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SPACE GROUPS AND ATOMIC PARAMETERS IN SOME GRAPHITE-ALKALI METAL LAMELLAR COMPOUNDS

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ABSTRACT

The recent discovery of a lamellar compound of sodium and graphite, similar to the well-known potassium and rubidium compounds, has stimulated renewed interest in the crystallography of these materials.

The crystallographic aspects of alkali metal - graphite lamellar compounds are reviewed here, and space groups and atomic parameters are derived for some of them.

NaC_{64}, KC_8, and RbC_8 crystallize in space group $C222_1$. If NaC_{64} is one of a series of sodium - graphite compounds, other members of the series would be expected to crystallize in the same space group. The remaining eight known potassium and rubidium compounds have a slightly different but similar structure. Experimental data for these are insufficient to permit a unique choice of space group.

I. INTRODUCTION

The definite layer structure of graphite with its large separation between layers gives rise to the phenomenon of lamellar compounds. In these, ordered layers of some foreign material are sandwiched in definite sequences between the layers of carbon atoms in the graphite structure. Generally, the latter are forced apart where such intrusion occurs.

Many materials are known to form lamellar compounds with graphite, but only those formed by the alkali metals will be considered here. Compounds of K, Rb, and Cs were first described by Fredenhagen and Cadenbach[1] and further investigated by Hérold[2] and by Schleede and Wellman.[3] The information resulting from these investigations concerning the stoichiometry and some of the structural features of these compounds was improved later by Rüdorff and Schulze,[4] who nevertheless did not avail themselves fully of the informational potential of the facts they so ably helped prove. Asher[5] too, while showing that the general picture of Rüdorff and Schulze is applicable also to NaC_{64}, did not go on to conclude that all these lamellar compounds are orthorhombic rather than hexagonal and to derive the space groups and atomic parameters for some of them. This has now been done by the author and is the subject of the present crystal structure review.

II. THE STRUCTURES AND THEIR INTERPRETATION

The following compounds are known:

KC_8	KC_{24}	KC_{36}	KC_{48}	KC_{60}
RbC_8	RbC_{24}	RbC_{36}	RbC_{48}	RbC_{60}

The cesium compounds are said to be analogous to these.[3]

The first member in each series has a metal-to-carbon ratio of 1:8, whereas the remaining ones proceed in increments of 1:12. Figure 1 shows a potassium layer in KC_8, projected onto the adjacent carbon layer. We propose to call this the octal structure, from the metal-to-carbon ratio. If the central metal atom from each hexagon of metal atoms is removed, the structure shown in Figure 2 results, which applies to the remaining compounds listed. We propose to call this the duodecimal structure. In KC_{24} there are two carbon layers between successive planes of metal atoms, three in KC_{36}, and so on. These compounds are often referred to as first, second, etc., stages, according to the number of graphite planes between layers of metal.

Rüdorff and Schulze deduced and Asher confirmed that the metal atoms are always aligned with the centers of carbon hexagons in the adjacent graphite planes, both above and below the plane of the metal atoms. In other words, the two carbon planes adjacent to the metal are in register (AA stacking) rather than in the normal AB stacking. This conclusion was reached on the basis of structure factor calculations. We may add that it does not appear possible to assign a space group if this were not so.

The first lamellar compound of sodium was reported by Asher.[5] He assigned the formula NaC_{64} to it and demonstrated that it has the octal rather than the duodecimal structure, with eight carbon layers between any two metal layers. In other words, if NaC_{64} were to be considered the eighth stage of an as yet hypothetical series, the decrease in the packing density of the metal layers, which occurs between the first and second stages of the K and Rb compounds, would not be found with Na. The existence of NaC_{64} has been confirmed in our laboratories, and we are in agreement with Asher's conclusions. Since

