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On the influence of binding electrons on X-ray intensities.

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The influence of the non-centrosymmetrical distribution of binding electrons on the scattering factor of the covalently bonded carbon atoms in diamond has been studied first by Ewald & Hönl (1936*a*, *b*). These authors calculated the electron distribution in diamond in zero approximation by means of wave mechanics and found that an electron density of axial symmetry is superimposed to the electron cloud of spherical symmetry of the C-atom. The superimposed charge was estimated at about $\frac{1}{2}$ electron per bond. The influence which this has on the X-ray intensity was taken care of by introducing a special term into the structure factor corresponding to the scattering power of this accumulation located at the center between two carbon atoms. In this way Ewald & Hönl calculated the structure factors for the reflexions of diamond in fair agreement with the observation. Later McWeeny (1954) performed a calculation of the scattering factor for the covalently bonded C-atom and showed that there exsits a difference with respect to the scattering factor of the C-atom in the valence state, which is restricted to a small region in reciprocal space of $0{\cdot}2 < \sin\theta/\lambda < 0{\cdot}5$. In this region the magnitude of the scattering factor of the bonded atom is a little smaller than that of the unbonded one and its magnitude depends also slightly upon the orientation of the atom with respect to the incident beam. An attempt to fit McWeeny's values for the bonded atom with the experimental values (Brill *et al.*, 1939) failed however. In particular the experimentally observed intensity of 111 is much too high. Remeasurement of this intensity (Brill *et al.*, 1959) confirmed the formerly observed value which is about 20% higher than it should be. This discrepancy disappears, however, if the structure factor of diamond is written in the form

$$F_H = f_c \sum_{1}^{8} \exp\left(-2\pi i H X_n\right) + f_\varepsilon \sum_{1}^{16} \exp\left(-2\pi i H X'_n\right), \quad (1)$$

where f_c is approximately* the atomic scattering factor for the carbon atom in the valence state, X and X' are the parameters for the carbon atoms and the points at the center between two carbon atoms respectively, and f_ε is the scattering factor of the electron accumulation due to the covalent bond. It is

$$f_\varepsilon = 0{\cdot}45 \exp\left(-8{\cdot}1 (\sin\theta/\lambda)^2\right). \quad (2)$$

The combination of equations (1) and (2) gives the values of F_{111} and also that of the 'forbidden' reflexion F_{222} in agreement with observation. Furthermore it renders the fact that the observed intensity of 220 agrees with the theoretical value calculated with McWeeny's scattering factor in the valence state, because in this case the contribution of the second term in equation (1) is zero. Equation (1) also reflects quite well the observed deviations of the atomic scattering factors from the smooth curve calculated in the usual way from the intensities of the reflexions 311, 400 and 331 (see Fig. 1). It leads also to the result that 622 is not observable since its F-value should be about 10^{-4}.

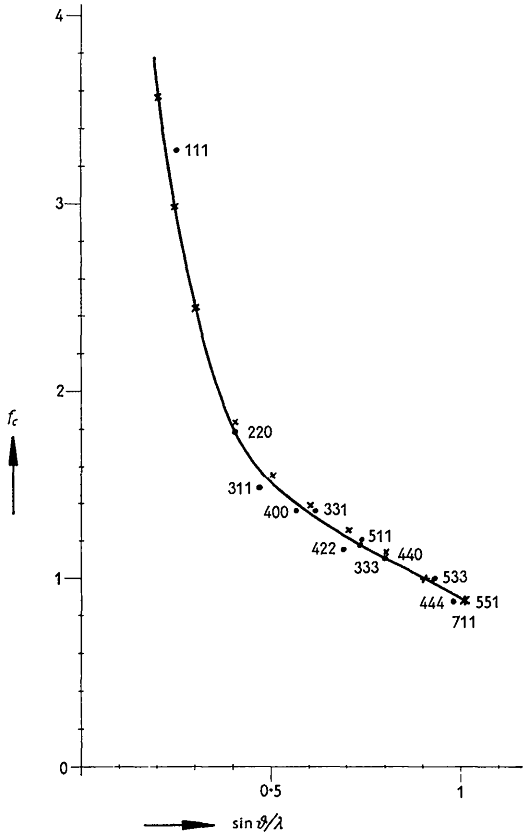

Fig. 1. Atomic scattering factor for diamond:

● experimental values, × theoretical values for the C-atom in the valence state after correcting for heat movement. The smooth curve is partially a compromise between experimental and theoretical values.

