QUARTERLY REVIEWS

APPLICATION OF ELECTRON DIFFRACTION TO THE STUDY OF THE CHEMICAL BOND IN CRYSTALS

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ELECTRON diffraction, the first experiments on which were carried out over thirty years ago,[1,2,3] has been the triumph of the wave theory of matter and is now a working method for investigating the structure of matter. It is used to study the structure of molecules in vapours and gases, in the phase analysis of oxide and other films on the surface of solids, in the study of the shape of submicroscopical crystals and their mutual orientation at epitaxy, or in phase transitions. In the post-war years, however, electron diffraction has found an increasingly independent place as a method for the study of the mutual arrangement of atoms in a crystal. The principal method used for atomic structure, *i.e.*, *X*-ray analysis, has in a number of cases proved to be insufficient, and to-day, along with it, extensive use is made of electron- and neutron-diffraction methods.

The development of structure analysis by electron diffraction is due, primarily, to Soviet authors,[3-6] and later to workers in many other countries.

The improvement of experimental techniques, as well as the evolution of the theory and practice of structure analysis by electron diffraction, enable us to attack and to solve problems of two types. The first of these is the geometrical problem, most important for structure analysis in general, *i.e.*, that of establishing the mutual arrangement of atoms, their co-ordination, lengths of chemical bonds, and valency angles. Such work, especially if carried out with sufficient accuracy, enables us to answer many questions concerning the nature of the chemical bond in a given crystal. The second problem, a more complicated and subtle one, involves the valency state of atoms and of the field of forces between them, and requires determination of the nature of their thermal motion, from which

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[1] Davisson and Germer, *Phys. Rev.*, 1927, **30**, 705.

[2] Thomson, *Proc. Roy. Soc.*, 1928, *A*, **117**, 600; **119**, *A*, 651; Thomson and Cochrane, "Theory and Practice of Electron Diffraction," London, 1939.

[3] Tartakovsky, *Doklady Akad. Nauk S.S.S.R.*, 1928, A.

[4] Lashkarev, "Diffrakzija Elektronov" (Electron Diffraction), Moscow, 1933.

[5] Pinsker, "Diffrakzija Elektronov" (Electron Diffraction), Moscow, 1947; London, 1953.

[6] Vainshtein, "Structurnaija Elektronographija" (Structure Analysis by Electron Diffraction), Moscow, 1956.

conclusions may be derived as to the force constants of some particular bond, etc.

We first give a very brief survey of the experimental techniques of electron-diffraction analysis. The electronograph is a vacuum apparatus. The electrons, from a hot tungsten wire, are accelerated by a voltage of 50—100 kv (corresponding to an electron wave-length, λ, of about 0·06—0·04 Å). The electron beam, formed with the aid of diaphragms and magnetic lenses, is passed through a thin ($\sim 10^{-6}$—10^{-5} cm.) film of the substance being investigated, the electrons thus being scattered and yielding a diffraction pattern, which is observed on a fluorescent screen and further recorded on photographic plates. Electron-diffraction cameras are usually constructed by the workers themselves, but are also produced commercially (*e.g.*, in the U.S.S.R. and Switzerland). Devices for observing electron diffraction are supplied with many electron microscopes. In Fig. 1 is shown the "EG" horizontal camera designed for study of the atomic structure of crystals at the Institute of Crystallography of the U.S.S.R. Academy of Sciences.[7,8]

Preparations of thin films are made by applying them on the thinnest possible support ($\sim 10^{-7}$ cm.) of celluloid, Formvar, etc. For this purpose, according to the nature of the substance investigated, it is precipitated from a solution or suspension, or from the gaseous phase in the form of a powder or smoke, or by sublimation in a vacuum. In contrast to the view sometimes expressed, it should be emphasised that the atomic structure of a given phase in thin films is found in the great majority of cases to be identical with its atomic structure in the bulk specimen, as shown by a comparision of data obtained from *X*-ray and electron-diffraction studies. Owing, however, to the very small volume of the crystals investigated, the temperature range of stability of some phase or other is sometimes found to be displaced. In thin films it is easier to produce the necessary transformations by means of thermal or chemical treatment, and this is often used in electron-diffraction analysis.

