1.3 Extinction due to face-centered lattice

Symmetry of face-centered lattice is described as follows,

$$\begin{split} \rho[T_F^{(i)}(\mathbf{r})] &= \rho[T_F^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2, 3\}.\\ T_F^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_F^{(1)}(\mathbf{r}) &= x\mathbf{a} + (y + \frac{1}{2})\mathbf{b} + (z + \frac{1}{2})\mathbf{c},\\ T_F^{(2)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} + y\mathbf{b} + (z + \frac{1}{2})\mathbf{c},\\ T_F^{(3)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} + (y + \frac{1}{2})\mathbf{b} + z\mathbf{c}. \end{split}$$

The extinction condition is described similarly to (B.2) [p.41] by the following equation,

$$\sum_{i=0}^{3} \exp[-i2\pi \mathbf{h} \cdot T_{F}^{(i)}(\mathbf{r})] = 0.$$
 (B.5)

Here, for mathematical convenience to calculate \sum in (B.5), let us define $f_F(\mathbf{h}, \mathbf{r})$ as follows,

$$f_F(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi [h(x + \frac{1}{4}) + k(y + \frac{1}{4}) + l(z + \frac{1}{4})]\}.$$

Therefore, the extinction condition is given as follows,

$$f_{F}(\mathbf{h}, \mathbf{r}) \{ \exp[-i\frac{\pi}{2}(-h-k-l)] + \exp[-i\frac{\pi}{2}(-h+k+l)] + \exp[-i\frac{\pi}{2}(+h-k+l)] + \exp[-i\frac{\pi}{2}(+h+k-l)] \}$$
(B.6)
$$= 2f_{F}(\mathbf{h}, \mathbf{r}) \{ \exp(+i\frac{\pi}{2}h) \cos[\frac{\pi}{2}(k+l)] + \exp(-i\frac{\pi}{2}h) \cos[\frac{\pi}{2}(k-l)] \} = 0.$$
(B.7)

Since $f_F(\mathbf{h}, \mathbf{r})$ is not zero in general, the extinction condition is represented as follows,

$$\cos[\frac{\pi}{2}(k+l)] = 0,\\ \cos[\frac{\pi}{2}(k-l)] = 0.$$

[(k + l is even) and (k - l is even)] is identical to [(both k and l are even) or (both k and l areod)] i.e. k + l = 2n. Here, h is an arbitrary integer. Since (B.6) is symmetrical for h, k and l, equations similar to (B.7) can be derived also for h + k, h - k and h + l, h - l. Then, The reflection condition (not distinguishing) as shown in Table B.4 [p.38] is given by

$$\begin{aligned} hkl : \quad h+k &= 2n, \\ hkl : \quad h+l &= 2n, \\ hkl : \quad l+k &= 2n. \end{aligned}$$

That is to say, reflection distinguishes when even and odd integers are mixed in h, k and l.

B.5.2 Extinction owing to glide axes

In cases of protein crystals, they do not have glide axis absolutely since they consist of only L amino acids but of not D amino acids (optical isomers of L amino acids).

B.5.2.1 Extinction due to axial glide plane

Symmetry due to c glide plane perpendicular to **b** axis whose height is $\frac{1}{4}$ **b**, is given by

$$\begin{split} \rho[T_{Bc}^{(i)}(\mathbf{r})] &= \rho[T_{Bc}^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}.\\ T_{Bc}^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_{Bc}^{(1)}(\mathbf{r}) &= x\mathbf{a} + (\frac{1}{2} - y)\mathbf{b} + (\frac{1}{2} + z)\mathbf{c}, \end{split}$$

Similarly to (B.2) [p.41], the extinction condition is given by

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_{Bc}^{(i)}(\mathbf{r})] = 0.$$
 (B.8)

Here, for mathematical convenience to calculate \sum in (B.8) [p.43], let us define $f_{Bc}(\mathbf{h}, \mathbf{r})$ as follows,

$$f_{Bc}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi[hx + k\frac{1}{4} + l(\frac{1}{4} + z)]\}.$$

$$\begin{split} f_{Bc}(\mathbf{h},\mathbf{r}) \times \\ & \left\{ \exp\{+i2\pi[k(\frac{1}{4}-y)+l\frac{1}{4}]\} \\ & +\exp\{-i2\pi[k(\frac{1}{4}-y)+l\frac{1}{4}]\} \right\} \\ & = 2f_{Bc}(\mathbf{h},\mathbf{r})\cos\{\frac{\pi}{2}[k(1-4y)+l]\} = 0. \end{split}$$

Since $f_F(\mathbf{h}, \mathbf{r})$ is not zero in general, reflections distinguish when the term of $\cos\{\}$ is zero, i.e. when h is arbitrary, k = 0 and l is odd, the reflection condition as shown in Table B.5 [p.38] is given by

$$h0l: l=2n$$

B.5.2.2 Extinction due to double glide plane (*e* glide plane)

