have the $4d^{10}$ configuration in the ground state and have a preference for the tetrahedral sites. The dsp^2 hybridization for In^{3+}, suggested by Goodenough & Loeb (1955), does not appear feasible on energy considerations. Recently Miller (1959) has calculated site preference energy in spinels for different cations, and accordingly it can be concluded that the 'inverse' structure is more stable than the 'normal' by about 11 kcal./g.mol. and hence the structure should be almost completely 'inverse' at room temperature.

Further discussion of the structure along with the infrared absorption analysis results will be published elsewhere.

Our thanks are due to Dr A. P. B. Sinha for valuable discussions.

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Tetrahedral structures in amorphous carbons.

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The two well-known crystalline forms of carbon are graphite and diamond (face-centered cubic). X-ray diagrams of amorphous carbon contain three or more diffuse bands. Heretofore emphasis has been placed on the fact that the angular positions of these bands correspond approximately to the positions of the (002), (100), (110), etc., reflections of graphite.

Strong peaks at the angular positions of the (00*l*) reflections of graphite lattice tend to support the presence of graphite-like layers (turbostratic) in carbons (Warren, 1941; Biscoe & Warren, 1942). However, some non-graphitizing (Franklin, 1951) carbons have weak peaks at these angular positions and qualitative and quantitative deductions regarding their structure are based on profile analyses of the scattering intensities in terms of the (*hk*) reflections of graphite-like layers and Fourier transforms of the scattering intensities (Franklin, 1950). The hardness, density and non-graphitizability of some carbons do not appear to be entirely compatible with a graphite-like structure. Therefore, theoretical work on the scattering intensities of tetrahedrally-bonded structures of carbon appeared desirable. Preliminary results are presented here, and full details will be published later.

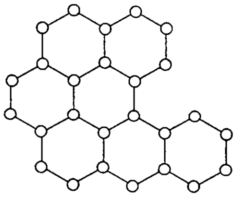
A graphite-like layer containing 26 carbon atoms (Fig. 1, Model No. 20) was first considered. The intensity $J(s)$ in atomic units, scattered at any angle 2θ, was computed by the Debye formula (Debye, 1915):

$$J(s)=\sum_{r}(n(r)/N)\sin 2\pi rs/(2\pi rs)$$

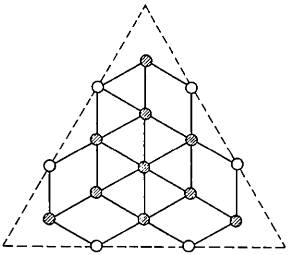
where $s=2\sin\theta/\lambda$, $n(r)$ is the number of interatomic distances of length r within the molecule, irrespective of direction, and N is the total number of atoms in the molecules. All carbon bonds were taken to be of equal length, 1·4174 Å (cf. Diamond, 1957) and all interbond angles to be 120°. After determining the interatomic distances and their number, intensity data were computed numerically on the Univac 120. The results are shown in Fig. 2 (solid line).

A molecule containing 26 carbon atoms arranged in a diamond type lattice shown in Fig. 1 (Model No. 12) was next considered. The molecule formed a tetrahedron. All carbon bonds were taken to be 1·5420 Å in length and all interbond angles 109° 28·4′, the tetrahedral bond angle. The computed curve is shown in Fig. 2 (dashed line).

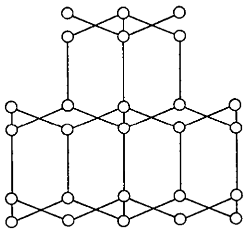
In a diamond lattice carbon atoms form cross-linked buckled layers composed of six-membered rings (chair type). Cross-linking is in such a manner that it yields a face centered cubic lattice, i.e., the projections on the (111) planes of the adjacent buckled layers do not superimpose. If the projections do superimpose a hexagonal



Model No. 20. Graphite-like layer



Model No. 12. Projection of tetrahedron on (111) plane of diamond lattice. Shaded circles show superimposed atoms.



Model No. 19. Projection of hexagonal lattice on (100) plane.

Fig. 1. Diagrams of models considered.