What are, then, the specific nature of electron-diffraction structure analysis and the features that distinguished it from the *X*-ray and neutron-diffraction methods?

They are, in the first place, the peculiar feature just mentioned, *viz.*, the possibility of determining atomic structure in thin films. In fact, to make a complete structure analysis with the aid of *X*-ray or neutron diffraction, single crystals no less than 0·1 mm. in size are required. Many natural and synthetic substances (*e.g.*, clay minerals), however, are found only in a highly disperse state, and hence their study by *X*-ray methods is difficult. On the other hand, they are a natural object for electron-diffraction studies. It is also advantageous to use the electron-diffraction method

[7] Vainshtein and Pinsker, *Kristallografiya*, 1958, **3**, 3.

[8] For review of modern electron diffraction apparatus, see Pinsker, *Pribori i technika experimenta* (Apparatus and experimental technique), 1959, **1**, 3.

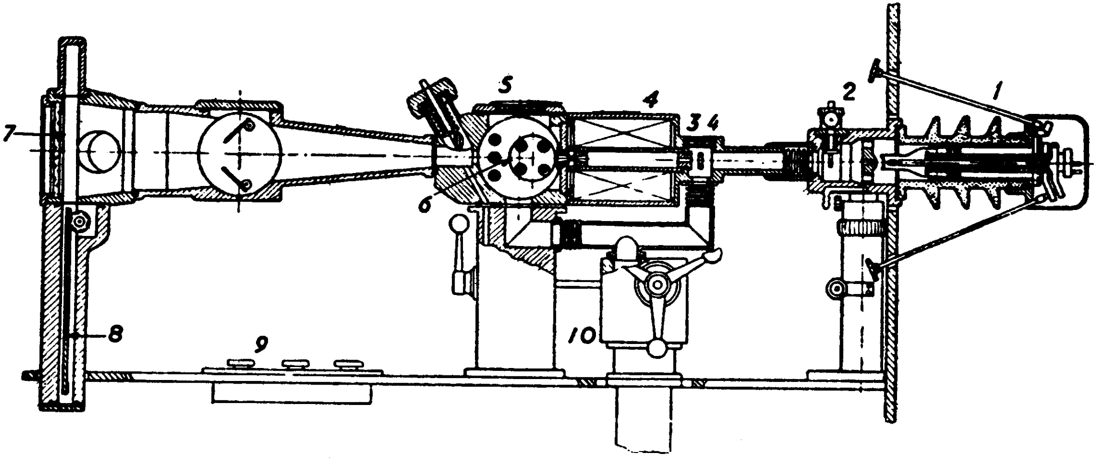

FIG. 1. *Electron-diffraction camera of the Institute of Crystallography of the Acad. Sci. U.S.S.R.* (1) Electron gun. (2) Anticathode. (3) Shutter. (4) Magnetic lens. (5) Central chamber. (6) Specimen. (7) Screen. (8) Photoplate. (9) Electrical panel. (10) Vacuum system.

for studying the structure of phases unstable in air (*e.g.*, some oxides or crystal hydrates) but stable in a high vacuum.

However, the fundamental distinctive feature of the electron-diffraction method and of its application to the analysis of atomic structure and a study of the chemical bond lies in the nature of the interaction between the electrons and the substance. Unlike *X*-rays, which are scattered by the electronic shells of atoms of a particular crystal, as well as neutrons, which are scattered by the nuclei of atoms, electrons are scattered on the electrostatic potential of the crystalline lattice. From this fact, which will be presently considered in detail, follow several peculiar features in the very principle of the electron-diffraction method.

Crystalline lattice potential and Fourier synthesis from electron-diffraction data.

The motion of electrons is described by the Schrödinger wave equation:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\psi(xyz)$ is the wave function, and E is the total and V the potential energy of the electron. The last is determined by the electrostatic potential $\phi(xyz)$ of the scattering object, so that $V = -e\phi$, where e is the charge of the electron. Hence the scattering of electrons by crystals, as well as by isolated molecules or atoms, is determined by the potential $\phi(r)$ of these objects.

