AN ATTEMPT AT AN ALGEBRAIC THEORY OF CRYSTAL STRUCTURE. PART 4.

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ABSTRACT

Since, for reasons to be examined in a later instalment of this work, the postulates of Euclid do not seem suited for the purpose, an attempt is made to classify regularities in the observed diffraction of X-rays by matter in the crystalline state on a 'Pythagorean', or purely numerical basis

Keywords: crystal structure, Yarmolyuk and Kripyakevich's rule.

"I am quite satisfied if we have the machinery for making predictions, even if we are unable to understand it clearly" (Einstein, 1953).

INTRODUCTION

It has been shown that in some cases the number of polyhedra that go to make up the postulated unit cell of a crystal, and the number of the cell's vertices, are proportional to the solutions of a simple Diophantine equation (Aboav, 1997; 1998a). These solutions do not describe the partition of the cell into its differently shaped polyhedra (Aboav, 1998b), though as we shall see in a moment a further numerical assumption makes such a description possible.

Relations depending on arithmetical operations, like the adding or multiplying of integers, will here be considered separately from those that depend on geometrical ones, such as the measurement of length and angle.

NUMERICAL

Pythagoras's discovery that the interval of 7 octaves is roughly equal to that of 12 major fifths, i.e. that $2^7 \sim (3/2)^{12}$, or

$$2^a \sim 3^b \qquad (1)$$

where $a = 19$, $b = 12$, may be regarded as a borderline case ($x = y = 1$) of a more general approximation

$$2^a x \sim 3^b y \qquad (2)$$

where x and y in this instance are integers, one of which is prime, and the other is either prime, or the product of 5 (or 7) and a prime number.

A pair of composite numbers, m and n, are now defined thus:

$$m = 2^a x / 2^7 \qquad (3)$$

and

$$n = 3^b y / 3^6 \qquad (4)$$

Since these numbers are co-prime, m is not a multiple of n. Their ratio m/n, here denoted by A, is equal to $(2^a x / 3^b y)(3^6 / 2^7)$. Hence, since $2^a x \sim 3^b y$, A is approximately equal to $3^6 / 2^7$, that is,

$$A \sim 5\ 7 \qquad (5)$$

The fraction $1 - 3^6 m / 2^7 n$, or $1 - 3^b y / 2^a x$, which is a measure of how closely $2^a x$ approximates $3^b y$, is here denoted by the Greek letter κ and called the *comma*:

$$\kappa = 1 - 3^6 n / 2^7 m \qquad (6)$$

[*Note*: In the above-quoted, celebrated instance of antiquity, where m and n are effectively put equal to 2^{12} and 3^6 respectively, $|\kappa| = 1 - 3^{12}/2^{19}$, or roughly $1/73$. Known to musicians as the *comma of Pythagoras*, this value of κ represents the small but perceptible interval between such notes as $D^\flat$ and $C^\#$ played on a violin.]

50 solutions to the approximate relation (2), here denoted by [a b]{x y}, are listed in col. 2 of Table 1, which shows the relevant values of the co-primes m and n (col. 3) and of the comma (col. 4). Solution No. 39, [6 6]{5.5.5 11}, in which x is neither prime, nor the product of 5 (or 7) and a prime as required, is exceptionally listed in the table to allow every value of [f 1 0] from $f = 1$ through $f = 10$ (see Eq. 10 below) to appear in it.

Table 1. *Partition of numbers m n proportional to solutions of 'Pythagorean' approximation $2^a x \sim 3^b y$.*

