Discussion

The patterns in Figs. 1–3 may be considered to be a composite of three superimposed nets each corresponding to the CuAu I tetragonal structure, in the three orientations drawn in Fig. 5. The three nets superimposed in this way account for the three spots observed at the {200} positions. The diffuse character of the diffraction spots in Figs. 1 and 2 can be interpreted respectively as a consequence of small domain size (Fig. 1) and imperfect order within the domains (Fig. 2).

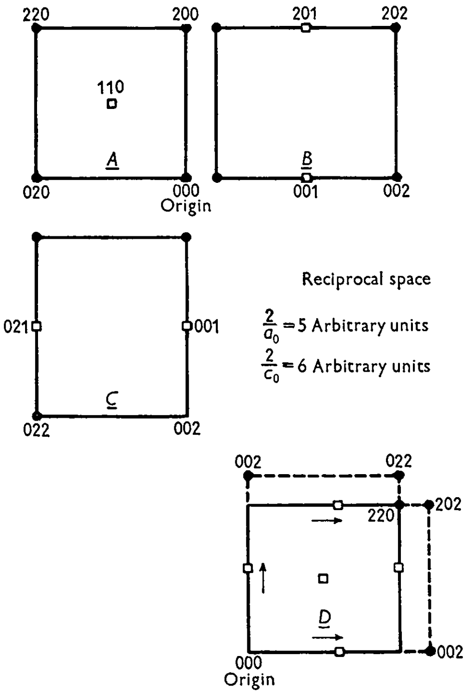

Fig. 5. Four figures in reciprocal space. In A the C axis is ⊥ to the paper and in B and C the axis is lying in opposite directions in this plane. The diagram D shows how, by superimposing these planes, the three spots can be accounted for in the pattern.

The splitting of the superstructure reflections (Figs. 2 and 3) into four symmetrically arranged intensity spots may be interpreted as arising from an elongated unit cell made up of five tetragonal cells in line with five more cells displaced $\frac{1}{2}a_0+\frac{1}{2}c_0$. This constitutes a multiple unit cell made up of ten ordered tetragonal cells bisected by an 'out-of-step' boundry and is identical with the cell proposed by Johannssen & Linde (1936) see Fig. 6. These effects are similar to diffuse X-ray effects given by Cu_3Au. Their interpretation is the same as that given by Guinier & Griffoul (1948).

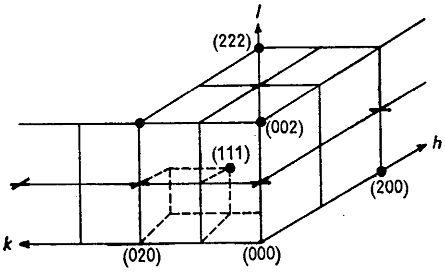

Fig. 6. Reciprocal lattice of AuCu II position of crosses as they appear in reciprocal space.

Throughout this study the author has had the benefit of many helpful suggestions from Dr B. W. Roberts.

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X-ray Scattering from CCl_4

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By using a recent development for the calculation of the X-ray scattering from a gas of non-spherical molecules the scattering factor for CCl_4 has been computed. In this way it was possible to establish some comparison with experiment regarding the 'valence' electron distribution in such a molecule when described by a Thomas–Fermi method. Further, a test was provided of the range of applicability of the general treatment used for evaluating the scattering factor.

1. Introduction

In a recent paper by Coulson & March (1956) a modified Thomas–Fermi (T.F.) treatment was developed for tetrahedral and octahedral molecules with heavy atoms in the outer positions. Whilst retaining within their approximation the simplicity of a centralfield problem, their scheme allowed the inner-shell and valence electrons to be treated separately and at the same time the exclusion principle to be imposed. This scheme was applied to CCl_4 by Banyard & March (1956), a comparison then being made between the distribution of valence electrons resulting from each of three methods. These were, firstly, the two methods proposed earlier by March (1952), viz. (i) a straightforward T.F. treatment in which the nuclear charges of the outer atoms were smeared out over the surface of a sphere whose radius was equal to the C–Cl bond length, and (ii) a more drastic 'compression model' whereby the T.F. method was applied to a system in which the *K*- and *L*-shell Cl electrons were first compressed into the nuclei and the smoothing approximation then applied to the effective nuclear charges. Finally, method (iii) was the modified T.F. scheme developed by Coulson & March (1956).

The discussion of Banyard & March (1956) makes it of interest to attempt some comparison with experiment for CCl_4, particularly with a view to gaining further insight into the usefulness of such methods for molecules having highly localized inner-shell electrons. The recent development of a general treatment for evaluating the X-ray scattering from a gas of non-spherical molecules provides us with a means of correlation with experiment. Further, the application of this treatment to CCl_4, with its heavy outer atoms, will provide a ready test of its range of applicability in determining the scattering factor for such a molecule.