M C 8x

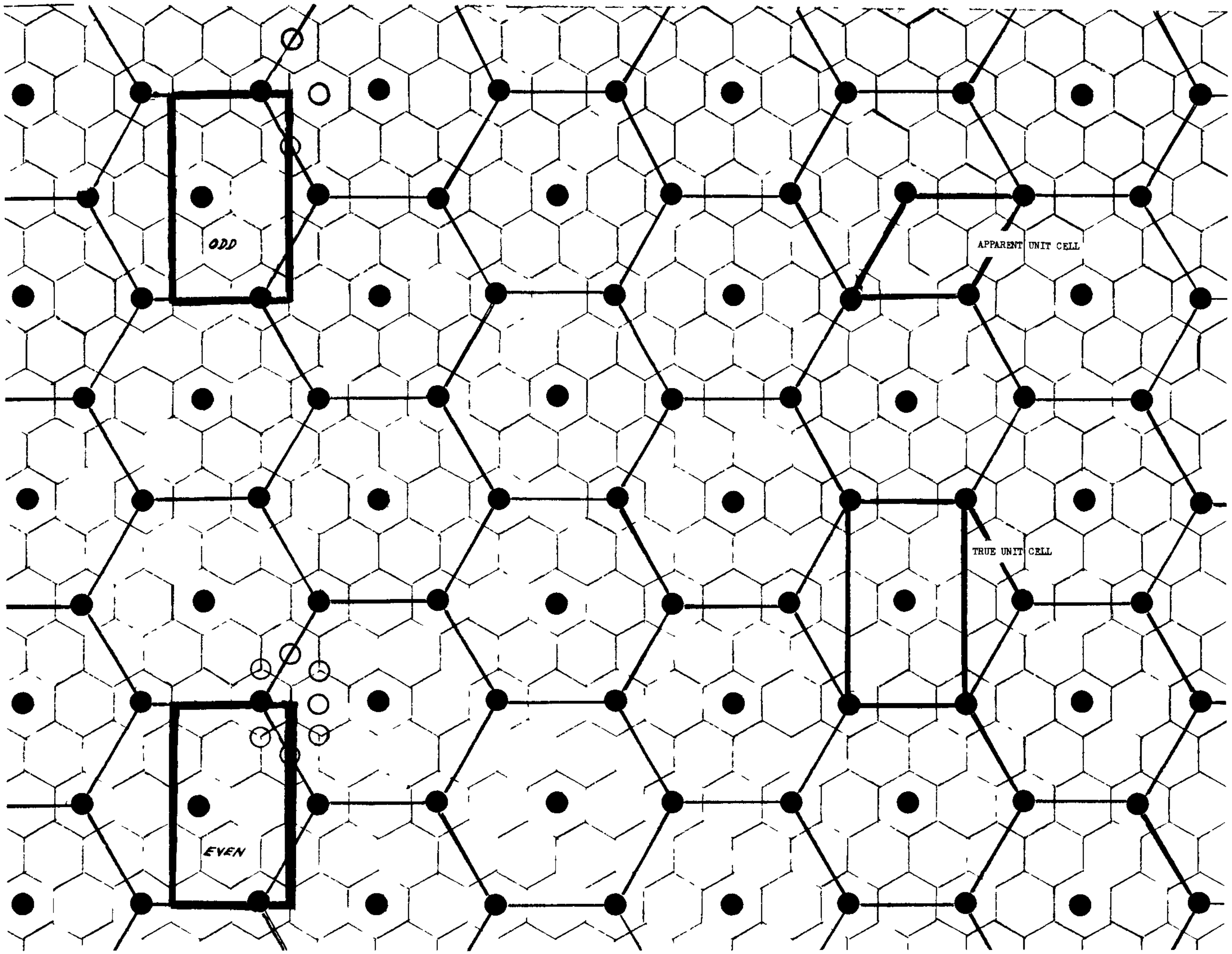

Figure 1. The Octal Structure

MC_{12n}

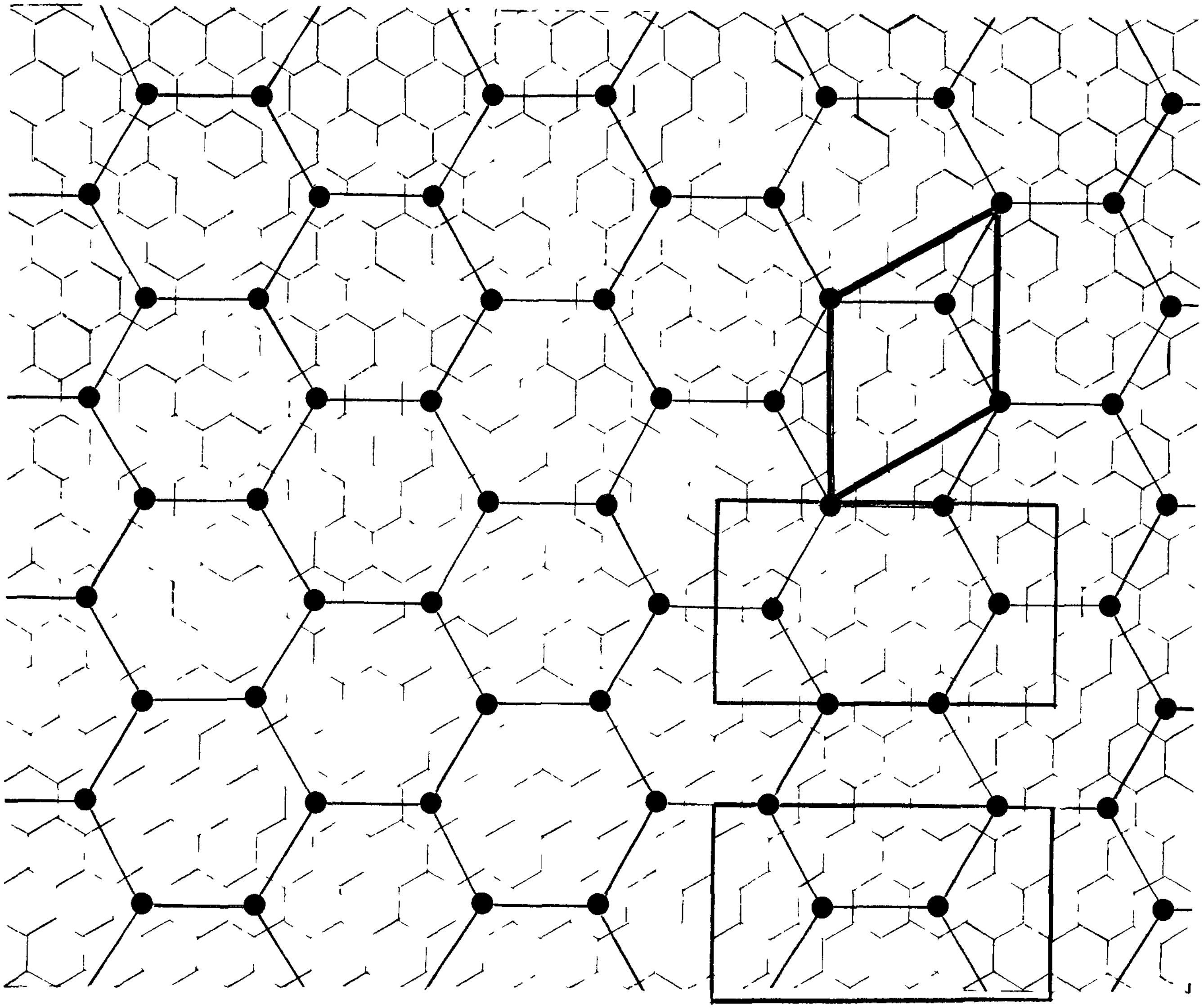

Figure 2. The Duodecimal Structure

there is no change in the separation of the carbon layers which do not have a metal layer between them, it is possible, on the basis of the one compound that has been analyzed, to calculate the X-ray diffraction patterns of an entire series of hypothetical compounds which differ only in the number of carbon planes between the metal planes. X-ray patterns which appear to match two of the calculated ones have been observed in our laboratories, but to date it has not been possible to confirm the compositions of the specimens by chemical means, nor is it as yet possible to reproduce these results at will.

