Reports of the Academy of Sciences of the USSR

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1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 132, No. 1

PHYSICAL CHEMISTRY

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ON THE DETERMINATION OF THE ELECTRON-DENSITY DISTRIBUTION IN CRYSTALS

In the works of Bragg (^{1}) the possibility of applying Fourier series for the purposes of X-ray structural analysis was first demonstrated. The further development of this method (^{2}, ^{3}) made it possible to pose the problem of the distribution of electron density between the atoms of solids from experimentally determined intensities of diffraction maxima on X-ray diffraction patterns. The question of the distribution of electron density in crystals, which determines the character, anisotropy, and energy of interatomic interaction, belongs to the most general problems of the physics and chemistry of solids.

Numerous works (^{4}-^{16}), as well as those mentioned in (^{16}), have been devoted to determining the distribution of electron density in solids.

To determine the distribution of electron density and to find the electron density $\rho(x, y, z)$ at an arbitrary point with coordinates x, y, z of an elementary cell of volume v, it is necessary to sum a three-dimensional Fourier series.

$$\rho(x, y, z) = \frac{1}{v} \sum_h \sum_k \sum_l F(hkl) \exp\left[-2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right)\right], \tag{1}$$

where $F(hkl)$ is the structure amplitude. The number of terms of the series is limited by the number of experimentally determined reflections.

The uncertainty arising from truncation of the series does not make it possible to obtain any clear idea of the actual distribution of electrons in the crystal lattice. Therefore, in a number of works, methods were proposed for eliminating the effect of series truncation by theoretical extrapolation of the f-curve to large values of the sum of the squares of the indices (^{4}), or by introducing the temperature factor e^{-2M} with considerable calculated temperatures of the order of 1000–10000° K (^{5}, ^{6}, ^{8}, ^{9}). Both the first and the second method introduce a considerable error into the results of calculating the electron-density distribution.

The application of the method proposed by Hosemann and Bagchi (^{7}) for determining electron density using operations of "convolution" and extrapolation of the f-curve creates a new possibility. This method, however, is also not free of known shortcomings.

As Nowacki indicates (^{18}), Reitz approximated the f-curve of the atomic scattering factor by a Gaussian function for calculating electron density. In this case the calculation of electron density was reduced to evaluating the Fourier integral and summing the series.

In the present work the possibility is shown of calculating the electron density by summing three-dimensional Fourier series, without introducing a temperature factor and without continuing the extrapolated f-curve, but using only values of the atomic scattering factor that can be obtained with CuKα and less hard radiations.

As is known (^{17}), the outer electrons of an atom introduce changes in the course of the f-curve mainly at small orders of reflection. At high orders of reflection their contribution becomes very small. Therefore the value of the atomic scattering factor can be divided into two parts, due to two groups of electrons with density distributions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$, where $\rho_1(\mathbf{r})$ is the principal part of the electron density, due to electrons located predominantly near the nucleus of each atom, and $\rho_2(\mathbf{r})$ is the remaining part of the electron density, due to electrons located predominantly in the outer part of the atoms. In this case the indicated division into ρ_1 and ρ_2 is not connected with any electron shells. Both functions are defined throughout space.

The distribution of electrons in the first part can, with sufficient approximation, be described by a Gaussian distribution function of the form

$$\rho_1'(r) = Ae^{-\alpha r^2}, \tag{2}$$

for which it is easy to calculate the scattering-factor curve as a function of the order of reflection.

Fig. 1. Change of the atomic scattering factor f as a function of the sum of the squares of the reflection indices of maximum diffraction. a—experimental f-curve of diamond (δ); f_1—calculated f-curve for electrons with a prescribed density distribution; b—experimental f-curve with the temperature factor introduced, with calculated temperature 7500°; f_2—difference of atomic scattering factors determined experimentally and calculated for electrons with the prescribed electron-density distribution

$$f_1 = \int_1^{\infty} Ae^{-\alpha r^2} 4\pi r^2 \frac{\sin \mu r}{\mu r}\, dr = A\frac{\pi^{3/2}}{\alpha^{3/2}} \exp\left[-\frac{\mu^2}{4\alpha}\right], \tag{3}$$

where $\mu = 4\pi \sin \vartheta / \lambda$.