2. Evaluation of the scattering factor

From a knowledge of the electron density within a molecule, Banyard & March (1957) have shown how the X-ray scattering factor, $f(\varkappa)$, may be determined for a gas of non-spherical molecules. Following their notation, they showed that the general expression

$$\bar{I}_s/I_e = f^2(\varkappa) = \iint \varrho(\mathbf{r}_1)\varrho(\mathbf{r}_2)\frac{\sin(\varkappa r_{12})}{\varkappa r_{12}}d\tau_1 d\tau_2 \qquad (1)$$

for the mean coherent scattering (see, for example, Pirenne (1946), p.57) as a function of $\varkappa = 4\pi(\sin\frac{1}{2}\theta)/\lambda$ can be reduced to the form

$$f^2(\varkappa) = \sum_{n=0}^{\infty}\sum_{m=-n}^{+n} f^*_{nm}(\varkappa)f_{nm}(\varkappa) \qquad (2)$$

where

$$f_{nm}(\varkappa) = (2\pi)^{3/2}\int_0^\infty \varrho_{nm}(r)\frac{J_{n+\frac{1}{2}}(\varkappa r)}{(\varkappa r)^{\frac{1}{2}}}r^2 dr \qquad (3)$$

and

$$\varrho(\mathbf{r}) = 2^{\frac{1}{2}}\sum_{n=0}^{\infty}\sum_{m=-n}^{+n}\varrho_{nm}(r)\Theta_{nm}(\theta)e^{im\varphi}. \qquad (4)$$

The valence-electron distribution for CCl_4 obtained by methods (i), (ii) and (iii) and the density of the two *K*-shell electrons of carbon possess spherical symmetry. However, it is realized that the localization of the ten *K*- and *L*-shell electrons centred on each Cl nucleus will appreciably influence the form of the scattering factor. Thus, the density of these regions of Cl inner-shell electrons described by Slater wave functions following method (iii) is expressed in the form of equation (4) taking the carbon nucleus as origin.

The scattering contribution from the $\Theta_{00}(\theta)$ term in the total electron-density expansion is seen from (3) to be

$$f_{00}(\varkappa) = \int_0^\infty \varrho_{00}(r)\frac{\sin(\varkappa r)}{(\varkappa r)}4\pi r^2 dr\,, \qquad (5)$$

where $\varrho_{00}(r)$ is the sum of (*a*) the density of the $2-1s$ inner-shell electrons of carbon, (*b*) the 40 Cl inner-shell electrons when averaged over angles, and (*c*) the distribution of the so-called 32 valence electrons. Thus, all the subsequent angular terms included in the present account arise from allowing the 40 Cl inner-shell electrons to retain their localized unperturbed form. Using the densities for (*a*), (*b*) and (*c*) obtained by method (iii) (see Banyard & March, 1956; Figs. 3, 1 and curve (1) of Fig. 4 respectively) the integrals were evaluated by standard numerical procedure for various values of $(\sin\frac{1}{2}\theta)/\lambda$; atomic units

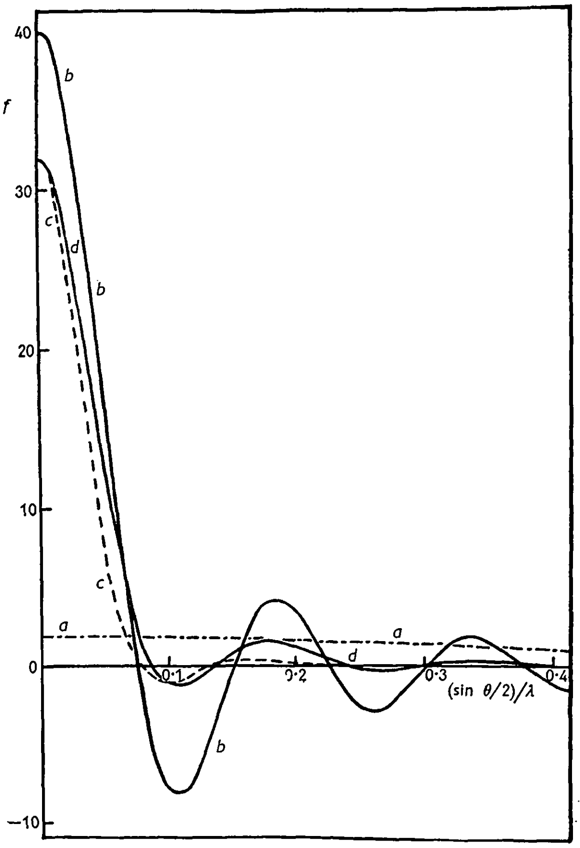

Fig. 1. Contributions to the X-ray scattering factor. Curve (*a*), the two 1*s* carbon electrons; curve (*b*), the averaged Cl inner-shell electrons; curves (*c*) and (*d*), the valence electron distributions from methods (iii) and (ii) respectively.

were used throughout this work. For comparison, the corresponding calculation was performed using the valence density obtained by the 'compression model', (ii) (see Banyard & March, 1956; curve (3) of Fig. 4). The results are shown here in Fig. 1. The scattering contribution using the valence distribution from (i) (see Banyard & March, 1956; curve (2) of Fig. 4) was not computed since it would closely resemble curve (*c*) of Fig. 1.