If the metal atoms are always aligned with the centers of carbon hexagons, then if the number of intervening carbon planes is even, one metal plane will be aligned with an A-type carbon layer and the next one with a B-type. Two successive metal layers will thus be non-identical, so that the c-axis is doubled. If the number of intervening carbon layers is odd, on the other hand, then two successive metal layers will both be aligned with an A-type carbon plane, and the doubling will not occur, so that one must distinguish between "odd" and "even" structures. (We are momentarily disregarding a further complication which will be discussed below.) This doubling of the c-axis for even structures was known both to Rüdorff and Schulze and to Asher. It should be pointed out that this arrangement changes the symmetry from hexagonal to orthorhombic. Thus, their Miller indices for other than 00ℓ planes and their unit cells should be transformed to orthorhombic units.

In graphite itself, the AB type stacking of successive layers involves the translation of every alternate layer parallel to a hexagon edge through a distance exactly equal to the length of such an edge. If this arrangement is projected parallel to the c-axis (Figure 3, left), it is seen to possess a three-fold axis of symmetry. The translation of the metal layers must be through exactly this same distance in order to maintain the proper alignment with the graphite planes. This distance, a full edge-length of the carbon hexagons, is only a quarter edge-length of the metal hexagons. Such an arrangement, shown in Figure 3, right, has only a two-fold axis instead of the three-fold one.*

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* The author is indebted to his colleague S. B. Austerman for this deduction.