Therefore, Symmetry due to double glide plane (*e* glide plane) whose height is zero, is described as follows,

$$\begin{split} \rho[T_{Be}^{(i)}(\mathbf{r})] &= \rho[T_{Be}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2, 3\}.\\ T_{Be}^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_{Be}^{(1)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} - y\mathbf{b} + z\mathbf{c},\\ T_{Be}^{(2)}(\mathbf{r}) &= x\mathbf{a} - y\mathbf{b} + (z + \frac{1}{2})\mathbf{c},\\ T_{Be}^{(3)}(\mathbf{r}) &= (x + \frac{1}{2})\mathbf{a} + y\mathbf{b} + (z + \frac{1}{2})\mathbf{c}, \end{split}$$

Similarly to (B.2) [p.41], the extinction rule is described by

$$\sum_{i=0}^{3} \exp[-i2\pi \mathbf{h} \cdot T_{Be}^{(i)}(\mathbf{r})] = 0.$$
 (B.9)

Here, for mathematical convinience to calculate \sum in (B.9), let us define $f_{Be}(\mathbf{h}, \mathbf{r})$ as follows,

$$f_{Be}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi[h(\frac{1}{4}+x) + l(\frac{1}{4}+z)]\}.$$

Therefore, the extinction condition can be described as follows,

$$\begin{aligned} f_{Be}(\mathbf{h}, \mathbf{r}) \times \\ & \left\{ \exp\{-i2\pi[-h\frac{1}{4} + ky - l\frac{1}{4}]\} \\ & + \exp\{-i2\pi[+h\frac{1}{4} - ky - l\frac{1}{4}]\} \\ & + \exp\{-i2\pi[-h\frac{1}{4} - ky + l\frac{1}{4}]\} \\ & + \exp\{-i2\pi[-h\frac{1}{4} - ky + l\frac{1}{4}]\} \\ & + \exp\{-i2\pi[+h\frac{1}{4} + ky + l\frac{1}{4}]\} \right\} \\ & = 2f_{Be}(\mathbf{h}, \mathbf{r}) \times \\ & \left\{ \exp(-i2\pi ky) \cos[\frac{\pi}{2}(h+l)] \\ & + \exp(+i2\pi ky) \cos[\frac{\pi}{2}(h-l)] \right\} = 0 \end{aligned}$$

Since $f_{Be}(\mathbf{h}, \mathbf{r})$ and $\exp(\pm i2\pi ky)$ are not zero in general, the above extinction condition is satisfied when $\cos[\frac{\pi}{2}(h+l)] = 0\cos[\frac{\pi}{2}(h-l)] = 0$. hkl reflections distinguishes when both h + land h - l are odd, i.e. when k is arbitrary and $[(\mathbf{h}, kareodd)or(h, k \text{ are even})]$. The reflection condition (not extinct) is given by

$$hkl: h+l=2n$$

With regard to other double glide planes, extinction rules as shown in Table B.5 [p.38] can be derived in a similar way.

B.5.2.3 Extinction due to diagonal glide plane

Symmetry due to diagonal glide plane (n glide plane) whose height is zero, is described as follows,

$$\begin{split} \rho[T_{Bn}^{(i)}(\mathbf{r})] &= \rho[T_{Bn}^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}.\\ T_{Bn}^{(0)}(\mathbf{r}) &= x\mathbf{a} + y\mathbf{b} + z\mathbf{c},\\ T_{Bn}^{(1)}(\mathbf{r}) &= (\frac{1}{2} + x)\mathbf{a} - y\mathbf{b} + (\frac{1}{2} + z)\mathbf{c}, \end{split}$$

The extinction condition is described similarly to (B.2) [p.41] as follows,

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_{Bn}^{(i)}(\mathbf{r})] = 0.$$
 (B.10)

Here, mathematical convenience to calculate \sum in (B.10), let us define $f_{Bn}(\mathbf{h}, \mathbf{r})$ as follows,

$$f_{Bn}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi[h(\frac{1}{4}+x)+l(\frac{1}{4}+z)]\}.$$

Therefore, the extinction condition is described as follows,

$$f_{Bn}(\mathbf{h}, \mathbf{r}) \times \left\{ \exp\{-i2\pi [-h\frac{1}{4} + ky - l\frac{1}{4}]\} + \exp\{-i2\pi [h\frac{1}{4} - ky + l\frac{1}{4}]\} \right\} \\ = 2f_{Bn}(\mathbf{h}, \mathbf{r}) \cos\{\frac{\pi}{2} [4ky - (h+l)]\} = 0.$$

Since $f_{Bn}(\mathbf{h}, \mathbf{r})$ is not zero in general, hkl reflections distinguish when the term of $\cos\{\}$ is zero. Therefore, the reflection condition (not extinct) is described as follows,

$$h0l: \quad h+l=2n$$

With regard to other orthogonal glide plane, reflection conditions as summarized in Table B.5 [p.38] can be derived.

B.5.3Extinction due to screw axes

Table B.6 [p.38] summarizes extinction rules due to p_q screw axes. Here $p \in \{2, 3, 4, 6\}$ and $q \in \{1, \cdots, p-1\}, p_q \text{ screw axis makes } p \text{ equiv-}$ alent points such that they translate by $q\mathbf{c}/p$, $(q\mathbf{a}/p \text{ or } q\mathbf{b}/p)$ when rotated by $2\pi/p$ around the axis. As summarized in Table B.6 [p.38], reflection condition [00l: l = 2n] is given by $2_1, 4_2$ and 6_3 screw axes since they make layers of atoms (molecules) whose spacing is c, (a or *b*).

