clude any physically relevant Shubnikov groups. The 28 non-crystallographic Shubnikov groups discussed above are listed in Table 2.

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High-Resolution Monochromatization of Neutrons by Multiple Bragg Reflection in Hexagonal Close-Packed Crystals*

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(*Received* 2 *October* 1968)

The conditions which give high-resolution monochromatization of neutrons by multiple Bragg reflection in hexagonal close-packed crystals have been studied theoretically. The role of reflections forbidden by special atomic positions has been clarified, and, contrary to a previous conclusion, it is found that these 'forbidden' reflections may be useful for high-resolution purposes. Detailed calculations of the necessary crystal orientations have been carried out for beryllium, magnesium and zinc. On the basis of somewhat arbitrary criteria the calculations show that these crystals can reflect a total of approximately 200 wavelengths in the range 0·7 to 4·9 Å (neutron energy 0·003 to 0·17 eV). Several orientations have been found at which *mosaic* crystals (with a sacrifice of angular resolution) should produce beams that are both intense and highly monochromatic.

Introduction

In a previous paper (hereinafter referred to as part I) it was pointed out that under suitable conditions in certain types of perfect crystals the phenomenon of multiple Bragg reflection (MBR) can provide highly monochromatic and highly collimated (semiparallel) beams of neutrons and X-rays at fixed wavelengths (Kottwitz, 1968*a*). The effect depends on the simulation of a forbidden (primary) reflection by the cooperative action of two allowed reflections (secondary and tertiary); this is the 'Umweganregung' phenomenon (Renninger, 1937). For each such simulation the reflected wavelength has a second-order extremum at a definite orientation (referred to in part I as the 'operating point') of the incident beam relative to the crystal. At such operating points even quite coarse external collimation can produce extremely high wavelength and angular resolution *provided* there is no 'interference', that is, provided no other simulation is close enough to make an impure contribution. Exploratory intensity measurements have been reported (Kottwitz, 1968*b*).

The main purpose of this paper is to present and discuss calculations of interference-free operating points for three hexagonal close-packed crystals: beryllium, magnesium and zinc. In contrast with the cubic diamond structure, for which the operating points are independent of lattice parameters, the h.c.p. structure permits various c/a ratios and thus requires separate calculations for each crystal. These particular crystals were chosen because they are suitable monochromators for neutrons (Bacon, 1962).

The general equations, nomenclature and conventions that provide the basis for this paper are identical with those in part I, and will be at most briefly described here. Attention will be concentrated on characteristics particularly relevant to the h.c.p. case.

Forbidden reflections in h.c.p. crystals

The h.c.p. structure (space group $P6_3/mmc$) has some reflections that are strictly forbidden by space-group symmetry; they are given by $hh\bar{2}hl$ with l odd. Calculations of operating points have been done for 0001, 0003, 0005, $11\bar{2}1$, $11\bar{2}3$ and $22\bar{4}1$. These are the preeminent candidates for use in high-resolution monochromatization by MBR.

The h.c.p. structure also has reflections that are only approximately 'forbidden' by special atomic positions; these are given by $hkil$ with l odd and $h-k=3n\neq 0$. They are represented in our calculations by $30\bar{3}1$, $30\bar{3}3$

* Work performed under U.S.A.E.C. Contract AT (45-1)-1830.

and $41\bar{5}1$. Furthermore at sufficiently low temperatures the operating points for these reflections probably are useful for high-resolution monochromatization of neutrons.

Since the last remark is contrary to the conclusion reached in § 5 of part I, it is necessary to clarify this point. It is customary to specify special positions for spherical scattering centers (*International Tables for X-ray Crystallography*, 1952). However, the condition of full spherical symmetry, while sufficient, is not *necessary* to nullify a reflection. Thus some of the special positions may be effective for less symmetrical scattering centers. This is so for the h.c.p. structure, since the elementary structure-factor calculation (Guinier, 1952) remains valid for all the 'forbidden' reflections when spheres are replaced by ellipsoids of revolution having axes parallel to the c axis. Now the nuclear 'cloud' in h.c.p. crystals has just this shape in the harmonic approximation, that is, at sufficiently low temperatures. The approximately 'forbidden' reflections may then become truly forbidden, thus making possible high-resolution monochromatization of neutrons by MBR. The electronic distribution, being more sensitive to the crystal structure, is likely to have an irregular shape; thus high-resolution monochromatization of X-rays by these approximately 'forbidden' reflections would not be possible. Similarly, at high temperatures the nuclear 'cloud', responding to the crystal structure, is not ellipsoidal, and high-resolution monochromatization of neutrons is no longer possible. In fact such weak 'forbidden' reflections are particularly useful in studying the spatial aspects of anharmonicity by neutron diffraction (Dawson & Willis, 1967).

Calculations for h. c. p. crystals

The calculations for Be, Mg and Zn were done on a UNIVAC 1108 computer with the FORTRAN V program *DBSKH2*. The program has essentially the same basic structure as that used in Part I for diamond-structure crystals. The only significant change was to add the calculation of θ_2 and θ_3, the Bragg angles (at the operating point) of the secondary and tertiary reflections, respectively. In the notation of Part I these quantities are given by

$$\tan\theta_2 = R/|\mathbf{K}_1 \,.\, \mathbf{K}_3| \qquad (1a)$$

$$\tan\theta_3 = R/|\mathbf{K}_1 \,.\, \mathbf{K}_2| \,. \qquad (1b)$$

They are related to the primary Bragg angle θ_p by

$$\theta_p = |\theta_2 - \theta_3| \,, \qquad (2a)$$

or

$$\theta_p = \text{smaller of } (\theta_2+\theta_3) \text{ and } (180^\circ - \theta_2 - \theta_3) \,, \qquad (2b)$$

the former equation applying when the senses of the secondary and tertiary reflections are opposite (parallel case) and the latter when they are similar (antiparallel case). The Bragg angles θ_2 and θ_3 provide useful semi-quantitative information about the resolution of a simulated reflection.