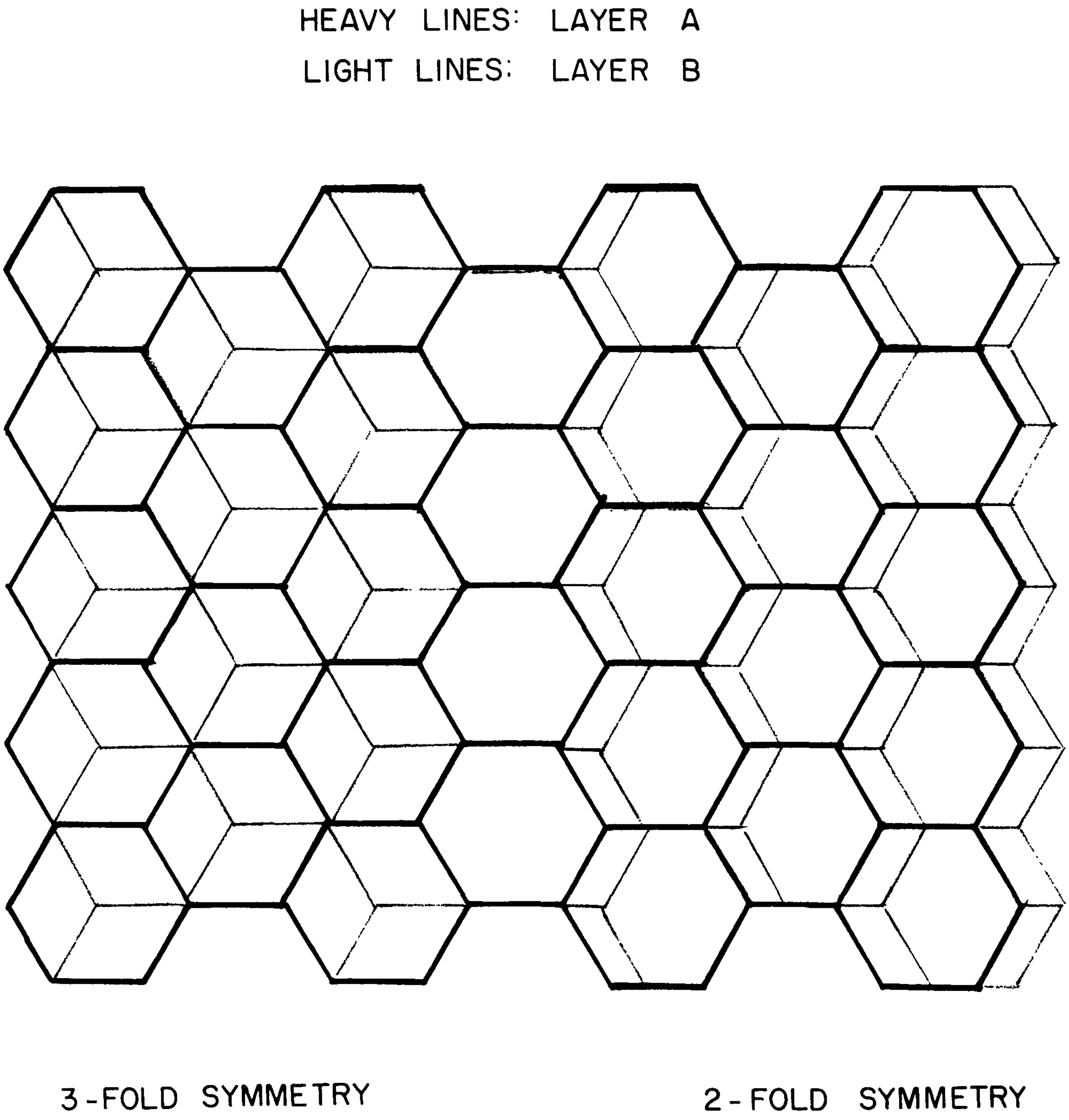

Figure 3. AB Type of Stacking

Thus, the symmetry of the lamellar compounds with even numbers of carbon planes is orthorhombic rather than hexagonal. In fact, it is quite impossible to describe the positions of the metal atoms in such compounds in terms of any hexagonal space group.

Actually, both "odd" and "even" structures are orthorhombic for the following reason. An examination of Figure 1 shows that there are metal atoms above one-fourth of the hexagons of the adjacent carbon plane. It is necessary to decide whether the atoms of the next metal layers are located over corresponding hexagons or over others. In the case of KC_8, the answer is known from the efforts of Schleede and Wellman[3] and has been confirmed by Rüdorff and Schulze.[4] The metal atoms in successive layers systematically occupy all available positions, leading to a quadrupling of the c dimension of the unit cell.

Since NaC_{64} has been found to follow the structural pattern of KC_8, one might expect to find the same quadrupling here. In accordance with this expectation, the indexing of NaC_{64} results in a better fit if the quadrupling of the c axis is assumed to occur. While this evidence is presumptive rather than conclusive, the quadrupling will be assumed to occur for the remainder of this discussion.* Since in the "even" structures the c-axis is already doubled, the new factor gives us a c-axis which comprises eight metal-to-metal spacings for "even" and four for "odd" structures. The open circles in Figure 1 show the shifts in the positions of the metal atoms from layer to layer for both cases, the sequence of translations being determined by the 2_1 axis. The origin of the unit cell is placed on the twofold screw axis in the center of the four or eight available positions. It is quite evident that this makes all of these compounds orthorhombic. In fact, all symmetry elements can now be deduced, and space group $C222_1$ can be uniquely chosen as the correct one for both odd and even octal structures. Figure 4 shows projections of the unit cell for a representative compound. The hypothetical NaC_{24} has been chosen merely to reduce the number of carbon planes that it is necessary to draw. Figure 5 is a

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* Should this assumption be in error, then the even structures would belong to space group Cmcm. No fit has been found for the odd structures in that case. Also, a structure factor calculation for NaC_{64} on the basis of space group Cmcm leads to calculated intensities drastically at variance with those observed, whereas satisfactory agreement is obtained on the basis of space group $C222_1$.

partial representation of the hypothetical compound NaC_{48} to illustrate the deduction of the z parameters for such a structure. Except for these remarks, no further explanation is required for the discussion of atomic parameters that follows.