No.	[a b]{x y}	m	n	κ	(6|5½) n_1	n_2	(6|5) n_1	n_2	(6|5½|5) n_1	n_2	n_3	(6½|6|5) n_1	n_2	n_3	d	e	f	g	h	(7|6½|6|5) n_1	n_2	n_3	n_4
01	[5 5]{23 3}	23	4	1/104	2	2	3	1	*	*	*	*	*	*	1	0	0	0	1	0	0	3	1
02	[7 5]{67 5.7}	201	35	1/121	17	18	26	9	25	2	8	2	23	10	8	1	0	1	7	0	2	23	10
03	[8 6]{89 31}	178	31	1/123	15	16	23	8	22	2	7	2	20	9	7	1	0	1	6	0	2	20	9
04	[7 8]{5.31 3}	155	27	1/126	13	14	20	7	19	2	6	2	17	8	6	1	0	1	5	0	2	17	8
05	[9 5]{11 23}	132	23	1/131	11	12	17	6	16	2	5	2	14	7	5	1	0	1	4	0	2	14	7
06	[7 6]{109 19}	109	19	1/138	9	10	14	5	13	2	4	2	11	6	4	1	0	1	3	0	2	11	6
07	[8 7]{43 5}	86	15	1/151	7	8	11	4	10	2	3	2	8	5	3	1	0	1	2	0	2	8	5
08	[7 6]{5.47 41}	235	41	1/157	19	22	30	11	29	2	10	2	27	12	8	3	0	3	5	0	6	21	14
09	[6 6]{149 13}	149	26	1/162	12	14	19	7	18	2	6	2	16	8	5	2	0	2	3	0	4	13	9
10	[7 4]{7 11}	63	11	1/179	5	6	8	3	7	2	2	2	5	4	2	1	0	1	1	0	2	5	4
11	[9 5]{31 5.13}	372	65	1/206	29	36	47	18	46	2	17	2	44	19	11	7	0	7	4	0	14	26	25
12	[6 7]{103 3}	103	18	1/213	8	10	13	5	12	2	4	2	10	6	3	2	0	2	1	0	4	7	7
13	[8 5]{41 43}	246	43	1/232	19	24	31	12	30	2	11	2	28	13	7	5	0	5	2	0	10	16	17
14	[9 7]{7.19 31}	532	93	1/228	41	52	67	26	66	2	25	2	64	27	15	11	0	11	4	0	22	34	37
15	[7 5]{101 53}	303	53	1/264	23	30	38	15	37	2	14	2	35	16	8	7	0	7	1	0	14	17	22
16	[10 6]{5 7}	40	7	1/301	3	4	5	2	4	2	1	2	2	3	1	1	0	1	0	0	2	2	3
17	[6 6]{7.31 19}	217	38	1/375	16	22	27	11	26	2	10	2	24	12	5	6	1	5	0	1	10	10	17
18	[7 5]{59 31}	177	31	1/397	13	18	22	9	21	2	8	2	19	10	4	5	1	4	0	1	8	8	14
19	[8 6]{157 5.11}	314	55	1/414	23	32	39	16	38	2	15	2	36	17	7	9	2	7	0	2	14	14	25
20	[4 6]{137 3}	137	24	1/438	10	14	17	7	16	2	6	2	14	8	3	4	1	3	0	1	6	6	11
21	[8 4]{13 41}	234	41	1/476	17	24	29	12	28	2	11	2	26	13	5	7	2	5	0	2	10	10	19
22	[9 7]{107 5.5}	428	75	1/503	31	44	53	22	52	2	21	2	50	23	9	13	4	9	0	4	18	18	35
23	[7 6]{97 17}	97	17	1/540	7	10	12	5	11	2	4	2	9	6	2	3	1	2	0	1	4	4	8
24	[8 8]{7.11 3}	154	27	1/680	11	16	19	8	18	2	7	2	16	9	3	5	2	3	0	2	6	6	13
25	[9 6]{67 47}	268	47	1/837	19	28	33	14	32	2	13	2	30	15	5	9	4	5	0	4	10	10	23
26	[6 5]{19 5}	57	10	1/1216	4	6	7	3	6	2	2	2	4	4	1	2	1	1	0	1	2	2	5
27	[8 6]{151 53}	302	53	1/2035	21	32	37	16	36	2	15	2	34	17	5	11	6	5	0	6	10	10	27
28	[9 7]{47 11}	188	33	1/3468	13	20	23	10	22	2	9	2	20	11	3	7	4	3	0	4	6	6	17
29	[7 6]{131 23}	131	23	1/16768	9	14	16	7	15	2	6	2	13	8	2	5	3	2	0	3	4	4	12
30	[5 7]{5.41 3}	205	36	-1/6562	14	22	25	11	24	2	10	2	22	12	3	8	5	3	0	5	6	6	19
31	[7 4]{31 7.7}	279	49	-1/3968	19	30	34	15	33	2	14	2	31	16	4	11	7	4	0	7	8	8	26
32	[8 6]{37 13}	74	13	-1/1894	5	8	9	4	8	2	3	2	6	5	1	3	2	1	0	2	2	2	7
33	[5 4]{43 17}	387	68	-1/1376	26	42	47	21	46	2	20	2	44	22	5	16	11	5	0	11	10	10	37
34	[7 5]{5.11 29}	165	29	-1/1006	11	18	20	9	19	2	8	2	17	10	2	7	5	2	0	5	4	4	16
35	[8 5]{73 7.11}	438	77	-1/813	29	48	53	24	52	2	23	2	50	25	5	19	14	5	0	14	10	10	43
36	[3 5]{7.13 3}	91	16	-1/728	6	10	11	5	10	2	4	2	8	6	1	4	3	1	0	3	2	2	9
37	[8 7]{5.29 17}	290	51	-1/629	19	32	35	16	34	2	15	2	32	17	3	13	10	3	0	10	6	6	29
38	[9 4]{3 19}	108	19	-1/512	7	12	13	6	12	2	5	2	10	7	1	5	4	1	0	4	2	2	11
39	[6 6]{5.5.5 11}	125	22	-1/421	8	14	15	7	14	2	6	2	12	8	1	6	5	1	0	5	2	2	13
40	[10 7]{7.7 23}	392	69	-1/401	25	44	47	22	46	2	21	2	44	23	3	19	16	3	0	16	6	6	41
41	[7 5]{89 47}	267	47	-1/393	17	30	32	15	31	2	14	2	29	16	2	13	11	2	0	11	4	4	28
42	[8 6]{71 5.5}	142	25	-1/371	9	16	17	8	16	2	7	2	14	9	1	7	6	1	0	6	2	2	15
43	[9 9]{5.23 3}	460	81	-1/348	29	52	55	26	54	2	25	2	52	27	3	23	20	3	0	20	6	6	49
44	[5 5]{53 7}	159	28	-1/339	10	18	19	9	18	2	8	2	16	10	1	8	7	1	0	7	2	2	17
45	[11 6]{11 31}	176	31	-1/317	11	20	21	10	20	2	9	2	18	11	1	9	8	1	0	8	2	2	19
46	[6 6]{193 17}	193	34	-1/301	12	22	23	11	22	2	10	2	20	12	1	10	9	1	0	9	2	2	21
47	[8 5]{5.7 37}	210	37	-1/289	13	24	25	12	24	2	11	2	22	13	1	11	10	1	0	10	2	2	23
48	[6 4]{29 23}	261	46	-1/265	16	30	31	15	30	2	14	2	28	16	1	14	13	1	0	13	2	2	29
49	[10 5]{13 5.11}	312	55	-1/251	19	36	37	18	36	2	17	2	34	19	1	17	16	1	0	16	2	2	35
50	[7 6]{17 3}	17	3	-1/198	1	2	2	1	*	*	*	*	*	*	0	1	1	0	0	1	0	0	2