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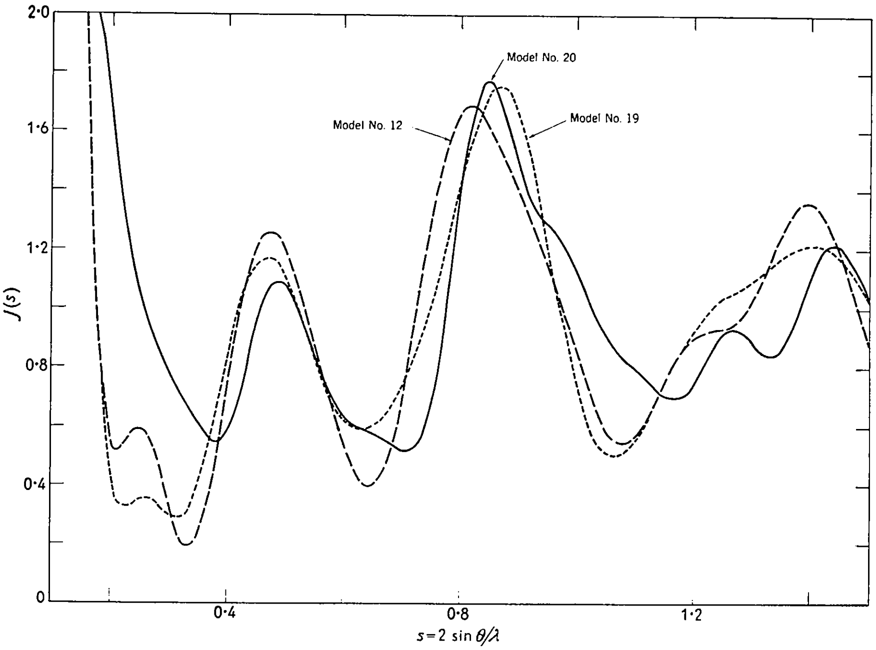

Fig. 2. Calculated X-ray scattering intensities of a graphite-like layer (solid line), a cubic diamond-like lattice (dashed line), and a hexagonal diamond lattice (dotted line) each containing 26 carbon atoms.

lattice is formed. A molecule composed of 26 carbon atoms forming a hexagonal lattice, Fig. 1 (Model No. 19) was also considered. For this structure bond distances and bond angles were taken to be the same as in regular diamond lattice. The computed curve is shown in Fig. 2 (dotted line).

It is seen that clusters of tetrahedrally bonded carbon atoms give rise to diffraction bands in approximately the same angular region where the two-dimensional (10) and (11) reflections of graphite-like layers occur, that is at s values of about 0·5 Å^{-1} and 0·85 Å^{-1}, respectively. The corresponding bands are the (111) and (220) bands of cubic diamond lattice and (100) and (110) bands of hexagonal diamond lattice. From the diffuse diffraction peaks that many amorphous carbons produce in these angular regions, it is very difficult to ascertain if graphite-like or diamond-like structures, or both, are present (cf. Fig. 8, Franklin (1950) and Fig. 2 of the present communication). Indeed, diamond-like structures may explain some of the difficulties that are encountered in matching the (10), (21) and (22) bands when experimental and theoretical curves are matched over the (11) band region assuming only graphite-like and amorphous structures.

A Fourier integral analysis made by Warren (1934) of the X-ray scattering intensities of a carbon black yielded atomic distribution curves which compared favorably with the atomic arrangement of a single graphite layer rather than that of diamond (both containing an infinite number of atoms). However, if one considers small crystallites containing finite numbers of atoms, a choice between graphite-like and diamond-like structures becomes very difficult, if not in favor of diamond lattice. For example, a tetrahedron containing 51 carbon atoms in a diamond lattice yields interatomic distances and distributions very close to those of carbon black obtained by Warren (1934). It is not suggested here that carbon blacks are composed of tetrahedrally-bonded structures; the blacks apparently have strong (002) reflections suggesting trigonal and π bonded structures. Rather, it is intended to demonstrate that Fourier transforms of the Debye equation may not always permit to distinguish between graphite-like and diamond-like structures. This is especially true if the Debye equation in its original form yields overlapping intensity curves ($J(s)$ functions).

The overlap of the X-ray scattering curves of diamond-like and graphite-like structures makes it equally difficult to ascertain the presence of diamond-like structures in amorphous carbons. Therefore other properties of carbons such as hardness, density, electronic absorption, graphitizability, etc. must be considered. Some amorphous carbons do not graphitize with heat treatment (Franklin, 1951); it appears reasonable to suppose that they contain diamond-like structures (cubic, hexagonal or both) in appreciable quantities.

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