The crystal potential $\phi(r)$ is a superposition of potentials of its individual atoms. The potential of each atom is determined by the distribution of charges: of the positive charge $+Ze$, concentrated in the nucleus, and of the negative charge of the electron shells $\rho_{\text{at}}(r)$.

As a consequence of the three-dimensional periodicity of the crystalline lattice, the potential of the crystal is a three-dimensional periodic function. The peaks of this function correspond to atoms, the positions of maxima being determined by the position of nuclei. As compared with the well-known electron-density function $\rho(r)$ obtained in *X*-ray analysis, the potential $\phi(r)$ has the following peculiar features.[9] $\phi(r)$ is a somewhat more diffuse function than $\rho(r)$, which follows from the relation of the Thomas–Fermi statistical theory of the atom:

$$\phi \sim \rho^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this expression it will be seen that the ratio of the potential peak heights to the electron density is different for crystals with different atomic numbers. The electron-density peak heights are proportional to Z^{α_x}, where $\alpha_x \gtrsim 1$ is somewhat greater than unity. The potential peak heights $\phi(0)$ are proportional to Z^{α_e}, where $\alpha_e \approx 0{\cdot}8$. Hence in crystals, it is

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[9] Vainshtein, *Trudy Inst. Krisk., Akad. Nauk S.S.S.R.*, 1954, **9**, 259.

easier to detect light atoms in the presence of heavy ones by electron-diffraction analysis than by *X*-ray analysis. Electron-diffraction is extensively used in determination of the positions of hydrogen atoms, in studying the position of nitrogen and carbon in metal nitrides and carbides, etc.

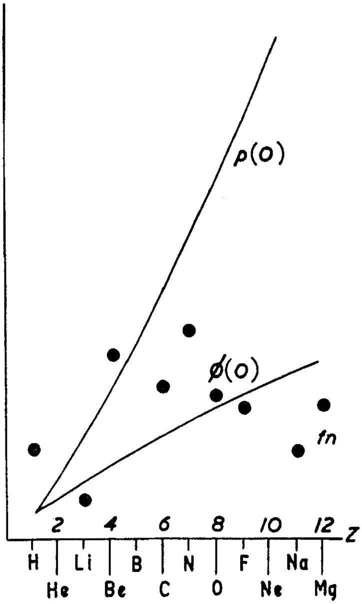

FIG. 2. *Curves of the detectability of atoms: in* X*-ray analysis* $\rho(0)$, *in electron diffraction* $\phi(0)$, *in neutron diffraction* f_n *(points).*

Fig. 2 shows curves of the relative detectability of atoms by electron diffraction, *X*-ray, and neutron-diffraction methods (points). The less the slope of the curve, the easier it is to locate a light atom in the presence of heavy ones. The most advantageous in this respect is the neutron-diffraction method, since the scattering of neutrons in general is not obviously dependent on the atomic number, while electron diffraction occupies an intermediate position between neutron-diffraction and *X*-ray analysis.

A remarkable characteristic of electron-diffraction, as well as of *X*-ray and neutron scattering, is that here the Fourier transform of the corresponding function, determining the scattering, is realised; that is, for the diffraction of electrons on the potential $\phi(r)$:[10,11]

$$\phi(xyz) = \frac{1}{F} \sum_{hkl} \Phi_{hkl} \exp\left[-2\pi i\,(hx + ky + lz)\right] \quad . \; . \; . \quad (3)$$

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[10] Vainshtein and Pinsker, *Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, 49.

[11] For reviews of Fourier methods in electron diffraction, see refs. 6 and 9 and also Cowley and Rees, *Reports Progr. Phys.*, London, 1958, **21**, 165.