Since by definition the comma cannot equal zero, relation (2) is necessarily approximate only. Exact numerical relations can, however, be found to depend on it by partitioning m and n into a finite number, s,

of positive integers m_s and n_s

$$m = \Sigma_s m_s \qquad (7)$$

and

$$n = \Sigma_s n_s \qquad (8)$$

such that $2m_s$ is a multiple of n_s for any value of s, that is,

$$m_s = A_s n_s \qquad (9)$$

where $A_s = p$ or $(p+^1/_2)$, p being a positive integer. The partitions depend on the chosen values of s and A_s; but the corresponding values of n_s are in general indeterminate.

Our attention is here confined to partitions for which s = 4, with the aim of determining whether, from among the solutions of Table 1, there exist partitions of that kind for which no value of n_s is greater than 3; and, if so, to express the partition of the remaining solutions in the table in terms of them, the underlying object being to base the sought-after partitions on the simplest possible assumptions. To that end the requisite partition coefficients are determined as follows.

n is first expressed as the sum of a pair of integers, n_1 and n_2 (col. 5), the chosen values of A_s needed to express m_s being those nearest to A (Eq. 5), namely $A_1 = 6$, and $A_2 = 5^1/_2$: $[(6|5^1/_2)]$; while in col. 6 the next nearest pair of values, $A_1 = 6$, and $A_2 = 5$: $[(6|5)]$ is used for the same purpose. The immediate aim is to identify solutions of relation (2) for which no value of n_s exceeds 3. As the data show, there are in this case only two such solutions, namely [5 5]{23 3} and [7 6]{17 3}, listed in the table at Nos. 01 and 50, respectively, with their values of n_s shown in *italics.*