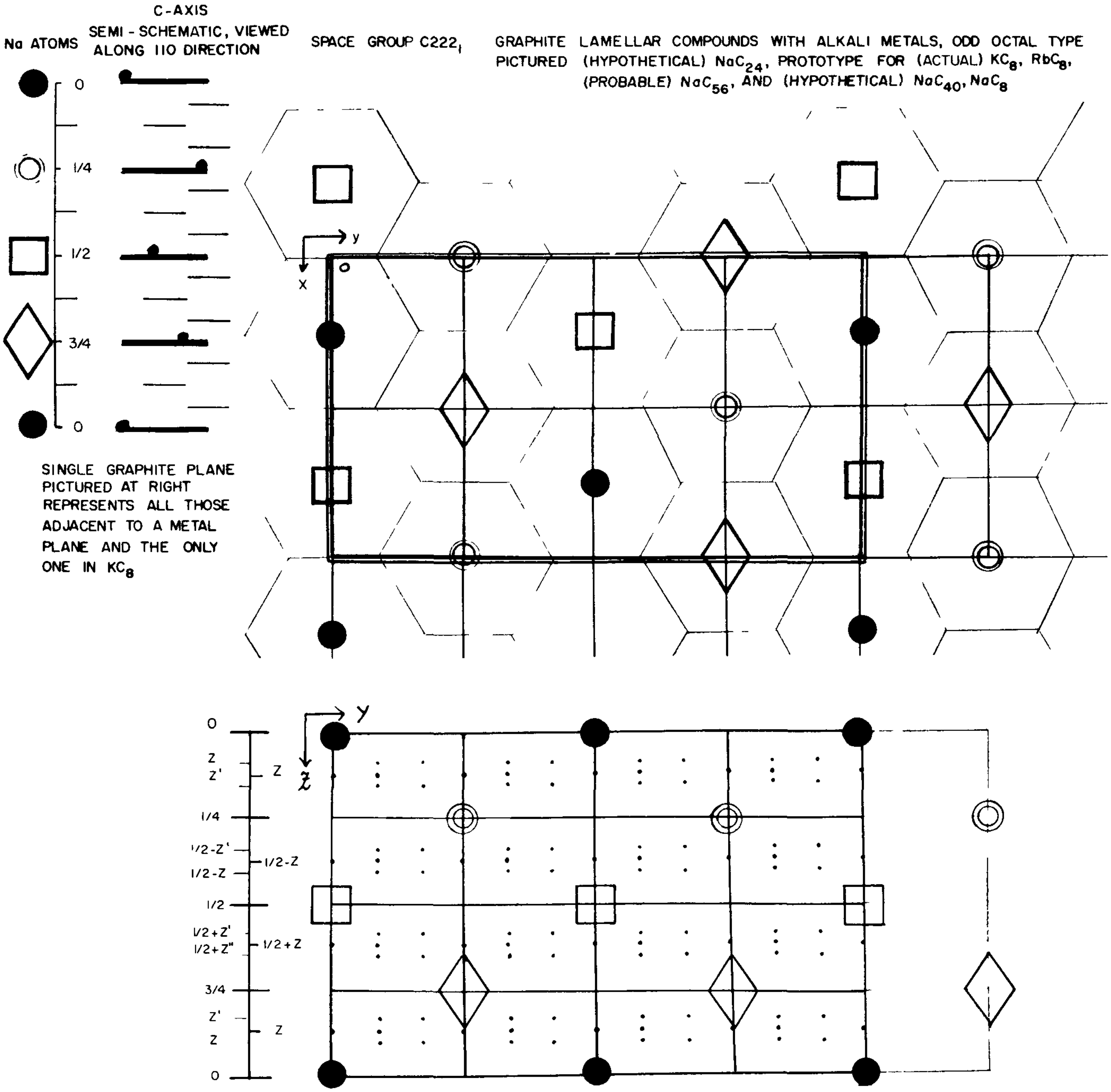

Figure 4. Projections of the Unit Cell

The number of z parameters and their numerical values both depend on the distance between the metal layer and the adjacent carbon layer and on the number of carbon layers between successive metal layers. The following diagram will illustrate this for the case of NaC_{48}.

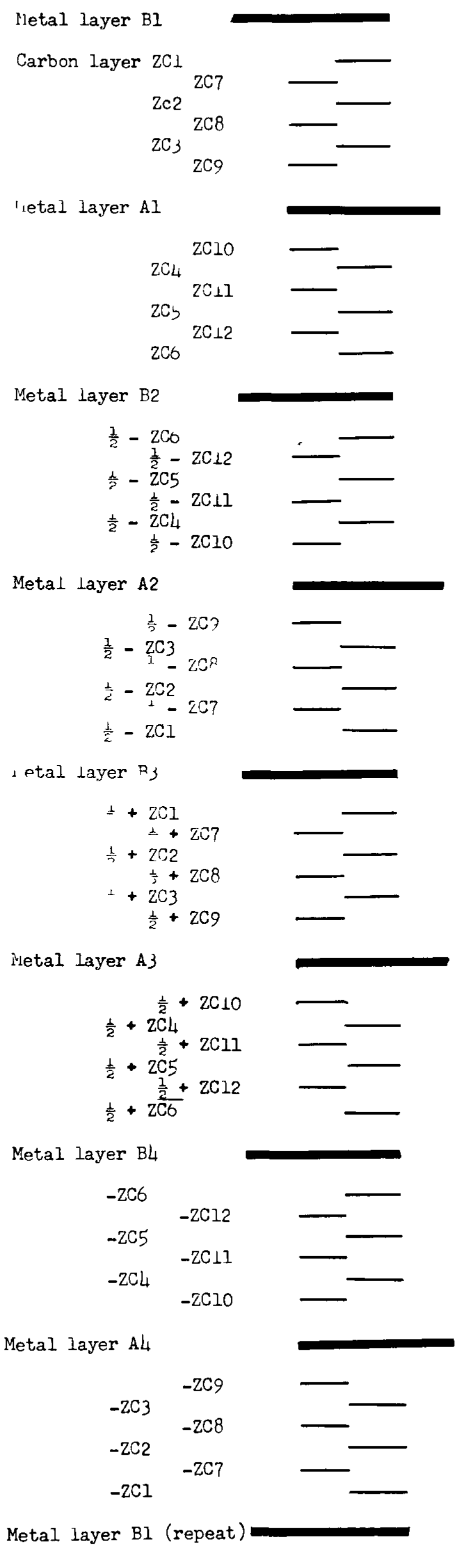

Figure 5. Partial Representation of NaC_{48} (Schematic side elevation of c-axis)

III. ATOMIC PARAMETERS ("OCTAL" STRUCTURES)

1) The space group is $C222_1$; the nomenclature and conventions are those of the International Tables for X-Ray Crystallography, 1952 edition.

2) Four metal atoms occupy the special set "a" of fourfold position x, 0, 0, where x = 1/4.

3) Four metal atoms occupy the special set "b" of fourfold position 0, y, 1/4, where y = 1/4.

4) In those compounds having the "even" structure, there are eight additional metal atoms in the general set "c" of eightfold positions x, y', z, where x = 1/4
y' = 1/6
z = 1/8

5) The carbon atoms are all in the general positions x, y, z of the eightfold set "c".