The Fourier coefficients, $F(hkl)$, the so-called structural amplitudes, are found directly from the intensities of the scattered beams, I_{hkl} [where h, k, l, indices of the reflecting crystal plane, are also indices of the Fourier series (3)]; V is the unit-cell volume. With kinematic scattering of electrons $F(hkl) = \kappa \sqrt{I_{hkl}}$; with dynamic scattering, $F(hkl) = \kappa\sqrt{(I_{hkl}Q)}$, where Q is a correction function, κ is a coefficient dependent on the type of electron-diffraction patterns (see electron-diffraction patterns I—IV) and the interplanar distance of the corresponding reflection.[12,13,*] Thus, by measuring the intensities of the diffraction spots on the patterns, finding from these the structural amplitudes $F(hkl)$, and summing the Fourier synthesis (3), we obtain the picture of the crystal lattice, the individual peaks of which correspond to atoms.

The essential principles of the Fourier method, which lies at the base of modern structure analysis, are easy to understand by analogy with the optics of visible rays. The formation of an image of the object in the optical microscope may be divided into two stages: (1) the formation of diffraction beams from the object, and (2) the bringing together of these beams into an image by means of lenses. As a result, an enlarged image of the object in the microscope is obtained. In the structure analysis of crystals only the first stage—the diffraction—is realised. The second stage cannot be attained for X-rays and neutrons, since no lenses for these are available. Lenses for electrons are available (the electron-microscope), but their resolving power is still far from being such as to permit us to see individual atoms. The second stage, however, *i.e.*, making the diffraction beams converge into the image of the object, may be realised by calculation, the summing of Fourier series, thus obtaining a "mathematical microscope" with magnifications of the order of hundreds of millions and a resolving power down to decimal fractions of an Å.

The Fourier synthesis is carried out in a number of different ways: as a projection of the structure on a plane, one- or two-dimensional sections of a three-dimensional potential distribution, etc.

By measuring the peak co-ordinates on the maps of Fourier syntheses, the co-ordinates of atoms are found directly, and information is obtained concerning the lengths of the chemical bonds, the angles between them, and other geometrical characteristics.

More detailed information may be gained by considering the shape of the atomic potential peaks and the distribution of the potential in interatomic space. To achieve this, the Fourier series (3) are reduced to the absolute scale, and the values of the potential are expressed directly in volts. The potential values in the peaks have magnitudes of the order of

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[12] Blackman, *Proc. Roy. Soc.*, 1939, *A*, **173**, 68.

[13] Vainshtein, *Kristallografiya*, 1956, **1**, 17, 150; 1957, **2**, 340.

[*] For the theory of intensities, the geometrical theory of electron-diffraction patterns, and other problems pertaining to the theory and procedures of electron-diffraction structural analysis, the reader is referred to the literature.[5,6,11–13]

some tens or hundreds of volts, while those in interatomic space are of the order of a few volts. It should be borne in mind that atoms in a crystal are in a state of thermal motion and that the pattern of the Fourier synthesis obtained is an average over time and over all the unit cells of a particular crystal. With mean-square displacements of atoms from the equilibrium position $\sqrt{\overline{\mu^2}} \approx 0{\cdot}3$ Å [which corresponds to a value of the thermal motion parameter or Debye factor† $(B = 8\pi^2\mu^2) \approx 2 \times 10^{-8}$ and is characteristic for many crystals], the potential peak height of an atom (*i.e.*, of the potential in its centre) may be evaluated by the formula

$$\phi(0) = 0{\cdot}5Z^{0{\cdot}8} \text{ (volts)} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

where Z is the atomic number. (The numerical coefficients in this formula change with a change of B.)

An important characteristic of the crystal is its mean inner potential, $\phi_m = F(000)/V$, determined by the zero term $F(000)$ of the Fourier series (3). This value may be either found experimentally from electron refraction[5,14] or estimated theoretically.[5,6,14] It is related to such a characteristic of the lattice as the energy of the output upon thermoelectronic emission.

At this point the potential in an atom should be considered in greater detail. First, we take as an example its simplest model in the shape of a spherical condenser with a charge $+Ze$ in the centre ("nucleus") and distributed about the sphere with a radius R of the charge $-Ze$ ("electron shell") [Fig. 3(*a*)]. The negative charge potential inside the sphere is constant and equal to $-Ze/R$, while outside the sphere it declines as $-Ze/r$, *i.e.*, as the potential of a point source placed at the origin of the co-ordinates. By adding this potential to the positive potential of the nucleus, the potential of the "atom" will be obtained as equal to $Ze/r - Ze/R$ inside the sphere, and to zero outside it. Consequently, the charge of the shell of a neutral atom fully screens the potential of the nucleus outside the shell and diminishes it inside the shell.