Again with the aim of identifying solutions for which no value of n_s exceeds 3, n is next expressed as the sum of three integers n_1, n_2, n_3 (cols. 7 and 8), the values of A_s for col. 7 being the closest to those already chosen, namely $A_1 = 6$, $A_2 = 5^1/_2$, and $A_3 = 5$: $[(6|5^1/_2|5)]$; while for col.8 the values $A_1 = 6^1/_2$, $A_2 = 6$, and $A_3 = 5$: $[(6^1/_2|6|5)]$ are chosen. With the partition of n into three numbers in this way the values of n_s are in general indeterminate. In the table therefore, where lack of space does not allow more than one of the possible partitions to be shown, n_2 in col. 7, and n_1 in col. 8, are given the same, arbitrarily chosen value 2. It will be seen that for the partition $(6|5^1/_2|5)$ (col. 7) there are no solutions, and that for the partition $(6^1/_2|6|5)$ (col. 8) there is only one solution --- [10 6]{5 7}, listed at No.16 --- for which no value of n_s is greater than 3.

Finally, by introducing the further, proximate coefficient, $A_1 = 7$, into the partition $(6^1/_2|6|5)$ of col. 8, which as we have seen already possesses one of the required solutions, we obtain the partition $(7|6^1/_2|6|5)$, in which n is expressed as the sum of four numbers n_1, n_2, n_3, and n_4. This partition has two further solutions for which no value of n_s is greater than 3. The components (n_1, n_2, n_3, n_4) of the three solutions, namely (*0 0 3 1*), (*0 2 2 3*) and (*1 0 0 2*), are listed in *italics* (Nos. 1, 16, 50) in the last column of Table 1.

These solutions enable the components of n for the remainder of the column to be expressed as sums of their products with positive integers f,g,h, which are functions of m and n only, thus:

$$(n_1+n_2+n_3+n_4) \equiv f(1\ 0\ 0\ 2)+g(0\ 2\ 2\ 3)+h(0\ 0\ 3\ 1)\ (10)$$

so that the components of n on the left-hand side of this identity may be equated to the sum of the corresponding products on the right-hand side as follows:

$$n_1 = f$$
$$n_2 = 2g$$
$$\qquad \qquad (11)$$
$$n_3 = 2g+3h$$
$$n_4 = 2f+3g+h.$$

Hence

$$m_1 = 7f$$
$$m_2 = 13g$$
$$m_3 = 12g+18h$$
$$m_4 = 10f+15g+5h;$$

so that

$$n = 3f+7g+4h$$
$$= 3u+4v, \qquad (12)$$

and

$$m = 17f+40g+23h$$
$$= 17u+23v, \qquad (13)$$

where $u = (f+g)$ and $v = (g+h)$. Hence $g \leq u$ and $g \leq v$. Moreover

$$m/n = (17u+23v)/(3u+4v)$$

i.e.

$$u(3m-17n) = v(23n-4m)$$

or

$$ud = ve \qquad (14)$$

where

$$d = (3m-17n),$$

and

$$e = (23n-4m);$$

so that

$$d+2e = 29n-5m$$
$$= 29(3f+7g+4h)-5(17f+4g+23h)$$

$$= 2f+3g+h,$$

from which it follows that

$$n_4 = 29n-5m. \qquad (15)$$

The choice of coefficients $(7|6^1/_2|6|5)$ thus makes one of the four numbers n_s, namely n_4, independent of the partition, the other three numbers, n_1, n_2, n_3, being in general indeterminate; though, as Eqs. (11) show, they are subject to the restrictions $n_1 < n_4$, and $n_2 \leq n_3$.

The following illustration, with Nos. 14, 19, and 27 taken as examples (Table 2), shows how the numbers d, e of Eq. (14), which are listed for each of the solutions of Table 1 (col. 9) facilitate the evaluation of f, g, h (col. 10).