The physical constants used in the calculations had the 1963 IUPAP values as follows: Planck's constant = $6{\cdot}6256\times10^{-34}$ J-sec, neutron mass = $1{\cdot}67482\times10^{-27}$ kg and electron charge = $-1{\cdot}60210\times10^{-19}$ C (*Physics Today*, 1964). Lattice parameters were taken from the recent compilation by Pearson (1967); they are shown in Table 1. It is interesting to note that these values of c/a accidentally cover the range of physical interest fairly well; Be has the smallest observed ratio, Zn has a value within 2% of the largest observed (Cd), while Mg has a value within 1% of that for close packing of spheres (1·6330).

Table 1. *Lattice parameters used in calculations*

Crystal	a (Å)	c (Å)	c/a
Be	2·286	3·584	1·568
Mg	3·2094	5·2105	1·6235
Zn	2·6649	4·9468	1·8563

A summary of some of the important input parameters and results for each simulated reflection is given in Table 2. The parameters $\alpha_{\min}$, $\alpha_{\max}$, $\theta_{\min}$, and $\theta_{\max}$, which specify the (α,θ)-rectangle to be scanned for operating points, were chosen as follows. The largest range of α ever required is 180°; however, if $\mathbf{K}_1$ is parallel to a symmetry axis or a symmetry plane, the necessary range of α may be reduced considerably.

Table 2. *Summary of input parameters and results for simulated h.c.p. reflections*

Column 2 gives the direct lattice vector that is perpendicular to the scattering plane when $\alpha=0$. Columns 3–6 give the input parameters defining the (α,θ)-rectangle investigated. Columns 7–9 give the number of operating points (including coincident ones) found in the rectangle. Columns 10–12 give the number of operating points (excluding coincidences) found to be free of interference.

Simulated reflection	Reference vector **Z**	$\theta_{\min}$ (°)	$\theta_{\max}$ (°)	$\alpha_{\min}$ (°)	$\alpha_{\max}$ (°)	Points tested Be	Mg	Zn	Points accepted Be	Mg	Zn
0001	[010]	6	90	0	30	56	52	44	4	4	5
0003	[010]	14	90	0	30	112	104	86	8	5	7
0005	[010]	23	90	0	30	114	106	86	9	8	11
$11\bar{2}1$	[$\bar{1}$10]	21	90	0	90	107	112	130	13	15	11
$11\bar{2}3$	[$\bar{1}$10]	28	90	0	90	104	101	104	11	11	12
$22\bar{4}1$	[$\bar{1}$10]	40	90	0	90	109	114	128	3	6	4
$30\bar{3}1$	[010]	35	90	0	90	117	120	137	7	9	7
$30\bar{3}3$	[010]	40	90	0	90	109	112	118	7	11	10
$41\bar{5}1$	[$\bar{1}$40]	61	90	−90	90	117	119	134	1	0	0

The value of θ_{min} is chosen empirically by a sequence of calculations, which indicate that there are very few, if any, interference-free operating points at smaller values of θ. The results in columns 7–12 of Table 2 show that only about 10% of the tested operating points are free of interference.

Detailed results on the interference-free operating points are given in Tables 3, 4, and 5. In all of these interference calculations the size of the diamond-shaped window was specified by: $\Delta\theta = 1°$, and $\Delta\beta = 2°$. The arbitrary criteria for accepting an operating point as interference-free were the same as in part I: θ_- and $\theta_+ \geq 0{\cdot}25°$, and β_- and $\beta_+ \geq 1°$. A detailed definition of these quantities is shown in Fig. 5 of part I.

Discussion of results

In Tables 3, 4, and 5 we note two striking features previously seen in the case of germanium, that is, a large range of values of θ_p and the frequent occurrence of coincident operating points. In addition, however, there is a new characteristic not present in the case of germanium. For the 0001, 0003 and 0005 reflections of each crystal there is at least one simulation which

Table 3. *Operating points free of interference for 9 simulated beryllium reflections*

The Bragg angle θ_p and azimuthal angle α in columns 3 and 4 specify the high-resolution orientation relative to the simulated reflection; λ and E in columns 5 and 6 give the corresponding wavelength and energy. θ_-, θ_+, β_- and β_+ in columns 7–10 give the size of the interference free region. In column 7 or 8, *** indicates that θ_- or $\theta_+ \geq 1°$; and in column 9 or 10, *** indicates that β_- or $\beta_+ \geq 2°$. Columns 11 and 12 give the values of the secondary and tertiary Bragg angles.