In reality, the electron shell has a complex, continuous structure, and the sketch in Fig. 3(*a*) should be "smoothed", as shown in Fig. 3(*b*). The distribution of electrons of the outer shells of atoms is not necessarily spherically symmetrical, which is, correspondingly, reflected in the shape of the potential peak. Therefore, in the general case it could be written as

$$\phi_{\text{at}}(r) = Ze/r - \phi\,[\rho_{\text{at}}(r)] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

where $\rho_{\text{at}}(r)$ is the atom electron density distribution. Should the atom be ionised, the equality of charges, and hence of the potential, beyond the "boundary" of the electron shell is disturbed, and this is revealed by the shape and height of the potential peak [see Fig. 3(*b*)]. Qualitatively, the

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[14] Tull, *Proc. Roy. Soc.*, 1951, *A*, **206**, 219, 232.

† This factor is used to compensate for the thermal movement of atoms by multiplying the value of the theoretical scattering factor f^0 calculated for atoms at rest by the term exp. $(-B \sin {}^2\theta/\lambda^2)$.

effect of negative ionisation is a decrease and a narrowing of the peak as compared to the neutral atom; and that of positive ionisation is an increase and a broadening of the peak.

An important characteristic of the atom is its "full potential"[6,15,16]

$$f_e(0) = \Sigma \phi_{at}(r) dV \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

the integral of the potential in the total volume—an analogue to the $F(000)$ value for a crystal. It is not difficult to show that the full potential for the model shown in Fig. 3 (*a*) is $f_e(0) \sim ZR^2$, *i.e.*, is dependent on the radius of the sphere inside which the field of the atom is enclosed. For the real atom

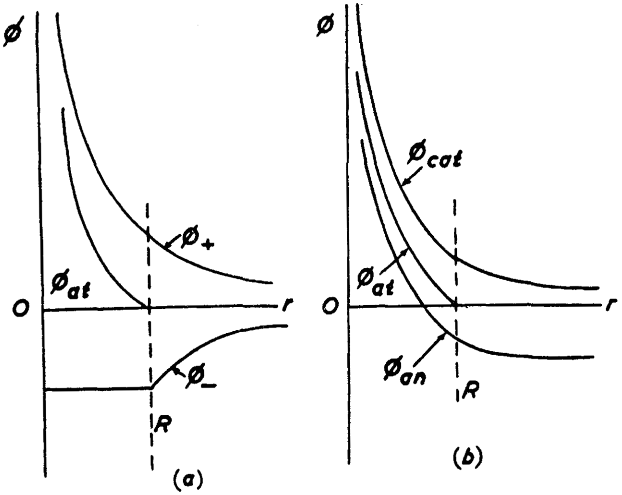

FIG. 3. (*a*) *Potential of the atom: superposition of the nucleus potential* ϕ_+ *and the electron-shell potential* ϕ_- (*for a model of atom in the form of spherical condenser*). (*b*) *Potential distributions in the neutral atom* ϕ_{at}, *the cation* ϕ_{cat}, *and the anion* ϕ_{an}.

$$f_e(0) \sim Z\bar{r}^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6')$$

where r^2 is the mean-square radius of the electron shell.[17] The $f_e(0)$ value, as will be shown below, has a distinct connection with a scattering of electrons. It should be noted that it is proportional to the molar diamagnetic susceptibility χ. Thus, by finding the shape of the potential peaks of the atoms from electron-diffraction data, a lot of information may be obtained concerning their state, and hence concerning the nature of the chemical bond too.