Table 2. *Some solutions for nos. 14, 19, 27 of Table 1.*

	no. 14	no. 19	no. 27
d	15	7	5
e	11	9	11
Eq(14)	$15u = 11v$	$7u = 9v$	$5u = 11v$
Sol^n	$u = 11, v=15$	$u = 9, v = 7$	$u = 11, v = 5$
f g h	0 11 4	2 7 0	6 5 0

Table 3. *Complete solutions for nos. 14, 19, 27 of Table 1.*

no. 14			no. 19			no. 27		
f	g	h	f	g	h	f	g	h
0	11	4	2	7	0	6	5	0
1	10	5	3	6	1	7	4	1
2	9	6	4	5	2	*8*	*3*	*2*
3	8	7	5	4	3	9	2	3
4	7	8	6	3	4	10	1	4
5	6	9	*7*	*2*	*5*	11	0	5
6	*5*	*10*	8	1	6			
7	4	11	9	0	7			
8	3	12						
9	2	13						
10	1	14						
11	0	15						

Whereas a single trio of numbers f, g, h as shown in the bottom line of Table 2 represents for these three examples a possible solution of the indeterminate equation (14), to obtain the complete solutions the trios with all possible values of g, in this case those for which $0 \leq g \leq 1$; $0 \leq g \leq 7$; and $0 \leq g \leq 5$, respectively (Table 3), have to be taken into account. These solutions are set out in full in Table 3, beginning in each case with the trio for which g has its largest value, i.e. for which g = 11, 7, or 5, respectively, and f or h = 0. Since for lack of space not all values of f,

g, h like those shown in Table 3 can be included in Table 1, only those for which f and/or h = 0 are listed. From these numbers and Eq. (10) a required partition of n (col. 11) can be obtained for each entry in the table, thus realizing the first aim of this investigation.

There remains to be seen, however, whether such a purely numerical system can contribute to the setting up of an axiomatic framework on which to base an adequate description of Nature.

PHYSICAL

The aspect of Nature to be considered here is the behaviour of light (or, more generally, of radiation) in the presence of matter in the crystalline state, the example chosen being the scattering of X-rays by some tetrahedrally close-packed alloys of the transition metals. Shoemaker and Shoemaker (1986) listed experimental data for 20 such alloys, some metrical properties of whose crystal structure have already been considered (Aboav, 1998b). Our attention is now briefly directed to the topology of the structure.

In Table 4, cols 2 and 3 are the same as cols 10 and 11 of Table 1. In col. 4 are listed the alloys investigated by Shoemaker and Shoemaker, while p, q, r, x, the numbers of 16-, 15-, 14-, and 12-hedra (called P, Q, R, X, respectively) per unit cell of the alloys are given in col. 6.

For each of these unit cells Yarmolyuk and Kripyakevich (1974) found an empirical formula for $P_pQ_q R_rX_x$ expressible as

$$P_p Q_q R_rX_x \rightarrow (PX_2)_i(Q_2R_2X_3)_j(R_3X)_k \qquad (16)$$

where i, j, k, whose values for the alloys of Shoemaker and Shoemaker are listed in col. 5 of Table 4, are integers. This apparent restriction on the relative values of p q r x is here referred to as the *rule of Yarmolyuk and Kripyakevich*. As the following fact suggests, the rule being a numerical one may not require a geometrical explanation.

From the above table it will be seen that to each value of [i j k] there corresponds an identical value of [f g h], and to each value of [p q r x] an identical value of [n_1 n_2 n_3 n_4]. When these identical numbers are placed in alignment, there appear gaps in the entries of cols. 4-6, which once again suggest that the experimental data may be incomplete (Aboav, 1998b). (Not all the values of [i j k] are equal to those of [f g h] shown in Table 1, those of Nos. 14, 19, and 27 equalling instead the values shown in *italics* in Table 3, which for lack of space could not, as we have already seen, be included in Table 1.).