Following Cundy (1937), the angular terms in the expansion of the Cl inner-shell density are

$$\Theta_{32}(\theta)\sin 2\varphi,\ \Theta_{40}(\theta),\ \Theta_{44}(\theta)\cos 4\varphi,\ \Theta_{60}(\theta),\ \Theta_{64}(\theta)\cos 4\varphi,\ \ldots .$$

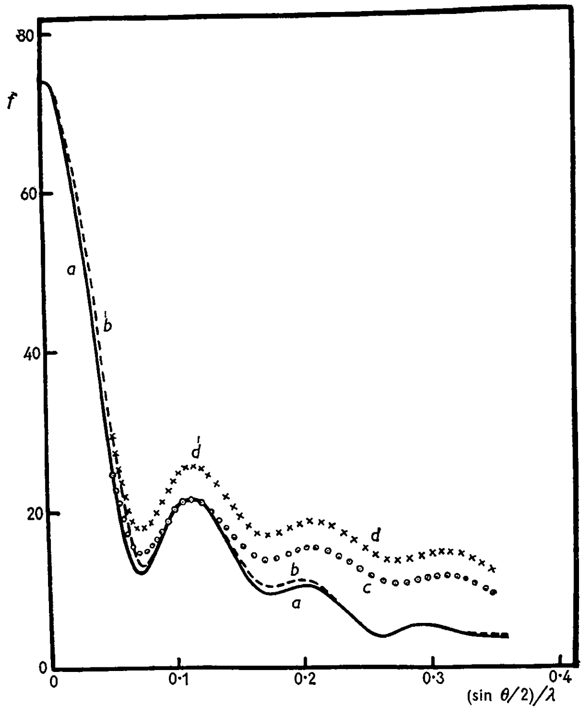

Fig. 2. X-ray scattering factor for CCl_4. Theoretical: Curves (*a*) and (*b*), using the distribution of valence electrons from methods (iii) and (ii) respectively. Experimental: Curves (*d*) and (*c*), extracted from the fitted experimental curves of van der Grinten and the present work respectively.

The functions $f_{nm}(\varkappa)$ of equation (3) were computed for various values of $(\sin\frac{1}{2}\theta)/\lambda$ for all terms up to $\Theta_{60}(\theta)$ inclusive. Using equation (2), the X-ray scattering factor for CCl_4 was determined. The results are presented as a function of $(\sin\frac{1}{2}\theta)/\lambda$ and are shown in Fig. 2. Curve (*a*) is for method (iii) and curve (*b*) is for the case when the valence electrons are described by (ii), namely the 'compression model'.

3. Discussion of experimental results

The graphical representation of the total scattered intensity from CCl_4 as a function of $(\sin\frac{1}{2}\theta)/\lambda$ obtained by van der Grinten (1933) (see Fig. 7) proves a suitable source of experimental data. Although the intensity scale is not quoted this can be evaluated since van der Grinten fitted his experimental curve to a total theoretical scattering curve calculated by using the expression in parenthesis from his equation (8). The incoherent part of the scattered intensity was calculated using the method of Heisenberg–Bewilogua (1931), whereas the mean coherent intensity was determined by the 'interference-like' treatment (see, for example, Pirenne, 1946, p. 58). The theoretical and fitted experimental intensity curves of van der Grinten are coincident in the region of the first maxima. A calculation of the total theoretical scattering for the corresponding values of $(\sin\frac{1}{2}\theta)/\lambda$ immediately fixed the intensity scale. Assuming, for the present, that we now know the absolute intensity scale, the mean coherent scattering was then extracted from the fitted experimental curve, the method of Heisenberg–Bewilogua being used for the incoherent intensity. Curve (*d*) of Fig. 2 shows the resulting coherent scattering factor plotted as a function of $(\sin\frac{1}{2}\theta)/\lambda$.

At this point it was thought profitable to present the experimental results in a slightly different manner. Following van der Grinten, his experimental curve was fitted in the region of the first maxima to the total theoretical intensity curve obtained here, this being the sum of the coherent scattering of § 2 and the incoherent intensity evaluated as before by the method of Heisenberg–Bewilogua. The mean coherent intensity was then extracted from this scaled experimental curve. The result is shown in curve (*c*) of Fig. 2 in the form of the scattering factor expressed as a function of $(\sin\frac{1}{2}\theta)/\lambda$. Experimental results for $(\sin\frac{1}{2}\theta)/\lambda < 0{\cdot}05$ were unobtainable from van der Grinten's work; thus curves (*c*) and (*d*) of Fig. 2 terminate at that value.