REFLECTION INDICES (HKIL) PRIMARY	SECONDARY	THETA (DEG)	ALPHA (DEG)	LAMBDA (Å)	ENERGY (EV)	THETA- (DEG)	THETA+ (DEG)	BETA- (DEG)	BETA+ (DEG)	THETA2 (DEG)	THETA3 (DEG)
0 0 0 1	1 0-1 0, 1 0-1 1	28.91543	.00000	3.46586	.006810	***	***	***	***	61.08, 90.00	90.00, 61.08
0 0 0 1	1 0-1-1, 1 0-1 2	18.93405	.00000	2.32587	.015121	***	***	***	***	42.15, 61.08	61.08, 42.15
0 0 0 1	2 0-2-1, 2 0-2 2	13.47578	.00000	1.67039	.029317	***	***	***	***	61.08, 74.56	74.56, 61.08
0 0 0 1	2 0-2-2, 2 0-2 3	10.72875	.00000	1.33439	.045940	.44	.31	***	***	50.36, 61.08	61.08, 50.36
0 0 0 3	1 0-1 1, 1 0-1 2	76.76492	.00000	2.32587	.015121	***	***	***	***	42.15, 61.08	61.08, 42.15
0 0 0 3	1 0-1 0, 1 0-1 3	58.89120	.00000	2.04572	.019547	***	***	***	***	31.11, 90.00	90.00, 31.11
0 0 0 3	2 0-2 1, 2 0-2 2	44.35508	.00000	1.67039	.029317	***	***	***	***	61.08, 74.56	74.56, 61.08
0 0 0 3	1 0-1-1, 1 0-1 4	36.73372	.00000	1.42905	.040056	***	***	***	***	24.35, 61.08	61.08, 24.35
0 0 0 3	3-1-2 1, 3-1-2 2	34.45634	19.10661	1.35183	.044763	***	.73	***	1.3	67.34, 78.21	78.21, 67.34
0 0 0 3	2 0-2-1, 2 0-2 4	32.40983	.00000	1.28062	.049880	***	.55	***	***	42.15, 74.56	74.56, 42.15
0 0 0 3	3-1-2-2, 3-1-2 5	23.56699	19.10661	.95531	.089635	.31	.38	***	1.6	43.77, 67.34	67.34, 43.77
0 0 0 3	4 0-4 1, 4 0-4 2	23.30220	.00000	.94517	.091567	.80	.74	1.2	1.2	74.56, 82.14	82.14, 74.56
0 0 0 5	-1 0 1 4, -1 0 1 1	85.43541	.00000	1.42905	.040056	***	***	***	***	61.08, 24.35	24.35, 61.08
0 0 0 5	-1 0 1 3, -1 0 1 2	73.25931	.00000	1.37284	.043403	***	***	***	***	42.15, 31.11	31.11, 42.15
0 0 0 5	1 0-1 0, 1 0-1 5	70.09626	.00000	1.34797	.045020	***	***	***	***	19.90, 90.00	90.00, 19.90
0 0 0 5	2 0-2 2, 2 0-2 3	68.55962	.00000	1.33439	.045940	***	***	***	***	50.36, 61.08	61.08, 50.36
0 0 0 5	2 0-2 1, 2 0-2 4	63.28913	.00000	1.28062	.049880	***	***	***	***	42.15, 74.56	74.56, 42.15
0 0 0 5	3-1-2 2, 3-1-2 3	54.72412	19.10661	1.17036	.059720	***	***	***	***	57.94, 67.34	67.34, 57.94
0 0 0 5	3-1-2 1, 3-1-2 4	51.65883	19.10661	1.12442	.064701	***	.88	***	***	50.13, 78.21	78.21, 50.13
0 0 0 5	4-1-3 1, 4-1-3 4	40.21062	13.89788	.92553	.095495	.72	.99	1.1	1.1	58.50, 81.29	81.29, 58.50
0 0 0 5	5 0-5 0, 5 0-5 5	28.91543	.00000	.69317	.170248	.33	.32	1.1	1.1	61.08, 90.00	90.00, 61.08
1 1-2 1	1 0-1-1	86.28675	32.34988	2.17335	.017318	***	***	***	***	38.83	54.88
1 1-2 1	2 0-2 0, 0 1-1 1	64.04487	62.24368	1.95825	.021332	***	***	***	1.3	81.55, 34.40	34.40, 29.64
1 1-2 1	1 0-1-2	62.52236	20.80858	1.93224	.021910	***	***	***	***	46.65	70.83
1 1-2 1	2 0-2-1	58.61374	43.53389	1.85924	.023664	***	***	***	***	76.98	44.40
1 1-2 1	2 0-2-2	50.20001	32.34988	1.67326	.029217	***	***	1.1	***	74.92	54.88
1 1-2 1	1 0-1-3	47.66199	15.18720	1.60989	.031562	***	***	***	***	51.90	80.44
1 1-2 1	1-1 0-2	42.99696	43.53389	1.48526	.037082	***	***	***	***	33.98	76.98
1 1-2 1	2 0-2-3	42.26796	25.40981	1.46487	.038121	.72	***	***	***	73.93	63.80
1 1-2 1	2 1-3-1	39.44392	20.80858	1.38369	.042726	.88	***	***	***	70.83	31.38
1 1-2 1	3-2-1-1	37.95540	72.47598	1.33953	.045589	.65	.52	1.3	1.9	66.12	75.93
1 1-2 1	4-1-3-1	29.41242	62.24368	1.06956	.071507	.52	***	1.5	1.3	80.17	50.76
1 1-2 1	2 1-3-5	28.33836	8.31590	1.03381	.076538	.26	.60	1.1	1.0	86.99	64.67
1 1-2 1	4-3-1-2	27.01827	69.39853	.98938	.083568	.29	.47	1.0	1.5	70.44	82.54
1 1-2 3	2 0-2 1	82.75818	51.40119	1.63859	.030466	***	***	***	***	59.17	38.07
1 1-2 3	2 0-2 2	81.41275	68.24168	1.63325	.030666	***	***	***	***	70.47	28.11
1 1-2 3	2 0-2 0, 0 1-1 3	75.02886	39.86709	1.59570	.032126	.49	***	***	***	53.71, 51.26	51.26, 23.77
1 1-2 3	1 0-1-1	74.92738	26.61511	1.59494	.032157	.29	***	***	1.3	27.40	77.67
1 1-2 3	2 1-3 0	60.77750	15.55639	1.44155	.039364	***	***	***	***	74.42	44.80
1 1-2 3	3-1-2 1	56.70802	68.24168	1.38069	.042911	***	***	***	***	70.47	52.82
1 1-2 3	3-1-2 2	55.26342	78.71409	1.35739	.044397	.88	***	1.0	***	79.39	45.34
1 1-2 3	3-1-2 0	54.40292	59.09139	1.34310	.045346	.76	***	***	1.6	63.83	61.77
1 1-2 3	3-2-1 0	48.24992	76.53262	1.23231	.053867	***	.75	***	***	55.43	76.32
1 1-2 3	3-2-1-1	43.83436	68.24168	1.14398	.062507	***	.80	1.5	1.3	51.34	84.82
1 1-2 3	3 1-4-2	38.58885	17.38966	1.03025	.077068	***	.49	2.0	1.5	78.88	62.53
2 2-4 1	2 0-2-4	66.19150	22.16506	1.03268	.076706	.51	.72	***	1.7	51.01	62.79
2 2-4 1	3-1-2-4	57.40269	39.17185	.95094	.090460	.69	.65	1.1	1.3	55.88	66.72
2 2-4 1	1 0-1-5	54.95053	9.90356	.92405	.095801	.26	.88	1.3	1.1	43.28	81.77
3 0-3 1	3-1-2-1	88.43138	41.00830	1.29752	.048589	.41	***	1.4	1.8	62.34	29.23
3 0-3 1	1-1 0-1	88.07111	53.80190	1.29727	.048608	***	.32	1.3	1.4	21.98	69.95
3 0-3 1	1 0-1-3	73.25931	.00000	1.24299	.052945	***	.92	1.7	1.7	37.42	69.32
3 0-3 1	2 0-2-4	62.05426	.00000	1.14665	.062216	***	***	1.4	1.4	59.66	58.28
3 0-3 1	1 0-1-6	44.13969	.00000	.90394	.100111	.69	.55	1.0	1.0	52.22	83.64
3 0-3 1	4 0-4-2	43.45155	.00000	.89269	.102651	.31	.69	1.2	1.2	69.32	25.87
3 0-3 1	4 0-4-3	43.14562	.00000	.88765	.103821	.38	.31	1.0	1.0	76.08	32.94
3 0-3 3	3-2-1 1	86.38150	74.40243	1.15298	.061534	.28	***	***	1.0	51.91	41.71
3 0-3 3	3-2-1 0	81.63258	60.82456	1.14299	.062615	***	.79	***	1.2	49.80	48.57
3 0-3 3	0 1-1 1	70.18661	74.40243	1.08690	.069245	***	***	1.2	***	18.28	51.91
3 0-3 3	4-1-3 1	69.65502	35.61920	1.08322	.069716	.86	.50	1.1	1.2	86.29	24.06
3 0-3 3	1 0-1-3	62.21760	.00000	1.02211	.078301	.93	***	1.1	1.1	29.98	87.81
3 0-3 3	4 0-4-2	54.65660	.00000	.94237	.092113	***	***	1.0	1.0	80.99	44.36
3 0-3 3	2 0-2-5	48.66059	.00000	.86740	.108724	.28	.62	1.6	1.6	48.33	83.01
4 1-5 1	2 1-3-6	64.95517	-5.98718	.77716	.135437	.42	***	1.6	***	56.34	58.70