It should be stressed that the possibility in principle of obtaining the exact pattern of the potential of a crystalline structure requires for its

[15] Vainshtein, *J. exp. theor. Phys.* (*U.S.S.R.*), 1953, **25**, 157.
[16] *Idem*, *Acta Cryst.*, 1958, **11**, 178.
[17] Vainshtein and Pinsker, *Trudy Inst. Krist., Akad. Nauk S.S.S.R.*, 1950, **6**, 163.

realisation a particularly high accuracy in experiment and in treating the experimental data. In most cases, therefore, workers restrict themselves to establishing the co-ordinates of atoms, while investigations in which the shape and height of the peaks are analysed are much scarcer. There is no doubt, however, that studies of this kind are highly promising. It is noteworthy that, by combining electron-diffraction data showing the distribution of the electron density of the crystal, it should be possible to determine the electronic energy distribution in a crystal.

We now discuss the accuracy of structure analysis by electron diffraction. One important property of the Fourier series should be noted. They include a large number of structure amplitudes *F*(*hkl*)—ranging from some tens to several hundreds—*i.e.*, as many of them as there are reflections observed from a given crystal. Owing to the statistical nature of errors in the measurement of the magnitude of amplitudes, and the large number of them, the resulting function $\phi(r)$ (see ref. 3) is but little susceptible to the errors of measurement of individual values of *F*(*hkl*). Therefore, even a visual estimate of the intensities of reflexions of electron-diffraction patterns permits us to determine, by employing the Fourier synthesis, the interatomic distances with an accuracy of 0·03—0·05 Å. In precision studies, with a microphotographic technique, this accuracy may be increased to 0·01 Å and even better, and the accuracy in determining the potential values to a matter of only some volts.

It should be noted that, although the treatment of diffraction data by the Fourier method yields the clearest result, *i.e.*, the map of the potential distribution, for an analysis of interatomic distances and of the state of atoms in electron-diffraction analysis, one may also directly consider the magnitudes of structure amplitudes, comparing them with their theoretical values. Examples of this will be cited below.

We now pass to a consideration of some examples of structure studies by means of the electron-diffraction method, in which problems of the chemical bond in crystals have been considered.

Electron-diffraction study of hydrogen atoms in crystals and of the hydrogen bond

Since they enter into the composition of a large number of organic and inorganic substances, hydrogen atoms largely determine the arrangement of their crystalline structure and a number of their physical properties: for instance, their property of forming hydrogen bonds plays a particularly important part in the structure of living matter, *e.g.*, proteins, nucleic acids, etc.

All the three modern diffraction methods permit the direct location of hydrogen atoms in crystals. The accuracy of these determinations is: for electron diffraction, 0·02—0·03 Å; for neutron diffraction, 0·01—0·02 Å, and for *X*-ray analysis, about 0·1 Å. The last method therefore hardly suffices to detect in the Fourier maps the exceedingly small electron density characteristic of a hydrogen atom. But the electron-density Fourier synthesis, as well as the potential Fourier synthesis in electron-diffraction analysis, enables conclusions to be drawn regarding the degree of ionisation of hydrogen in some particular compound. The most accurate method, neutron-diffraction, yields only the co-ordinates of nuclei, but it is most convenient for a study of the thermal motion of atoms.

The C–H Distance.—For a long time the idea has prevailed that this distance is about the same in all organic compounds and is about 1·08—1·09 Å. However, in the course of the first study of n-paraffins by electron-diffraction it was discovered that this distance was really greater. Recently,[18] a precision electron-diffraction study of n-paraffins, $C_{18}H_{38}$, $C_{28}H_{58}$, and $C_{30}H_{62}$, has been carried out. Electron-diffraction patterns have been obtained from films of paraffin prepared by crystallisation on a support from a solution in toluene (electron-diffraction pattern I).

On the basis of a microphotometric intensity measurement, a Fourier potential projection has been constructed along the aliphatic chain [Fig. 4(*a*)]. In this projection, the C–H distances are displayed in an undistorted way. To eliminate certain effects inherent in the procedure used, the so-called "difference syntheses" were employed, *i.e.*, the peaks of heavy atoms were removed from the potential map [Fig. 4(*b*)].