Similarly, reflection conditions [000l:l =3n for $3_1, 3_2, 6_2, 6_4$ screw axes, [00l: l = 4n]for $4_1, 4_3$ screw axes and [000l: l = 6n] for 6_1 , 6₅screw axes can be derived. For mathematical proof of reflection conditions for three- and six-fold screw axes, refer to Appendix C [p.48], please.

In the following description, mathematical proofs of extinction rules due to 2_1 , 4_1 and 4_2 screw axes.

B.5.3.1 Extinction due to 2_1 screw axis

Symmetry of 2_1 screw axis in the direction of **c** located at $\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}$, is described as follows,

$$\rho[T_{2_1}^{(i)}(\mathbf{r})] = \rho[T_{2_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}.$$

$$T_{2_1}^{(0)}(\mathbf{r}) = (\frac{1}{2} + x)\mathbf{a} + (\frac{1}{2} + y)\mathbf{b} + z\mathbf{c},$$

$$T_{2_1}^{(1)}(\mathbf{r}) = (\frac{1}{2} - x)\mathbf{a} + (\frac{1}{2} - y)\mathbf{b} + (\frac{1}{2} + z)\mathbf{c}.$$

The extinction condition is described similarly to (B.2) [p.41] as follows,

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_{2_1}^{(i)}(\mathbf{r})] = 0.$$
 (B.11)

Here, for mathematical convinience to calculate \sum of (B.11), let us define $f_{2_1}(\mathbf{h}, \mathbf{r})$ as follows,

$$f_{2_1}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi [h\frac{1}{2} + k\frac{1}{2} + l(\frac{1}{4} + z)]\}.$$

Therefore, summation in (B.11) can be de- Therefore, summation in (B.12) can be deformed to give the following extinction condi-

tion,

$$f_{2_1}(\mathbf{h}, \mathbf{r}) \times \left\{ \exp\{-i2\pi [hx + ky - l\frac{1}{4}]\} + \exp\{-i2\pi [-hx - ky + l\frac{1}{4}]\} \right\}$$
$$= f_{2_1}(\mathbf{h}, \mathbf{r}) \times \cos\{\frac{\pi}{2} [4(hx + ky) - l]\} = 0.$$

Since term of $\cos\{ \}$ is zero when h, k = 0 and lis odd, the reflection condition (not extinct) is given by

$$00l: l = 2n.$$

Similarly, the reflection conditions due to c and a screw axes can be obtained as summarized in Table B.6 [p.38].

B.5.3.2 Extinction due to 4_1 screw axis

Symmetry due to 4_1 screw axis that is located at the origin, can be described as follows,

$$\begin{split} \rho[T_{4_1}^{(i)}(\mathbf{r})] &= \rho[T_{4_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2, 3\}.\\ T_{4_1}^{(0)}(\mathbf{r}) &= +x\mathbf{a} + y\mathbf{b} + \frac{1}{8}\mathbf{c},\\ T_{4_1}^{(1)}(\mathbf{r}) &= -y\mathbf{a} + x\mathbf{b} + \frac{3}{8}\mathbf{c},\\ T_{4_1}^{(2)}(\mathbf{r}) &= -x\mathbf{a} - y\mathbf{b} + \frac{5}{8}\mathbf{c},\\ T_{4_1}^{(3)}(\mathbf{r}) &= +y\mathbf{a} - x\mathbf{b} + \frac{7}{8}\mathbf{c}. \end{split}$$

Here, the extinction condition is described similarly to (B.2) [p.41] as follows,

$$\sum_{i=0}^{3} \exp[-i2\pi \mathbf{h} \cdot T_{4_1}^{(i)}(\mathbf{r})] = 0.$$
 (B.12)

Here, let us define $f_{4_1}(\mathbf{h}, \mathbf{r})$ as follows,

$$f_{4_1}(\mathbf{h}, \mathbf{r}) = \exp(-i2\pi l \frac{1}{2}).$$

tion,

$$f_{4_{1}}(\mathbf{h}, \mathbf{r}) \times \left\{ \exp[-i2\pi(+hx + ky - l\frac{3}{8})] + \exp[-i2\pi(-hy + kx - l\frac{1}{8})] + \exp[-i2\pi(-hx - ky + l\frac{1}{8})] + \exp[-i2\pi(-hx - ky + l\frac{3}{8})] \right\} = 2f_{4_{1}}(\mathbf{h}, \mathbf{r}) \times \left\{ \exp(+i2\pi l\frac{1}{8}) \cos\{\frac{\pi}{2}[4(hx + ky) - l]\} + \exp(-i2\pi l\frac{1}{8}) \cos\{\frac{\pi}{2}[4(hy - kx) + l]\} \right\} = 0.$$

When h, k = 0 and l is even, $\cos\{ \}$ in the first and second terms of the above equation have an identical value (1 or -1). Under an assumption that this condition is satisfied, let us discuss the condition that the above equation gives value of zero as follows,

$$\exp(-i2\pi l \frac{1}{8}) + \exp(-i2\pi l \frac{1}{8}) \\ = 2\cos(\frac{\pi}{2} \cdot \frac{l}{2}) = 0.$$

The above equation means that reflections distinguish when l/2 is odd. Therefore, the reflection condition (not extinct) can be described as follows,

$$00l: l = 4n$$

Similarly, reflection condition due to 4_3 screw axis can be obtained.