4. Discussion of results

Convergence of the series (2) when applied to CCl_4 was by no means as rapid as that found on application to other molecules, for example H_2O (see Banyard & March, 1957). This is not so surprising since the intense localization of charge about the Cl nuclei naturally increases the importance of the angular terms in the expansion of the density. It should perhaps be emphasized here that in the present work all angular terms in the density expansion, i.e. terms not involving $\Theta_{00}(\theta)$, arise solely from the existence of the localized Cl inner-shell electrons. By including those terms stated in § 2 convergence of (2) to within graphical accuracy was obtained for $(\sin\frac{1}{2}\theta)/\lambda < 0{\cdot}14$. It was interesting to note not only how the inclusion of higher angular terms caused the convergence to extend to larger values of $(\sin\frac{1}{2}\theta)/\lambda$, but also how their inclusion by means of (2) caused the maxima and minima in the subsequent scattering curve to move steadily towards higher values of $(\sin\frac{1}{2}\theta)/\lambda$. This is thought to explain why, for example, the third 'peak' in the theoretical scattering curve is situated at a smaller value of $(\sin\frac{1}{2}\theta)/\lambda$ than is the corresponding 'peak' of the experimental curves. The lack of coincidence on the $(\sin\frac{1}{2}\theta)/\lambda$ scale of equivalent regions between the experimental and theoretical curves was found to be indicative of the lack of convergence of series (2) in that region of $(\sin\frac{1}{2}\theta)/\lambda$.

In the absence of any absolute scale associated with van der Grinten's experimental curve, it initially seemed worth while to make a comparison between our theoretical curve (*a*) and the corresponding fitted curve (*c*) of experiment, see Fig. 2. Even allowing for the lack of convergence, which is in fact small in the region of the second minima although increasing considerably as we approach the third maxima, the agreement is not good. This, coupled with the excellent correspondence obtained between the curves of van der Grinten (see his Fig. 7 or Pirenne, 1946, Fig. 52) over such a large range of $(\sin\frac{1}{2}\theta)/\lambda$ leads one to suppose that curve (*d*) of Fig. 2 based on his results might well be regarded as a measure of the absolute experimental scattering.

Although the agreement between the theoretical and fitted experimental curves of van der Grinten was so good, the use of the 'interference-like' treatment for calculating his theoretical scattering curve is less fundamental than that described here, in which use was also made of the results of Banyard & March (1956).

The difference between the contributions to the total coherent scattering factor provided by the valence electrons when described by methods (ii) and (iii) (see curves (*d*) and (*c*) of Fig. 1 respectively) is reflected in the corresponding scattering curves of Fig. 2. From Fig. 2 we see that the valence-electron distribution given by method (ii) results in a scattering curve (*b*) which appears to be in slightly better agreement with experiment than that obtained from the results of method (iii). However, it must be remembered that (ii), i.e. the 'compression model', is basically less sound than method (iii) since it violates the exclusion principle.

To obtain some indication of the importance of angular terms associated with the distribution of valence electrons in CCl_4, the theoretical curve (*a*) of Fig. 2 was fitted to the experimental curve (*d*) by introducing a semi-empirical multiplicative factor common to all angular terms in the density expansion (4). This is effectively assuming that the overall form of the angular terms for the valence electrons will be very roughly like that for the inner-shell electrons. It should be noted that normalization of the charge distribution is unaffected as this depends only on the first, or radially symmetric, term. Curve (*a*) was fitted only over the range $0{\cdot}08 < (\sin\frac{1}{2}\theta)/\lambda < 0{\cdot}14$ for in this work $(\sin\frac{1}{2}\theta)/\lambda \sim 0{\cdot}14$ was the limit of convergence of series (2); further, in this region the contribution to the scattering factor from the angular terms is far more important than that arising from the spherically symmetric density term. A factor of about 1·2 was found to produce an excellent fit with curve (*d*). This value does not seem unreasonable, and suggests that angular terms associated with the valence electron distribution may be roughly one-fifth as important as those arising from the Cl inner-shell density.

The conclusions which can be drawn from the present work are two-fold. Firstly, that in order to obtain a good description of the valence electron distribution in CCl_4 it appears essential to introduce into any subsequent treatment at least the first few angular terms having the symmetry of the molecule. Secondly, that the application of the expansion of the density in spherical harmonics to the calculation of X-ray scattering has here reached about the limit of its convergence from a practical point of view. Nevertheless, it should be realized that the highly localized inner-shell electrons in CCl_4 afford an extremely stringent test of the method, and evidently the technique has a wide applicability.

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