has θ_2 (or θ_3)$=90°$. Thus one of the relevant pair of cooperating reflections is a complete back-reflection.*

* In order to show that such an intermediate back-reflection is impossible for diamond-structure simulations, we first note from equation (1*b*) that $\theta_3=90°$, only if

$$\mathbf{K}_1 \cdot \mathbf{K}_2 \equiv h_1h_2+k_1k_2+l_1l_2=0 .$$

However, the indices are restricted as follows: (1) h_1,k_1, and l_1 are each even, and $h_1+k_1+l_1=4n+2$; and (2) h_2,k_2, and l_2 are each odd. These restrictions readily give $\mathbf{K}_1 \cdot \mathbf{K}_2 = 4m+2\neq 0$. The proof for θ_2 is analogous.

Now it is a well-known consequence of Bragg's equation that $d\lambda/d\theta=0$ at $\theta=90°$. This means that the extremely good wavelength resolution characteristic of a perfect crystal can be obtained even with a mosaic crystal having a small but finite angular spread. Thus highly monochromatic beams of relatively high intensity can be produced. However, it must be noted that such a result is obtained by sacrificing angular resolution.

The foregoing discussion would adequately account for a simple operating point, that is, one corresponding

Table 4. *Operating points free of interference for* 8 *simulated magnesium reflections*

See caption of Table 3.