B.5.3.3 Extinction due to 4_2 screw axis

Symmetry due to 4_2 screw axis at the origin can be describes as follows,

$$\begin{split} \rho[T_{4_2}^{(i)}(\mathbf{r})] &= \rho[T_{4_2}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2, 3\} \\ T_{4_2}^{(0)}(\mathbf{r}) &= +x\mathbf{a} + y\mathbf{b} + \frac{1}{4}\mathbf{c}, \\ T_{4_2}^{(1)}(\mathbf{r}) &= -y\mathbf{a} + x\mathbf{b} + \frac{3}{4}\mathbf{c}, \\ T_{4_2}^{(2)}(\mathbf{r}) &= -x\mathbf{a} - y\mathbf{b} + \frac{1}{4}\mathbf{c}, \\ T_{4_2}^{(3)}(\mathbf{r}) &= +y\mathbf{a} - x\mathbf{b} + \frac{3}{4}\mathbf{c}. \end{split}$$

A point translates by $\frac{2}{4}$ **c** when rotating by $\frac{2\pi}{4}$ around the axis. Here, note that the heights of $T_{4_2}^{(2)}(\mathbf{r})$ and $T_{4_2}^{(3)}(\mathbf{r})$ are $\frac{5}{4}$ **c** and $\frac{7}{4}$ **c** which are equivalent to $\frac{1}{4}$ **c**, $\frac{3}{4}$ **c** due to translation symmetry of unit cell.

The, the extinction condition is described similarly to (B.2) [p.41] as follows,

$$\sum_{i=0}^{3} \exp[-i2\pi \mathbf{h} \cdot T_{4_2}^{(i)}] = 0.$$
 (B.13)

Here, for mathematical convenience to calculate \sum in (B.13), let $f_{4_2}(\mathbf{h}, \mathbf{r})$ be dfined as follows,

$$f_{4_2}(\mathbf{h}, \mathbf{r}) = \exp[-\mathrm{i}2\pi(l\frac{1}{2})].$$

 $f_{4_2}(\mathbf{h}, \mathbf{r})$ Therefore, deforming the \sum of (B.13), the extinction condition can be obtained as follows,

$$\begin{split} f_{4_2}(\mathbf{h},\mathbf{r}) \times \\ & \left\{ \exp[-\mathrm{i}2\pi(+hx+ky-l\frac{1}{4})] \right. \\ & \left. +\exp[-\mathrm{i}2\pi(-ky+hx+l\frac{1}{4})] \right. \\ & \left. +\exp[-\mathrm{i}2\pi(-hx-ky-l\frac{1}{4})] \right. \\ & \left. +\exp[-\mathrm{i}2\pi(+kx-hy+l\frac{1}{4})] \right\} \end{split}$$

$$= 2f_{4_2}(\mathbf{h}, \mathbf{r}) \times$$

$$\left\{ \exp(+i2\pi l \frac{1}{4}) \cos[2\pi (hx + ky)] + \exp(-i2\pi l \frac{1}{4}) \cos[2\pi (kx - hy)] \right\}$$

$$= 0.$$

The above extinction can be discussed when the content of cos[] is zero. Under the assumption that the above condition is satisfied, the above equation can be further deformed as follows,

$$\exp(-i2\pi l\frac{1}{4}) + \exp(+i2\pi l\frac{1}{4}) = 2\cos(\frac{\pi}{2}l) = 0.$$

Therefore, the reflection condition (not extinct) can be described as follows,

$$00l: \quad l=2n.$$

Reflection condition due to 6_3 screw axis is the same as the above description. With regard to this, refer to §C.2.5 [p.53] in Appendix C, please.

Appendix C

Reflection indeices and extinction rules in the cases of trigonal and hexagonal crystals

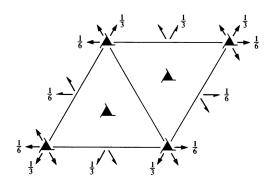


Figure C.1: International Tables for Crystallography (2006) Vol.A, Symmetric elements. $P3_121(\#152)$.

Read this chapter when the reader has time, please.

In cases of trigonal and hexagonal crystal system, reflection vectors are usually indexed by four integers, $h \ k \ i \ l(h + k + i = 0)$. This chapter describes the reasonableness of this way of indexing and the extinction rules due to threeand six-fold screw axes.

C.1 Cases of trigonal system

C.1.1 Diagram shown in International Tables for Crystallography (2006) Vol.A

Fig. C.1 is a diagram in *International Ta*- screw axis. About this, bles for Crystallography (2006) Vol.A that in \S C.1.4 [p.50], please.