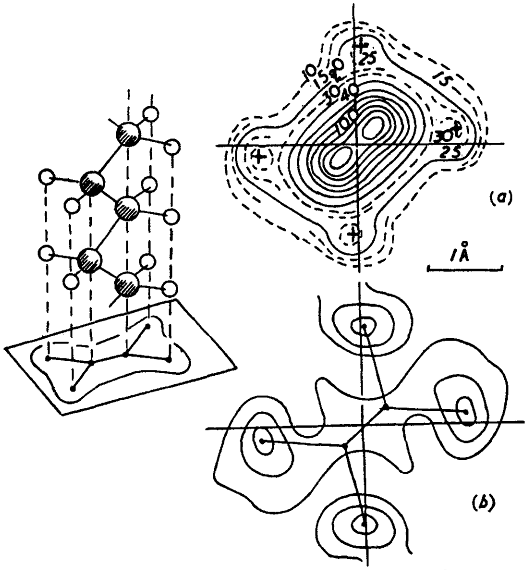

FIG. 4. *Fourier projection of potential of* $C_{30}H_{62}$ (in volt Å). (*a*) C and H atoms; (*b*) C atoms subtracted.

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[18] Vainshtein, Lobatshev, and Stasova, *Kristallografiya*, 1958, 3, 452.

The average C–H distance has been found to be $1{\cdot}12_5$ Å. The accuracy of this determination, estimated by several different methods, is ± 0·015 Å. It is noteworthy that in the lower paraffins (n-pentane, -hexane, -heptane), as shown by data of electron-diffraction analysis in gases,[19] this distance is 1·120 ± 0·006 Å.

An analysis of peak heights has shown that no ionisation of hydrogen atoms is observed. At the same time the shape of the peaks of these atoms indicates that their thermal oscillations take place chiefly in the form of oscillations about carbon atoms, as centres, while the oscillations along the C–H bond are less pronounced. The same is observed in the CH_2 group of the diketopiperazine structure (see p. 116).

The increase in the C–H distance above the value of 1·09 is not confined to paraffins. An electron-diffraction structure analysis of hexamethylenetetramine[20] has given a value of 1·14 ± 0·10 Å for this distance, and neutron-diffraction has given a value[21] of 1·13 ± 0·02 Å. Thus, for the tetrahedral atom of carbon there is a distinct tendency towards an increase in the C–H distance to about 1·12—1·13 Å as compared with the value of 1·08 Å. At the same time, structure-analysis data for the C–H distance in the aromatic ring[22] show that in this case the distance of 1·08 Å is retained. The increase in the C–H distance upon a weakening of the adjacent bonds of the carbon atom has been observed by the spectroscopic method.[23] In this way, it may be inferred that the presence of a smaller number of other stronger bonds to the carbon atom (*e.g.*, $\equiv$C–H) produces a measurable shortening of the C–H bond, and in the tetrahedral configuration this bond is the longest and consequently the weakest. This kind of mutual influence of bonds reminds one of conjugation phenomenon, with the distinction that in conjugation the given ordinary bond is surrounded on each side by stronger bonds, while in the instance considered the adjacent bonds which exercise an influence are located only on one side of it.

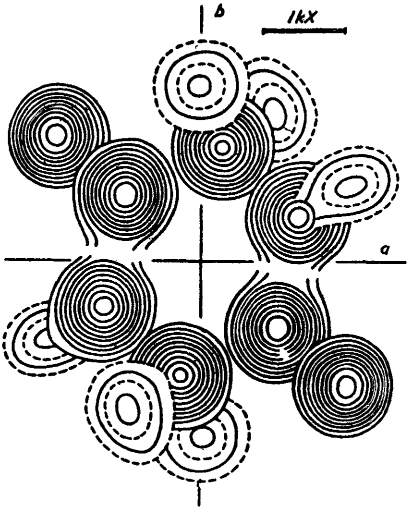
It has been already pointed out that electron-diffraction, as well as neutron-diffraction studies yield the co-ordinates of nuclei. Remarkably they have diverged from the data of *X*-ray analysis. *X*-Ray determinations of the C–H distances (as well as of O–H, N–H), regardless of their rather low accuracy, reveal a systematic shortening of the distance from the carbon atom to the electron-density peak of the hydrogen atom of about 0·85—1·05 Å. Theoretical analysis[24] shows that such a shortening, *i.e.*, a displacement of the electron-density maximum of the bonded hydrogen atom towards the carbon atom, may actually take place. It is qualitatively accounted for by movement of a part of the electron cloud