REFLECTION INDICES (HKIL) PRIMARY	SECONDARY	THETA (DEG)	ALPHA (DEG)	LAMBDA (Å)	ENERGY (EV)	THETA− (DEG)	THETA+ (DEG)	BETA− (DEG)	BETA+ (DEG)	THETA2 (DEG)	THETA3 (DEG)
0 0 0 1	1 0-1 0, 1 0-1 1	28.07667	.00000	4.90467	.003401	***	***	***	***	61.92, 90.00	90.00, 61.92
0 0 0 1	1 0-1-1, 1 0-1 2	18.77597	.00000	3.35419	.007271	***	***	***	***	43.15, 61.92	61.92, 43.15
0 0 0 1	2 0-2-1, 2 0-2 2	13.14274	.00000	2.36950	.014570	***	***	***	***	61.92, 75.07	75.07, 61.92
0 0 0 1	1 0-1-2, 1 0-1 3	11.14651	.00000	2.01457	.020156	.36	***	***	***	32.00, 43.15	43.15, 32.00
0 0 0 3	1 0-1 1, 1 0-1 2	74.92930	.00000	3.35419	.007271	***	***	***	***	43.15, 61.92	61.92, 43.15
0 0 0 3	1 0-1 0, 1 0-1 3	57.99914	.00000	2.94581	.009427	***	***	***	***	32.00, 90.00	90.00, 32.00
0 0 0 3	2 0-2 1, 2 0-2 2	43.01059	.00000	2.36950	.014570	***	***	***	***	61.92, 75.07	75.07, 61.92
0 0 0 3	1 0-1-1, 1 0-1 4	36.81237	.00000	2.08141	.018882	***	***	1.7	1.7	25.11, 61.92	61.92, 25.11
0 0 0 3	3-1-2-2, 3-1-2 5	23.26969	19.10661	1.37231	.043437	.80	.57	***	***	44.77, 68.04	68.04, 44.77
0 0 0 5	-1 0 1 4, -1 0 1 1	87.03429	.00000	2.08141	.018882	***	***	1.7	1.7	61.92, 25.11	25.11, 61.92
0 0 0 5	-1 0 1 3, -1 0 1 2	75.14822	.00000	2.01457	.020156	***	***	***	***	43.15, 32.00	32.00, 43.15
0 0 0 5	1 0-1 0, 1 0-1 5	69.44726	.00000	1.95154	.021479	***	***	***	***	20.55, 90.00	90.00, 20.55
0 0 0 5	2 0-2 2, 2 0-2 3	66.74139	.00000	1.91482	.022310	***	***	***	***	51.34, 61.92	61.92, 51.34
0 0 0 5	3-1-2 2, 3-1-2 3	53.12854	19.10661	1.66733	.029425	***	***	***	***	58.83, 68.04	68.04, 58.83
0 0 0 5	3-1-2 1, 3-1-2 4	50.28395	19.10661	1.60321	.031826	***	.79	***	***	51.12, 78.60	78.60, 51.12
0 0 0 5	1 0-1-1, 1 0-1 6	44.57217	.00000	1.46271	.038234	.96	.65	1.1	1.1	17.35, 61.92	61.92, 17.35
0 0 0 5	4 0-4 2, 4 0-4 3	36.73881	.00000	1.24670	.052630	***	.57	1.1	1.1	68.20, 75.07	75.07, 68.20
1 1-2 1	1 0-1-1	87.61075	33.17881	3.06457	.008710	***	***	1.6	***	38.67	53.72
1 1-2 1	1 0-1-2	64.05402	21.42068	2.75808	.010753	***	***	***	***	46.51	69.43
1 1-2 1	2 0-2-1	58.77435	44.44408	2.62289	.011891	***	***	***	***	77.60	43.63
1 1-2 1	1-1 0-1	52.35574	62.98760	2.42869	.013868	***	***	1.9	***	29.68	82.04
1 1-2 1	1 0-1-3	49.04656	15.65409	2.31651	.015244	***	.35	1.4	***	51.85	79.11
1 1-2 1	1-1 0-2	43.71258	44.44408	2.11958	.018208	***	***	***	***	33.99	77.60
1 1-2 1	3-1-2 0	43.08036	75.69988	2.09499	.018638	***	***	1.7	***	85.65	51.27
1 1-2 1	2 0-2-3	42.99673	26.12288	2.09172	.018696	.77	***	***	***	74.54	62.46
1 1-2 1	3-1-2-1	41.68316	62.98760	2.03974	.019661	***	.51	***	***	82.04	56.28
1 1-2 1	3-1-2-2	38.64252	52.59496	1.91536	.022298	***	***	1.9	1.8	79.40	61.95
1 1-2 1	2 0-2-4	36.56302	21.42068	1.82717	.024502	.27	***	1.5	***	74.00	69.43
1 1-2 1	2 1-3 0	33.51797	33.17881	1.69372	.028515	***	.39	***	1.8	53.72	20.20
1 1-2 1	1 0-1-5	32.71264	10.11092	1.65761	.029771	.41	.92	1.3	***	58.15	89.14
1 1-2 1	4-3-1 0	28.94434	85.83460	1.48442	.037124	.26	***	1.4	***	74.33	76.73
1 1-2 1	2 1-3-6	25.80835	7.45033	1.33536	.045874	.31	.88	1.4	1.7	85.97	68.22
1 1-2 3	2 0-2 1	81.81508	51.91783	2.33327	.015026	***	***	***	***	60.32	37.86
1 1-2 3	2 0-2 2	80.34419	68.60481	2.32389	.015147	***	***	***	***	71.37	28.28
1 1-2 3	1 0-1-1	76.17517	27.04277	2.28900	.015613	***	***	1.2	***	27.82	76.00
1 1-2 3	2 0-2 0, 0 1-1 3	74.63507	40.39036	2.27303	.015833	***	***	***	***	54.87, 50.50	50.50, 24.14
1 1-2 3	2 1-3 0	59.95112	15.83292	2.04046	.019647	***	.69	***	***	76.21	43.84
1 1-2 3	3-1-2 1	55.88924	68.60481	1.95173	.021475	***	***	***	***	71.37	52.74
1 1-2 3	1 0-1-2	55.72859	20.03279	1.94801	.021557	.82	***	***	***	30.83	86.55
1 1-2 3	3-1-2-1	49.38578	51.91783	1.78944	.025546	.78	***	***	***	60.32	70.29
1 1-2 3	3-2-1 0	47.75503	76.77114	1.74504	.026863	***	***	***	1.3	56.16	76.09
1 1-2 3	2 0-2-3	44.53988	23.04434	1.65341	.029923	***	***	1.9	1.1	49.63	85.83
1 1-2 3	4 0-4-3	32.30026	29.56123	1.25963	.051556	.50	.96	1.7	1.2	77.49	70.21
2 2-4 1	0 2-2 3	87.11003	37.18783	1.58399	.032603	.39	***	1.2	***	46.88	40.23
2 2-4 1	2 0-2-3	79.11527	28.45474	1.55747	.033723	.66	***	***	1.8	45.86	55.02
2 2-4 1	2 0-2-4	67.75458	22.85560	1.46796	.037961	.46	.89	1.7	1.8	50.56	61.69
2 2-4 1	3 1-4-3	61.64625	25.36991	1.39574	.041991	.86	***	1.3	1.7	82.08	36.27
2 2-4 1	2 1-3-5	58.74320	9.36583	1.35580	.044501	.41	.85	1.3	1.8	66.39	54.87
2 2-4 1	2 0-2-5	58.70038	19.02760	1.35518	.044542	.32	***	1.5	1.0	54.36	66.94
3 0-3 1	1 0-1 3	86.07581	.00000	1.82006	.024694	.56	***	1.3	1.3	38.16	47.92
3 0-3 1	2 0-2 3	85.51735	.00000	1.81875	.024729	***	.56	1.7	1.7	56.93	28.58
3 0-3 1	2 0-2-3	76.44624	.00000	1.77353	.026007	***	***	***	***	54.81	48.75
3 0-3 1	3-1-2-3	66.42141	23.27582	1.67202	.029260	.69	***	1.4	1.4	68.44	45.14
3 0-3 1	2 0-2-4	63.70010	.00000	1.63549	.030582	***	.89	***	***	59.36	56.93
3 0-3 1	3-2-1-3	60.77871	41.96954	1.59217	.032269	***	***	***	1.2	62.33	56.89
3 0-3 1	3-1-2-4	57.57753	18.83798	1.53995	.034494	.75	***	***	1.9	70.32	52.10
3 0-3 1	1 0-1-7	40.10352	.00000	1.17518	.059231	.62	.65	1.9	1.9	54.81	85.09
3 0-3 1	5-2-3 0	39.11927	67.98696	1.15104	.061742	.39	.43	1.3	1.2	64.50	25.38
3 0-3 3	3-2-1 1	85.96109	74.79800	1.63083	.030757	.30	***	***	1.1	52.36	41.68
3 0-3 3	3-2-1 0	81.51443	61.47756	1.61699	.031286	***	***	***	***	50.32	48.17
3 0-3 3	1-1 0-1	80.46425	50.81328	1.61230	.031468	.63	.90	1.9	1.4	19.19	80.34
3 0-3 3	3-1-2-2	73.22353	22.23968	1.56531	.033386	.99	.56	1.3	1.4	53.45	53.33
3 0-3 3	2-2 0-1	72.30721	61.47756	1.55756	.033719	***	***	1.5	1.3	35.45	72.24
3 0-3 3	0 1-1 1	70.69144	74.79800	1.54293	.034361	***	***	1.5	1.4	18.34	52.36
3 0-3 3	2 0-2-3	68.68643	.00000	1.52307	.035263	***	***	1.8	1.8	44.57	66.74
3 0-3 3	4-3-1 2	60.92984	84.82443	1.42894	.040062	.40	.39	1.3	***	75.14	43.93
3 0-3 3	1 0-1-4	53.28536	.00000	1.31057	.047626	.70	.48	1.2	1.2	33.75	87.03
3 0-3 3	2 0-2-5	50.05343	.00000	1.25338	.052071	***	.42	1.0	1.0	48.73	81.21
3 0-3 3	4-1-3-4	49.73545	13.78469	1.24753	.052560	.51	.29	1.5	1.4	70.09	60.17