It must be concluded, therefore, that the procedure adopted by Ewald & Hönl (1936), which is represented by equation (1), seems to be well suited to represent the observation. Indeed, the reliability factor is 0·084 if the first term of equation (1) alone is used to calculate the theoretical intensities on the assumption that all orders higher than 331 have been measured correctly, i.e., that their intensities agree with the calculated ones. However, the reliability factor becomes 0·04 if the full equation (1) is used with the same f_c-values and also otherwise the same assumptions. Of course, the influence of the binding electrons is especially large in the case of diamond because its characteristic temperature is so high. For organic compounds with more pronounced temperature

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* It has to be taken into account that f_c must approach a value smaller than 6 if $\sin\theta/\lambda$ approaches zero to fulfill the condition $\frac{1}{8}F_{000} = 6{\cdot}0$.

vibrations the binding electrons may not influence the reliability factor to the same extent. But, whenever the reliability factor is used as a criterion for the determination of parameters and the intensities have been measured at low temperatures, the asymmetry of the carbon atom will play a role, and formulas corresponding to equation (1) should be used. It should also be taken into account that, if the elementary cell is very large, the intensities of low orders may be appreciably influenced by the binding electrons and even forbidden reflexes may appear.

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Crystal data for some naphthalene derivatives.

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The interesting results obtained from the analyses of the crystal structures of several derivatives of anthracene have prompted investigations of the structures of some naphthalene derivatives. It is hoped to carry out complete analyses of several crystals and to compare the bond lengths in the naphthalene skeletons with those in the parent molecule. In the meantime the crystal data are outlined here.

Crystal data

1-Naphthoic acid, $C_{11}H_8O_2$.

Monoclinic, $a = 31{\cdot}12$, $b = 3{\cdot}87$, $c = 6{\cdot}92$ Å, $\beta = 92{\cdot}2°$.
Volume of the unit cell $= U = 832{\cdot}8$ Å^3,
D_m (measured density) $= 1{\cdot}380$ g.cm.$^{-3}$,
$Z = 4$, D_x (calculated density) $= 1{\cdot}373$ g.cm.$^{-3}$.
Space group $P2_1/a$–C_{2h}^5.

2-Naphthoic acid, $C_{11}H_8O_2$.

Monoclinic, $a = 30{\cdot}59$, $b = 5{\cdot}00$, $c = 5{\cdot}63$ Å, $\beta = 92{\cdot}6°$.
$U = 858{\cdot}8$ Å^3, $D_m = 1{\cdot}320$ g.cm.$^{-3}$, $Z = 4$, $D_x = 1{\cdot}332$ g.cm.$^{-3}$.
Space group $P2_1/n$–C_{2h}^5.

1,2-Dichloronaphthalene, $C_{10}H_6Cl_2$.

Monoclinic, $a = 15{\cdot}11$, $b = 3{\cdot}92$, $c = 14{\cdot}86$ Å, $\beta = 96{\cdot}0°$.
$U = 875{\cdot}4$ Å^3, $D_m = 1{\cdot}494$ g.cm.$^{-3}$, $Z = 4$, $D_x = 1{\cdot}495$ g.cm.$^{-3}$.
Space group $P2_1/n$–C_{2h}^5.

1,4-Dibromonaphthalene, $C_{10}H_6Br_2$.

Monoclinic, $a = 27{\cdot}45$, $b = 16{\cdot}62$, $c = 4{\cdot}09$ Å, $\beta = 91{\cdot}9°$.
$U = 1864{\cdot}9$ Å^3, $D_m > 2{\cdot}00$ g.cm.$^{-3}$, $Z = 8$, $D_x = 2{\cdot}037$ g.cm.$^{-3}$.
Space group $P2_1/a$–C_{2h}^5.

1,5-Dinitronaphthalene, $C_{10}H_6N_2O_4$.

Monoclinic, $a = 7{\cdot}76$, $b = 16{\cdot}32$, $c = 3{\cdot}70$ Å, $\beta = 101{\cdot}8°$.
$U = 458{\cdot}7$ Å^3, $D_m = 1{\cdot}578$ g.cm.$^{-3}$, $Z = 2$, $D_x = 1{\cdot}579$ g.cm.$^{-3}$.
Space group $P2_1/a$–C_{2h}^5.

Crystal data for 1-naphthoic acid have been reported previously (McCrone, 1953), the axial lengths agreeing well with those of the present investigation, but the crystal system being reported as orthorhombic. The *h0l* Weissenberg films of all the crystals of 1-naphthoic acid examined in the present analysis do indeed exhibit orthorhombic symmetry at first sight, but closer examination of both the positions and intensities of the reflexions leaves no doubt that the crystals are monoclinic, but twinned on (100).

The structure analysis of 1,5-dinitronaphthalene has been completed (Trotter, 1960), and has shown that the molecule is not completely planar as previously reported (Sevastyanov, Zhdanov & Umansky, 1948). Details of the other structures will be reported in later communications.

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