Table 4. *Relation of numerical solutions of Table 1 to the crystal structure of some tetrahedrally close-packed alloys (Shoemaker and Shoemaker, 1986).*

No.	f	g	h	n_1	n_2	n_3	n_4	Alloy	i	j	k	p	q	r	x
01	0	0	1	0	0	3	1	CrAl	0	0	1	0	0	3	1
02	0	1	7	0	2	23	10								
03	0	1	6	0	2	20	9								
04	0	1	5	0	2	17	8								
05	0	1	4	0	2	14	7								
06	0	1	3	0	2	11	6								
07	0	1	2	0	2	8	5	CrFe	0	1	2	0	2	8	5
08	0	3	5	0	6	21	14								
09	0	2	3	0	4	13	9								
10	0	1	1	0	2	5	4								
11	0	7	4	0	14	26	25								
12	0	2	1	0	4	7	7								
13	0	5	2	0	10	16	17								
14	0	11	4	0	22	34	37	MnSi	6	5	10	6	10	40	37
15	0	7	1	0	14	17	22								
16	0	1	0	0	2	2	3	ZrAl	0	1	0	0	2	2	3
17	1	5	0	1	10	10	17								
18	1	4	0	1	8	8	14								
19	2	7	0	2	14	14	25	MnFeSi	7	2	5	7	4	19	25
20	1	3	0	1	6	6	11								
21	2	5	0	2	10	10	19								
22	4	9	0	4	18	18	35								
23	1	2	0	1	4	4	8								
24	2	3	0	2	6	6	13								
25	4	5	0	4	10	10	23								
26	1	1	0	1	2	2	5								
27	6	5	0	6	10	10	27	MrCrCo	8	3	2	8	6	12	27
28	4	3	0	4	6	6	17								
29	3	2	0	3	4	4	12								
30	5	3	0	5	6	6	19								
31	7	4	0	7	8	8	26								
32	2	1	0	2	2	2	7	MoCo	2	1	0	2	2	2	7
33	11	5	0	11	10	10	37								
34	5	2	0	5	4	4	16								
35	14	5	0	14	10	10	43								
36	3	1	0	3	2	2	9								
37	10	3	0	10	6	6	29								
38	4	1	0	4	2	2	11	VNiSi	4	1	0	4	2	2	11
39	5	1	0	5	2	2	13								
40	16	3	0	16	6	6	41								
41	11	2	0	11	4	4	28								
42	6	1	0	6	2	2	15	VCoSi	6	1	0	6	2	2	15
43	20	3	0	20	6	6	49	MgZnAl	20	3	0	20	6	6	49
44	7	1	0	7	2	2	17								
45	8	1	0	8	2	2	19								
46	9	1	0	9	2	2	21								
47	10	1	0	10	2	2	23	MnCoSi	10	1	0	10	2	2	23
48	13	1	0	13	2	2	29								
49	16	1	0	16	2	2	35	MgZn	16	1	0	16	2	2	35
50	1	0	0	1	0	0	2	MgZn	1	0	0	1	0	0	2

It is remarkable that, despite their different origin, relations (2) and (16) should furnish identical groups of numbers, either of which can be used to describe the same topological property of a crystal's structure. This identity is not to be expected, since relation (2) has nothing to do with the notions of geometry that

play a seemingly essential part in our customary interpretation of the X-ray photograph of a crystal. A doubt therefore arises as to whether this phenomenon requires such notions for its description.

Such doubts are not new: indeed, a century-and-a-half has elapsed since Riemann (1854), recognizing that the rules of everyday geometry do not necessarily apply in cases where, as for example in Haüy's (1784) 'molecular' picture of a crystal, the scale is so reduced that the notions of the solid body and the ray of light are no longer valid, expressed the opinion:

"...es ist also sehr wohl denkbar, dass die Massverhältnisse des Raumes im Unendlichkleinen den Voraussetzungen der Geometrie nicht gemäss sind, und dies würde man in der That annehmen müssen, sobald sich dadurch die Erscheinungen auf einfacherer Weise erklären liessen." (Riemann, 1854).

("….it is thus quite conceivable that relations of size on an infinitesimally small scale are not in accord with the postulates of geometry, and this one would indeed have to assume, as soon as it allowed the phenomena to be more simply accounted for.")

This doubt, which haunts us still, is not easy to allay; for, in seeking to be rid of it, not only are we faced with the task of finding suitable assumptions to take the place of those laid down in the *Elements*, but history has left little or no trace of the discoveries and decisions known to have been made by Pythagoras and his successors in the 2 centuries before the publication of that great work, discoveries and decisions which must have played no small part in determining the path Euclid was eventually to follow and which would help us immeasurably in our present task, could we but know what they were. All we can do, alas, is to guess what they may have been and try to reconstruct the route by which Euclid arrived at his assumptions, an undertaking we venture to hazard in the next instalment of this work.

(to be continued)

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