to a case of only 3 beams. However, all of the instances of intermediate back-reflections in Tables 3, 4, and 5 occur for coincident operating points corresponding to cases of 4 beams. Thus the argument must be modified to show that all non-vanishing 'routes' of multiple reflection going from the incident to the final beam include at least one back-reflection. For this purpose it is convenient to consider the first operating point in Table 3 as an example. There are four independent indirect routes, which may be identified with the following sequences of reflections:

$$(10\bar{1}0)+(\bar{1}011) \tag{3a}$$
$$(10\bar{1}1)+(\bar{1}010) \tag{3b}$$
$$(10\bar{1}0)+(0001)+(\bar{1}010) \tag{3c}$$
$$(10\bar{1}1)+(000\bar{1})+(\bar{1}011)\,. \tag{3d}$$

The first and second sequences correspond to the simulations given in Table 3; both include back-reflections and thus give good wavelength resolution. The third and fourth sequences are not high-resolution simulations. Fortunately, however, they contribute nothing, since the middle links in both sequences have vanishing structure factors. Thus high-resolution monochromat-

Table 5. *Operating points free of interference for* 8 *simulated zinc reflections*

See caption of Table 3.

REFLECTION INDICES (HKIL) PRIMARY	SECONDARY	THETA (DEG)	ALPHA (DEG)	LAMBDA (Å)	ENERGY (EV)	THETA- (DEG)	THETA+ (DEG)	BETA- (DEG)	BETA+ (DEG)	THETA2 (DEG)	THETA3 (DEG)
0 0 0 1	1 0-1 0, 1 0-1 1	25.01085	.00000	4.18291	.004675	***	***	***	***	64.99, 90.00	90.00, 64.99
0 0 0 1	1 0-1-1, 1 0-1 2	18.00635	.00000	3.05833	.008746	***	***	***	***	46.98, 64.99	64.99, 46.98
0 0 0 1	2 0-2-1, 2 0-2 2	11.88032	.00000	2.03678	.019719	.44	***	***	***	64.99, 76.87	76.87, 64.99
0 0 0 1	1 0-1-2, 1 0-1 3	11.43766	.00000	1.96192	.021252	***	.44	***	***	35.55, 46.98	46.98, 35.55
0 0 0 1	2 0-2-2, 2 0-2 3	9.97376	.00000	1.71354	.027859	.51	***	***	***	55.02, 64.99	64.99, 55.02
0 0 0 3	1 0-1 1, 1 0-1 2	68.02804	.00000	3.05833	.008746	***	***	***	***	46.98, 64.99	64.99, 46.98
0 0 0 3	1 0-1 0, 1 0-1 3	54.45486	.00000	2.68333	.011361	***	***	***	***	35.55, 90.00	90.00, 35.55
0 0 0 3	2 0-2 1, 2 0-2 2	38.14138	.00000	2.03678	.019719	***	***	***	***	64.99, 76.87	76.87, 64.99
0 0 0 3	1 0-1-1, 1 0-1 4	36.80399	.00000	1.97568	.020957	***	***	1.8	1.8	28.19, 64.99	64.99, 28.19
0 0 0 3	2 0-2-1, 2 0-2 4	29.88666	.00000	1.64328	.030293	***	***	***	***	46.98, 76.87	76.87, 46.98
0 0 0 3	2 0-2-2, 2 0-2 5	24.38006	.00000	1.36132	.044141	.41	***	***	***	40.61, 64.99	64.99, 40.61
0 0 0 3	4 0-4-1, 4 0-4 4	18.35824	.00000	1.03869	.075822	.47	.93	1.6	1.6	64.99, 83.35	83.35, 64.99
0 0 0 5	1 0-1 1, 1 0-1 4	86.82569	.00000	1.97568	.020957	***	***	1.8	1.8	28.19, 64.99	64.99, 28.19
0 0 0 5	1 0-1 0, 1 0-1 5	66.79569	.00000	1.81865	.024732	***	***	***	***	23.20, 90.00	90.00, 23.20
0 0 0 5	2 0-2 2, 2 0-2 3	59.99545	.00000	1.71354	.027859	***	***	***	***	55.02, 64.99	64.99, 55.02
0 0 0 5	2 0-2 1, 2 0-2 4	56.14773	.00000	1.64328	.030293	***	***	***	***	46.98, 76.87	76.87, 46.98
0 0 0 5	3-1-2 2, 3-1-2 3	47.30524	19.10661	1.45431	.038676	***	.48	1.7	1.9	62.12, 70.57	70.57, 62.12
0 0 0 5	1 0-1-1, 1 0-1 6	45.33033	.00000	1.40721	.041309	***	.35	1.4	1.4	19.66, 64.99	64.99, 19.66
0 0 0 5	3-1-2-1, 3-1-2 6	36.61413	19.10661	1.18015	.058733	***	.79	1.5	***	43.39, 80.00	80.00, 43.39
0 0 0 5	4-1-3 2, 4-1-3 3	35.72457	13.89788	1.15535	.061282	.68	.75	1.5	1.1	68.78, 75.49	75.49, 68.78
0 0 0 5	4 0-4 2, 4 0-4 3	32.41566	.00000	1.06071	.072706	.29	***	***	***	70.71, 76.87	76.87, 70.71
0 0 0 5	4 0-4 1, 4 0-4 4	31.66346	.00000	1.03869	.075822	***	.47	1.6	1.6	64.99, 83.35	83.35, 64.99