6) The x and y parameters for the carbon atoms are common to all compounds in the series.

7) The z parameters differ from compound to compound, both as to numerical values and to how many such parameters there are.

8) In the "odd" structures, the number of z parameters equals the number of carbon planes between two succeeding metal layers. In the "even" structures, because of the doubling of the c-axis, there are twice as many.

9) Each time the set "c" is used, it creates eight carbon atoms at four different levels, i. e. two per layer in each of four different layers.

10) Since there are 16 carbon atoms per layer per unit cell, the set must be used eight times, with eight sets of x and y, to create full layers four at a time.

11) If the carbon layer adjacent to the zero-plane metal layer is called type A, then all A-type carbon layers have the following x and y parameters.

0, 1/12	1/4, 1/6
0, 5/12	1/4, 1/3
0, 7/12	1/4, 2/3
0, 11/12	1/4, 5/6

The B-type layers have the following coordinates:

0, 1/4	1/4, 0
0, 5/12	1/4, 1/6
0, 3/4	1/4, 1/2
0, 11/12	1/4, 2/3

The z parameters depend on a knowledge of the layer separations. In graphite, successive planes are spaced 3.35 Å apart. This distance remains unchanged in the lamellar compounds except where a metal layer is inserted. The distances between layers of metal and carbon, as found experimentally, are shown below.

Metal	Vertical layer Distance (Å)	Closest approach, metal to carbon* (Å)
Na	2.29	2.69
K	2.70	3.05
Rb	2.83	3.16
Cs	2.97	3.30

---

* The distances of closest approach between metal and carbon have been shown[4] to be approximated quite well by the sums of the Goldschmidt metallic radii for coordination number 12 and the covalent radius for carbon. It may be pertinent to point out that even better agreement is obtained by adding the ionic radii of the metals to one-half the layer separation in graphite. Hennig,[6] who has investigated the electrical properties of many lamellar compounds, has concluded that the intercalated material is fractionally ionized, the fraction being close to one-third in the case of alkali metals.

The preceding information is sufficient to calculate the z parameters for any desired compound. As an example, the calculation is performed here for a sixth-stage sodium compound, the hypothetical NaC_{48}.

c_o = 170.64 Å, and the z parameters, in fractions of c_o, are

(A-type)	(B-type)
ZC1 = 0.01342	ZC7 = 0.03305
ZC2 = 0.05268	ZC8 = 0.07232
ZC3 = 0.09195	ZC9 = 0.1116
ZC4 = 0.1581	ZC10 = 0.1384
ZC5 = 0.1973	ZC11 = 0.1777
ZC6 = 0.2366	ZC12 = 0.2169

The derivation of these parameters is shown schematically in Figure 5.

APPENDIX
STRUCTURE FACTORS

It is likely that a few additional members of a sodium family of lamellar compounds will be found. When observed, their identification will be aided by the fact that their X-ray patterns can be predicted (page 5). In addition, a knowledge of the structure factors would be helpful.

A complete structure factor computation for sodium - graphite lamellar compounds has been carried out with the aid of a computer. In those compounds that are relatively dilute in sodium — such as NaC_{64} — the sodium contribution to the X-ray intensities is always small, and strong reflections are strong because of a large contribution from the carbon atoms. In such compounds, only the following lines will be strong (indices based on orthorhombic cell):

Class of reflection	Even structures	Odd structures
00ℓ	if $\ell = 8n$	if $\ell = 4n$
40ℓ	if $\ell = 0$ or $8n$	if $\ell = 0$ or $4n$
26ℓ		
66ℓ		

The following will be medium to strong:

04ℓ	for all values of ℓ, except $\ell = 2 + 4n$ and $\ell = 17$	for all values of ℓ, except $\ell = 2 + 4n$
22ℓ		
08ℓ		
44ℓ		
42ℓ		
48ℓ		

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