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The quantities α and A are determined from two lines (h_1, k_1, l_1) and (h_2, k_2, l_2) with intensities I_1 and I_2, for $h^2 + k^2 + l^2 > 27$:

$$\alpha = \pi^2 \left(\frac{h_2^2 - h_1^2}{a^2} + \frac{k_2^2 - k_1^2}{b^2} + \frac{l_2^2 - l_1^2}{c^2} \right) \frac{1}{\ln \frac{I_1 C_1}{I_2 C_2}}, \tag{4}$$

$$A = \frac{\sqrt{C_1 I_1}}{(\pi/\alpha)^{3/2}} \exp\left[\frac{\pi^2}{\alpha} \left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2} \right) \right], \tag{5}$$

where C_1 and C_2 are products of the experimentally accounted-for factors.

As we noted above, the f-curve of the first part of the electrons $f_1(hkl)$ at large values of the indices must merge with the experimentally

obtained f-curve. For $h^2 + k^2 + l^2 = 0$ ($\mu = 0$) the value $f_1(0,0,0)$ is equal to the number of electrons in the first part.

Figure 1 shows that, in the case of diamond, the merging of the f_1-curve of the first part of the electrons and the experimentally determined f-curve, within the limits of experimental accuracy, already occurs beginning with the sum of squares $h^2 + k^2 + l^2 = 27$.

Curve f_2 in Fig. 1 represents the difference $f - f_1 = f_2$, due to the electrons of the second part with the unknown distribution ρ_2.

The electron density at any point of the crystal $\rho(\mathbf{r})$ can be represented in the form

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}) = \sum_j \rho_j \exp[-\alpha_j (\mathbf{r} - \mathbf{r}_{0j})^2] +$$

Fig. 2. Calculated values of electron density in the diamond lattice in the [111] direction.

Figure 2: Fig. 2. Calculated values of electron density in the diamond lattice in the [111] direction.

$$+\frac{1}{v}\sum_h\sum_k\sum_l F_2\exp[-2\pi i\mathbf{r}\mathbf{H}]. \tag{6}$$

$\rho_1(\mathbf{r})$ is the given density, obtained by summing the density ρ_1' over all atoms of the lattice; ρ_2 is the required difference between the true and the given densities.

In practice, the calculation of the electron-density distribution reduces to summing the series $\frac{1}{v}\sum_h\sum_k\sum_l F_2\exp(-2\pi i\mathbf{r}\mathbf{H})$.

Figure 2 shows the calculated distribution of electron density in the [111] direction of diamond.

Fig. 2. Calculated values of electron density in the diamond lattice in the [111] direction. *A*—at the calculation temperature (7500° K). *a*—ordinary method of summing series (1); *b*—by the proposed method. *B*—at 20° C, calculated by the new method without introducing the temperature factor

According to the data presented, the radius of the carbon ion in diamond is 0.20–0.25 Å, and the degree of ionization corresponds to $C + 4.0$.

In the intervals between the coordinates 1/2, 1/2, 1/2 and 3/4, 3/4, 3/4, the electron density is close to zero within the accuracy of the experimental data. In the interval from $0, 0, 0$ to 1/4, 1/4, 1/4, the minimum electron density is 1.53 el/Å^3; this value is approximately 5 times higher than for silicon in the same position, which is apparently due to the character and energy of the interatomic bond.

The actual distribution of electrons near the nucleus differs somewhat from that specified, owing to the correction calculated from the difference between the experimental and the specified atomic scattering factors. In the intervals between atoms, the value of the specified density is negligibly small and the actual electron density practically coincides with ρ_2.

In Fig. 3 are shown the curves of variation of the calculated electron density at the points $0, 0, 0$; $1/8, 1/8, 1/8$; and $1/2, 1/2, 1/2$ as a function of the calculated temperature. As is seen from the graph presented, the introduction of the temperature factor very strongly affects the obtained values of the electron density at the point $0, 0, 0$, and to a lesser extent at the points $1/8, 1/8, 1/8$ and $1/2, 1/2, 1/2$. It should be noted, however, that extrapolating the curves obtained by introducing temperature factors down to room temperature does not appear possible.

Fig. 3. Variation of the calculated values of electron density as a function of the calculated temperature. *a*—at the point $0, 0, 0$, calculated by the new method; *b* —at the point $1/8, 1/8, 1/8$; *c*—at the point $1/2, 1/2, 1/2$; a'—at the point $0, 0, 0$, calculated by the conventional method

The method described opens up new possibilities in determining electron density and in solving the problem of the chemical bond in solids.

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Received
5 I 1960

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