0 0 0 5	4 0-4-1, 4 0-4 6	28.33200	.00000	.93906	.092763	.53	.99	1.9	1.9	55.02, 83.35	83.35, 55.02
1 1-2 1	0 1-1 2	87.54361	36.49949	2.57082	.012377	***	***	1.8	***	49.62	37.92
1 1-2 1	1 0-1-2	69.96664	23.93971	2.41749	.013997	***	***	***	***	45.75	64.28
1 1-2 1	2 0-2 0, 0 1-1 1	63.05635	65.74927	2.29388	.015546	***	.88	***	1.1	83.69, 33.26	33.26, 29.80
1 1-2 1	1 0-1-3	54.55733	17.59488	2.09637	.018614	***	.87	1.8	***	51.38	74.07
1 1-2 1	1-1 0-1	53.88729	65.74927	2.07877	.018930	***	***	***	1.5	29.80	83.69
1 1-2 1	1-1 0-2	46.31672	47.98226	1.86085	.023623	***	***	***	***	33.46	79.78
1 1-2 1	2 0-2-3	45.66443	29.02855	1.84050	.024149	.94	***	***	***	76.75	57.59
1 1-2 1	1 0-1-4	44.18661	13.85540	1.79351	.025431	***	.46	***	***	55.35	80.46
1 1-2 1	2 0-2-4	39.54987	23.93971	1.63848	.030471	.37	***	***	***	76.17	64.28
1 1-2 1	2 1-3-3	36.22874	13.85540	1.52078	.035370	***	.32	***	1.1	80.46	44.23
1 1-2 1	5-3-2 0	24.28874	83.57439	1.05844	.073018	.27	.63	***	***	88.27	67.44
1 1-2 3	1 0-1-1	80.87191	28.86169	2.04651	.019532	***	***	***	***	29.29	69.84
1 1-2 3	2 0-2 1	78.40239	54.02991	2.03044	.019842	***	***	***	***	64.61	36.99
1 1-2 3	2 0-2 2	76.59262	70.05555	2.01626	.020122	***	***	***	1.6	74.59	28.82
1 1-2 3	2 0-2 0, 0 1-1 3	73.10180	42.57045	1.98326	.020797	***	***	***	***	59.24, 47.66	47.66, 25.45
1 1-2 3	2 0-2-1	64.51844	34.56478	1.87113	.023365	***	***	***	***	56.36	59.12
1 1-2 3	1 0-1-2	61.11913	21.48876	1.81496	.024833	***	***	***	***	32.53	86.35
1 1-2 3	3-1-2 2	51.77868	79.71633	1.62841	.030849	.47	.87	***	***	81.79	46.43
1 1-2 3	3-1-2 0	51.73225	61.44015	1.62737	.030888	.35	***	2.0	***	68.88	59.39
1 1-2 3	2 1-3-2	48.94388	11.96859	1.56300	.033485	***	***	1.9	***	71.80	59.25
1 1-2 3	1 0-1-3	48.05289	17.02452	1.54164	.034419	.50	.78	***	1.6	35.07	83.12
1 1-2 3	2 1-3-3	43.83463	10.41024	1.43555	.039694	***	.81	***	***	68.58	67.59
1 1-2 3	4-1-3-2	35.63606	46.66613	1.20766	.056089	.39	.97	1.2	2.0	77.02	67.35
2 2-4 1	2 0-2-3	84.74224	31.71368	1.31497	.047307	.49	***	1.8	***	44.06	51.20
2 2-4 1	0 2-2 3	82.59803	40.86372	1.30952	.047702	***	.58	1.8	1.4	43.83	38.77
2 2-4 1	3-2-1-1	63.68664	76.98293	1.18370	.058382	.83	.42	1.1	1.1	43.55	72.77
2 2-4 1	1 0-1-6	55.13579	9.81635	1.08351	.069679	***	.50	1.0	1.8	44.25	80.62
3 0-3 1	2 0-2-3	83.20055	.00000	1.50961	.035895	.67	***	***	***	52.98	43.82
3 0-3 1	1 0-1-3	82.52794	.00000	1.50740	.036000	***	.67	***	***	34.18	63.29
3 0-3 1	0 1-1 1	80.13886	66.07818	1.49785	.036461	***	***	***	***	20.98	59.16
3 0-3 1	1 0-1 3	79.46570	.00000	1.49468	.036615	.95	***	1.5	1.5	33.85	45.62
3 0-3 1	2-2 0-1	75.57461	70.46146	1.47238	.037733	***	.38	1.0	***	40.93	63.50
3 0-3 1	2 0-2-4	70.18711	.00000	1.43031	.039985	***	***	1.6	1.6	57.96	51.86
3 0-3 1	1 0-1 2	56.14773	.00000	1.26258	.051315	***	.40	1.0	1.0	21.97	34.18
3 0-3 3	2 0-2-2	88.19345	.00000	1.39361	.042119	.60	***	***	***	41.78	50.02
3 0-3 3	1 0-1-2	87.59189	.00000	1.39307	.042152	***	.60	***	***	24.38	68.03
3 0-3 3	3-1-2-1	86.26394	30.33811	1.39134	.042257	***	.95	***	1.6	54.08	39.66
3 0-3 3	3-2-1 0	81.09281	63.97857	1.37749	.043111	.93	***	***	1.7	52.15	46.76
3 0-3 3	2-2 0-1	73.66026	63.97857	1.33799	.045694	***	***	1.4	***	36.54	69.80
3 0-3 3	0 1-1 1	72.41454	76.28247	1.32915	.046304	***	.88	1.4	1.9	18.53	53.89
3 0-3 3	2-2 0-4	51.89765	39.32926	1.09719	.067951	***	***	1.1	1.5	40.56	87.54
3 0-3 3	4 0-4-3	51.05605	.00000	1.08444	.069559	.36	.33	1.0	1.0	84.65	44.30
3 0-3 3	5-3-2 0	49.34522	60.33582	1.05779	.073108	.57	.62	1.5	1.1	87.35	43.31
3 0-3 3	2 0-2-7	43.58185	.00000	.96122	.088535	.41	***	1.6	1.6	52.89	83.53