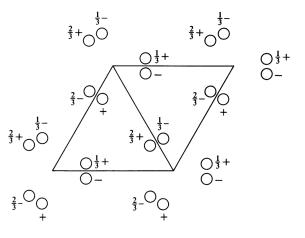


Figure C.2: International Tables for Crystallography (2006) Vol.A, Positions of atoms. $P3_121(\#152)$.

shows symmetric elements of space group $P3_121(\#152)$. Fig. C.2 shows atomic coordinates of $P3_121(\#152)$.

The unit cell is usually taken to be a rhombus that consists of two regular triangles as shown in Figs. C.1 and C.2. Space group $P3_121(\#152)$ has three-fold screw axis in the direction of **c** axis and two-fold screw axis perpendicular to **c** axis. However, in the case of trigonal system, there is no extinction due to the two-fold screw axis. About this, refer to the description in §C.1.4 [p.50], please.

C.1.2 Real and reciprocal coordinates

Fig. C.3 shows real and reciprocal primitive translation vectors in the cases of trigonal and hexagonal crystal system.

a, **b** and **c** axes are usually taken such that the angle spanned by **a** and **b** axes is 120° and **c** is parallel to three-fold rotation or screw axis. There are three way of taking **a** and **b** axes as shown in Fig. C.3 i.e. combinations of \mathbf{a}_0 and \mathbf{b}_0 axes, \mathbf{a}_1 and \mathbf{b}_1 axes and \mathbf{a}_2 and \mathbf{b}_2 axes.

reciprocal primitive vectors are defined as follows:

$$\mathbf{a}^* = rac{\mathbf{b} imes \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} imes \mathbf{c})},$$

 $\mathbf{b}^* = rac{\mathbf{c} imes \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} imes \mathbf{c})},$
 $\mathbf{c}^* = rac{\mathbf{a} imes \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} imes \mathbf{c})}.$

About the reasonableness of the above definition, refer to Appendix A [p.30], please.

By following the above definition, in Fig. C.3, real (black) and reciprocal (gray) primitive translation vectors are drawn. Referring to this figure, the following relations can easily be understood,

$$egin{aligned} \mathbf{a}_0^* &= -\mathbf{b}_1^* \ &= -\mathbf{a}_2^* + \mathbf{b}_2^* \ \mathbf{b}_0^* &= \mathbf{a}_1^* - \mathbf{b}_1^* \ &= -\mathbf{a}_2^*. \end{aligned}$$

From the above relations, reciprocal lattice vector $h\mathbf{a}_0^* + k\mathbf{b}_0^* + l\mathbf{c}^*$ can also be represented as follows:

$$h\mathbf{a}_0^* + k\mathbf{b}_0^* + l\mathbf{c}^*$$

= $k\mathbf{a}_1^* + i\mathbf{b}_1^* + l\mathbf{c}^*$
= $i\mathbf{a}_2^* + h\mathbf{b}_2^* + l\mathbf{c}^*$,
where, $h + k + i = 0$.

By using four indices h, k, i and l (h+k+i=0) to describe reflections, we can easily understand the equivalence of reflections due to three-fold symmetry. For example, a reflection described as 1 1 0 by using $\mathbf{a}_0^*-\mathbf{b}_0^*-\mathbf{c}^*$ coordinate system is equivalent to 1 $\overline{2}$ 0 by $\mathbf{a}_1^*-\mathbf{b}_1^*-\mathbf{c}^*$ system and also to $\overline{2}$ 1 0 by $\mathbf{a}_2^*-\mathbf{b}_2^*-\mathbf{c}^*$ system. This reflection 1 1 $\overline{2}$ 0 described using four indices can easily be understood to be equivalent to 1 $\overline{2}$ 1 0 and $\overline{2}$ 1 1 0.

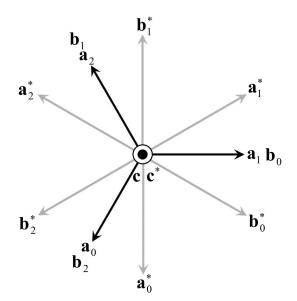


Figure C.3: Real (black) and reciprocal (gray) primitive translation vectors.

C.1.3 Derivation of extinction rule due to 3_1 screw axis

Similarly to the description in Appendix B §B.5 [p.41], the extinction due to 3_1 screw axis can be derived as follows.

Symmetry due to 3_1 screw axis at the origin is described as follows:

$$\rho[T_{3_1}^{(i)}(\mathbf{r})] = \rho[T_{3_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2\}.$$

$$T_{3_1}^{(0)}(\mathbf{r}) = x\mathbf{a}_0 + y\mathbf{b}_0 + z\mathbf{c},$$

$$T_{3_1}^{(1)}(\mathbf{r}) = x\mathbf{a}_1 + y\mathbf{b}_1 + (\frac{1}{3} + z)\mathbf{c},$$

$$T_{3_1}^{(2)}(\mathbf{r}) = x\mathbf{a}_2 + y\mathbf{b}_2 + (\frac{2}{3} + z)\mathbf{c}.$$
 (C.1)

On the other hand, referring to Fig. C.3, the following relations are evident.