ization can be obtained even with a mosaic crystal. Analogous considerations are valid for 9 other operating points in Tables 3, 4 and 5.

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A Method of Calculating Molecular Crystal Structures

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(*Received* 30 *September* 1968)

A novel method of calculating the molecular position in a lattice of known dimensions is presented. The repulsive lattice energy is approximated by a sum of quadratic nonbonded interatomic potential functions and the lattice energy sum is minimized by full-matrix least squares. The convergence range from arbitrary trial models is greater than the previously used steepest descent method using (exp–6) nonbonded potentials. Greatly increased speed of convergence is also obtained because of the inclusion of off-diagonal terms and the small number of repulsive interactions which are considered. The calculated packing models are sufficiently accurate to serve as a starting point for structure factor least-squares refinement based on diffraction data.

Introduction

A situation frequently encountered in the study of molecular crystals by diffraction methods is that the molecular structure is already known approximately, or at least, plausible predictions of the molecular structure can be made from expected bond distances and angles. In order to verify the model and to refine the molecular structure from the diffraction data it is necessary to locate the molecules in the unit cell of the crystal. In addition, the packing structure may be of considerable interest in itself even if the molecular structure is accurately known. For example, several different packing structures may be observed for the same molecular structure. Or, chemical and physical interactions between molecules may be closely related to their mode of packing in the crystal.

The most obvious procedure which can be used to obtain the crystal packing of molecules is to minimize the lattice energy, neglecting thermal effects, using the best available representation of the non-bonded energy* between the molecules, and assuming pairwise additivity (Williams, 1965*a*). The most important contribution to the attractive energy in molecular crystals is the London dispersion energy, which has an inverse sixth power dependence on the interatomic separation. This term has the physical meaning of instantaneous dipole–dipole polarization. Terms involving quadrupoles or higher may safely be neglected as an initial approximation.

Several investigators (Kitaigorodskii, 1965; Craig, Mason, Pauling & Santry, 1965) have shown that the contribution to the lattice energy from electrostatic dipoles or quadrupoles is small for typical molecular crystals. Further, the rate of change of electrostatic energy effects with respect to molecular position is small.

The repulsive energy is of primary importance in determining the molecular position, provided the observed lattice constants are retained. The repulsive energy is due to overlap of filled electron shells and is a consequence of the required antisymmetry of the wave function for the system. The increase in repulsion energy with decreasing interatomic separation, d, may be fitted by a d^{-n} term, with n chosen for best fit, or to an exponential $\exp(-Cd)$ term, with C chosen for best fit.

The pairwise sum for the lattice energy based on the usual models for the nonbonded energy, such as the

* For a general discussion of nonbonded energy see, for example, Hirschfelder, Curtiss & Bird (1954).