$$a_1 = b_0,$$

 $b_1 = -a_0 - b_0,$
 $a_2 = -a_0 - b_0,$
 $b_2 = a_0,$

Substituting the above equation into (C.1),

$$\rho[T_{3_1}^{(i)}(\mathbf{r})] = \rho[T_{3_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2\}.$$

$$T_{3_1}^{(0)}(\mathbf{r}) = x\mathbf{a}_0 + y\mathbf{b}_0 + z\mathbf{c},$$

$$T_{3_1}^{(1)}(\mathbf{r}) = -y\mathbf{a}_0 + (x - y)\mathbf{b}_0 + (\frac{1}{3} + z)\mathbf{c},$$

$$T_{3_1}^{(2)}(\mathbf{r}) = (-x + y)\mathbf{a}_0 - x\mathbf{b}_0 + (\frac{2}{3} + z)\mathbf{c},$$

I

The extinction condition can be described similarly to (B.2) [p.41] as follows:

$$\sum_{i=0}^{2} \exp[-i2\pi \mathbf{h} \cdot T_{3_{1}}^{(i)}(\mathbf{r})] = 0.$$
 (C.2)

Here, for mathematical convenience to calculate \sum of (C.2), let us define $f_{3_1}(\mathbf{h}, \mathbf{r})$ as follows:

$$f_{3_1}(\mathbf{h}, \mathbf{r}) = \exp[-\mathrm{i}2\pi(lz)].$$

Therefore, (C.2) can be deformed as follows:

$$\begin{split} f_{3_1}(\mathbf{h},\mathbf{r}) \times \\ &\left\{ \exp\{-\mathrm{i}2\pi[hx+ky]\} \right. \\ &\left. + \exp\{-\mathrm{i}2\pi[-hy+k(x-y)+l\frac{1}{3}]\} \right. \\ &\left. + \exp\{-\mathrm{i}2\pi[+h(-x+y)-kx+l\frac{2}{3}]\} \right\} = 0. \end{split}$$

Since terms [hx + ky], [-hy + k(x - y)] and [h(-x+y)-kx] in exp{ } of the above equation depend on value of x and y, the extinction can be discussed only when h = k = i = 0. Under this condition, the extinction condition can be described as follows:

$$1 + \exp(-i2\pi l\frac{1}{3}) + \exp(-i2\pi l\frac{2}{3}) = 0.$$

The second and third terms of on the lefthand side of the above equation are 1 and 1 not giving extinction when l = 3n, $\exp(-i2\pi\frac{1}{3})$ and $\exp(-i2\pi\frac{2}{3})$ giving extinction and $\exp(-i2\pi\frac{2}{3})$ and $\exp(-i2\pi\frac{1}{3})$ giving extinction. Therefore, the reflection condition can be described as follows:

$$000l: \quad l=3n.$$

With similar consideration, the same reflection condition for 3_2 can be derived.

C.1.4 On the absence of extinction due to 2_1 screw axis perpendicular to c.

In Fig. C.1 [p.48], there are 2_1 screw axes perpendicular to **c** at positions of $x = \frac{1}{2}$ and $y = \frac{1}{2}$. However, these 2_1 screw axes cause no extinction. The reason is that the angle spanned by **a** and **a**^{*} and that spanned by **b** and **b**^{*} are not zero (not parallel). About this, refer to the following description, please.

Symmetric operation due to rotation around \mathbf{a}_0 is represented by movement of point on a plane perpendicular to \mathbf{a}_0 . Referring to Fig. C.3, reciprocal vectors perpendicular to \mathbf{a}_0 are \mathbf{c}_0^* and \mathbf{b}_0^* . A real vector parallel to \mathbf{b}_0^* is represented by a linear combination of \mathbf{a}_0 and \mathbf{b}_0 , as $\frac{1}{2}\mathbf{a}_0 + \mathbf{b}_0$. Therefore, Symmetry due to 2_1 screw axis in the direction of \mathbf{a}_0 located at $(y, z) = \frac{1}{2}, \frac{1}{3}$ is represented as follows:

$$\begin{split} p[T_{2_1}^{(i)}(\mathbf{r})] &= \rho[T_{2_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1\}, \\ T_{2_1}^{(0)}(\mathbf{r}) &= x \mathbf{a}_0 \\ &+ (\frac{1}{2} + y)(\frac{1}{2} \mathbf{a}_0 + \mathbf{b}_0) \\ &+ (\frac{1}{3} + z) \mathbf{c} \\ &= (x + \frac{1}{4} + \frac{1}{2} y) \mathbf{a}_0 \\ &+ (\frac{1}{2} + y) \mathbf{b}_0 \\ &+ (\frac{1}{3} + z) \mathbf{c}, \\ T_{2_1}^{(1)}(\mathbf{r}) &= (\frac{1}{2} + x) \mathbf{a}_0 \\ &+ (\frac{1}{2} - y)(\frac{1}{2} \mathbf{a}_0 + \mathbf{b}_0) \\ &+ (\frac{1}{3} - z) \mathbf{c} \\ &= (x + \frac{3}{4} - \frac{1}{2} y) \mathbf{a}_0 \\ &+ (\frac{1}{2} - y) \mathbf{b}_0 \\ &+ (\frac{1}{3} - z) \mathbf{c}. \end{split}$$

The extinction condition (while not existing) is represented similarly to (B.2) [p.41] as follows:

$$\sum_{i=0}^{1} \exp[-i2\pi \mathbf{h} \cdot T_{2_1}^{(i)}(\mathbf{r})] = 0.$$
 (C.3)

Here, for mathematical convenience to calculate \sum of (C.3), let us define $f_{2_1}(\mathbf{h}, \mathbf{r})$ as follows:

$$f_{2_1}(\mathbf{h}, \mathbf{r}) = \exp\{-i2\pi \left[h(\frac{1}{2} + x) + k\frac{1}{2} + l\frac{1}{3}\right]\}.$$

Therefore, \sum of (C.3) can be deformed as fol-

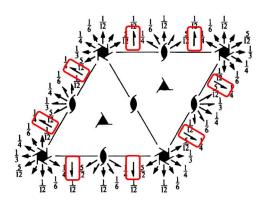


Figure C.4: International Tables for Crystallography (2006) Vol.A, Symmetric elements. $P6_{1}22(\#178).$

lows:

$$f_{2_1}(\mathbf{h}, \mathbf{r}) \times \left\{ \exp\{-i2\pi [h(\frac{1}{4} - \frac{1}{2}y) - ky - lz]\} + \exp\{-i2\pi [-h(\frac{1}{4} - \frac{1}{2}y) + ky + lz]\} \right\}$$

= $f_{2_1}(\mathbf{h}, \mathbf{r}) \times \cos\{2\pi [h(\frac{1}{4} - \frac{1}{2}y) - ky - lz]\} = 0.$

The above equation reveals that there is no extinction due to 2_1 screw axis perpendicular to \mathbf{c} since terms of h, k and l all depend to values of y or z. The second term $-h\frac{1}{2}y$ in $\cos\{ \}$ of the above equation exists since \mathbf{a}_0 is not parallel to \mathbf{a}_0^* . If there were a reciprocal primitive vector parallel to the screw axis, we can discuss the extinction under the condition that k, l = 0. When there is no reciprocal primitive vector parallel to the screw axis, there is no extinction due to it.

In a similar way, it can be verified that there is no extinction due to screw axes parallel to \mathbf{b}_0 or $a_0 + b_0$.

C.2Case of hexagonal system

C.2.1 Figure shown in International Tables for Crystallography (2006) Vol.A

Fig. C.4 is a drawing for space group By using the above coordinates, positions that

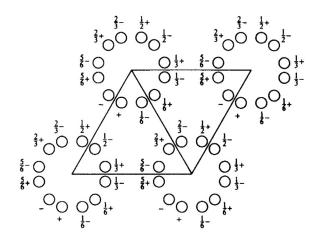


Figure C.5: International Tables for Crystallography (2006) Vol.A, Positions of atoms. $P6_{1}22(\#178).$

tallography (2006) Vol.A that shows symmetric elements. Fig. C.5 shows coordinates of atoms.

The unit cell is usually taken similarly to that in the case of trigonal system as shown in Fig. C.1 [p.48] and C.2 [p.48]. There are 2_1 screw axes perpendicular to c. However they do not cause extinction similarly to the case of trigonal system.

C.2.2Coordinates for describing sixfold screw axes

For describing positions of atoms that are rotated by $\frac{i}{6}2\pi$ ($i \in \{0, 1, 2, 3, 4, 5\}$) from the original position, let us prepare combinations of \mathbf{a}_i and \mathbf{b}_i as follows:

\mathbf{a}_i	\mathbf{b}_i	i
\mathbf{a}_0	\mathbf{b}_0	0
$\mathbf{a}_0 + \mathbf{b}_0$	$-\mathbf{a}_0$	1
\mathbf{b}_0	$-\mathbf{a}_0 - \mathbf{b}_0$	2
$-\mathbf{a}_0$	$-\mathbf{b}_0$	3
$-\mathbf{a}_0 - \mathbf{b}_0$	\mathbf{a}_0	4
$-\mathbf{b}_0$	$\mathbf{a}_0 + \mathbf{b}_0$	5

 $P6_{1}22(\#178)$ in International Tables for Crys- is rotated by $\frac{i}{6}2\pi$ $(i \in \{0, 1, 2, 3, 4, 5\})$ from the

original position can be written as follows:

From (C.4), the extinction condition is obtained as follows:

$$\begin{array}{ll} x_0 = x, & y_0 = y, \\ x_1 = x - y, & y_1 = x, \\ x_2 = -y, & y_2 = x - y, \\ x_3 = -x, & y_3 = -y, \\ x_4 = -x + y, & y_4 = -x, \\ x_5 = y, & y_5 = -x + y. \end{array}$$

a. — a.

C.2.3 Derivation of extinction rule due to 6_1 screw axis

origin in the direction of **c**, is described as follows:

$$f_{6_{1}}(\mathbf{h}, \mathbf{r}) \times \\ \left\{ \exp\{-i2\pi[hx + ky]\} \right\} \\ + \exp\{-i2\pi[h(x - y) + kx + l\frac{1}{6}]\} \\ + \exp\{-i2\pi[-hy + k(x - y) + l\frac{2}{6}]\} \\ + \exp\{-i2\pi[-hx - ky + l\frac{3}{6}]\} \\ + \exp\{-i2\pi[h(-x + y) - kx + l\frac{4}{6}]\} \\ + \exp\{-i2\pi[hy + k(-x + y) + l\frac{5}{6}]\} \right\} = 0.$$

Symmetry due to 6_1 screw axis located at the The extinction can be discussed only when h =k = i = 0. Under this condition, the above extinction condition can be described as follows:

$$\begin{split} \rho[T_{6_1}^{(i)}(\mathbf{r})] &= \rho[T_{6_1}^{(0)}(\mathbf{r})], \quad i \in \{0, 1, 2, 3, 4, 5\}.\\ T_{6_1}^{(0)}(\mathbf{r}) &= x\mathbf{a}_0 + y\mathbf{b}_0 + z\mathbf{c},\\ T_{6_1}^{(1)}(\mathbf{r}) &= (x - y)\mathbf{a}_0 + x\mathbf{b}_0 + (\frac{1}{6} + z)\mathbf{c},\\ T_{6_1}^{(2)}(\mathbf{r}) &= -y\mathbf{a}_0 + (x - y)\mathbf{b}_0 + (\frac{2}{6} + z)\mathbf{c},\\ T_{6_1}^{(3)}(\mathbf{r}) &= -x\mathbf{a}_0 - y\mathbf{b}_0 + (\frac{3}{6} + z)\mathbf{c},\\ T_{6_1}^{(4)}(\mathbf{r}) &= (-x + y)\mathbf{a}_0 - x\mathbf{b}_0 + (\frac{4}{6} + z)\mathbf{c},\\ T_{6_1}^{(5)}(\mathbf{r}) &= y\mathbf{a}_0 + (-x + y)\mathbf{b}_0 + (\frac{5}{6} + z)\mathbf{c}. \end{split}$$

Similarly to (B.2) [p.41], the extinction condition is described as follows:

$$\sum_{i=0}^{5} \exp[-i2\pi \mathbf{h} \cdot T_{6_1}^{(i)}(\mathbf{r})] = 0.$$
 (C.4)

For mathematical convenience, let us define $f_{6_1}(\mathbf{h}, \mathbf{r})$ as follows:

$$f_{6_1}(\mathbf{h}, \mathbf{r}) = \exp[-\mathrm{i}2\pi(lz)].$$

$$1 + \exp(-i2\pi l \frac{1}{6}) + \exp(-i2\pi l \frac{2}{6}) + \exp(-i2\pi l \frac{3}{6}) + \exp(-i2\pi l \frac{4}{6}) + \exp(-i2\pi l \frac{4}{6}) + \exp(-i2\pi l \frac{5}{6}) = 0.$$
 (C.5)

When l = 6n, reflections do not distinguish. When l = 6n + i $(i \in \{1, 2, 3, 4, 5\})$, reflections distinguish since phase interval of the six term is an identical value $-2\pi \frac{i}{6}$. The reflection condition (not extinct) can be described a follows,

$$hkil: l = 6n.$$

Similarly, the same reflection condition can be derived also for 6_1 screw axis.

In Fig. C.4, 2_1 and 3_1 screw axes in the direction of \mathbf{c} are found. However, the logical product of reflection conditions due to 6_1 , 2_1 and 3_1 screw axes gives the same reflection condition as described in the above equation.

C.2.4 **Derivation of the extinction** can be derived for 6_4 screw axis. due to 6_2 screw axis

The extinction condition due to 6_2 screw axis is given similarly to (C.5) [p.52] as follows:

$$1 + \exp(-i2\pi l \frac{1}{3}) + \exp(-i2\pi l \frac{2}{3}) + 1 + \exp(-i2\pi l \frac{1}{3}) + \exp(-i2\pi l \frac{1}{3}) + \exp(-i2\pi l \frac{2}{3}) = 0$$

When l = 3n, reflections do not distinguish since the six term have an identical value unity. When l = 3n + i $(i \in \{1, 2\})$, reflections distinguish since phase interval of the six term is an identical value $-2\pi \frac{i}{3}$. Then, the reflection condition (not extinct) is given by

$$hkil: l = 3n$$

In a similar way, the same reflection condition

C.2.5Derivation of extinction rule due to 6_3 screw axis

An equation for 6_3 screw axis that corresponds to (C.5) [p.52] is given by

$$1$$

$$+ \exp(-i2\pi l\frac{1}{2})$$

$$+1$$

$$+ \exp(-i2\pi l\frac{1}{2})$$

$$+1$$

$$+ \exp(-i2\pi l\frac{1}{2}) = 0.$$

When l is even, all terms are unity giving no extinction. When l is odd, reflections distinguish since phase interval of the six terms is an identical value $-2\pi \frac{1}{2}$ giving extinction. Therefore, the reflection condition (not extinct) is given by

$$hkil: l = 2n.$$

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