[19] Bartell, Report on the Symposium on Electron Diffraction in Leningrad, 1959.
[20] Lobatshev, *Trudy Inst. Krist., Akad. Nauk S.S.S.R.*, 1954, **10**, 167.
[21] Andersen, *Acta Cryst.*, 1957, **10**, 107.
[22] Bacon and Curry, *Proc. Roy. Soc.*, 1956, *A*, **235**, 552.
[23] Herzberg and Stoicheff, *Nature*, 1955, **175**, 79.
[24] Tomiie, *J. Phys. Soc. Japan*, 1958, **13**, 1030.

to the bond. The shift increases with increase in the degree of ionic nature of the bond, as well as with an increase in the thermal oscillations of the atoms.

A lack of coincidence in the positions of electron-density maximum and the nucleus is observed only for hydrogen atoms, but not for other, heavier atoms. It should also be noted that distances between nuclei in electron-diffraction and neutron-diffraction determinations are found, as a rule, to be 0·02—0·03 Å longer than those given by spectroscopic data. This discrepancy may possibly be due to another cause, *i.e.*, to the anharmonicity of the thermal oscillations of the nuclei of molecules.[25] As a result of anharmonicity, the distribution function of the probability of the position of nuclei is non-symmetrical, and its centre of gravity (mean position of the hydrogen nucleus), as determined by neutron-diffraction and by electron-diffraction, does not coincide with the position of the potential-energy minimum determined spectroscopically. This problem, however, has not yet been fully resolved.

The N–H Distance.—Fig. 5 shows a three-dimensional potential synthesis of diketopiperazine.[26] This structure (I) is rich in hydrogen bonds, and the object of studying it was to locate hydrogen atoms, although it had already been investigated by means of *X*-rays.[27]



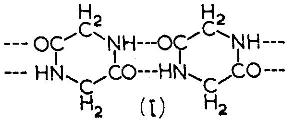


FIG. 5. *Three-dimensional Fourier synthesis of potential of diketopiperazine molecule.* Continuous line drawn at intervals of 15 volts; broken lines 7·5 volts.

In a ring, the angles of which differ but little from 120°, the distances are

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[25] Ibers, *Acta Cryst.*, 1959, **12**, 251.

[26] Vainshtein, *Trudy Inst. Krist., Akad. Nauk S.S.S.R.*, 1954, **10**, 49; *J. Phys. Chim., U.S.S.R.*, 1955, **29**, 327.

[27] Corey, *J. Amer. Chem. Soc.*, 1938, **60**, 1598.

(in Å): C–N, $1{\cdot}38_6$; N–CH_2, $1{\cdot}40_3$; C–CH_2, $1{\cdot}44_4$; C–O, $1{\cdot}22_4$ (the mean-square error in these determinations is 0·008 Å). The C–H distances in the CH_2 group are 1·09 and 1·11 Å (± 0·03 Å), and the bond angle is near the tetrahedral value, *i.e.*, 107°. The hydrogen atom forming the bond between the N and O of neighbouring molecules is covalently linked to the nitrogen atom and is 0·98 ± 0·03 Å distant from it. The hydrogen bonds of NH · · · O deviate slightly from rectilinearity; their lengths are 2·84 Å.

The elongated shape of the peaks of hydrogen atoms indicates a different nature for the oscillations in the CH_2 group (around C) and in the NH group (along the hydrogen bond). The values of the potential in the centre of C, N, and O atoms are close to each other, being about 160 v. Their equality is accounted for by the fact that, although in the C, N, O series the atomic number Z increases, the mean-square radius of the electron shell simultaneously increases, that is, the screening of the nuclear potential is augmented too [see equation (6)]. The $\phi(0)$ potential of hydrogen atoms in the CH_2 group is 32 and 33, and in the NH group 36 v. The increase of this potential indicates, as discussed above, the ionisation of this atom. A theoretical calculation shows that such a potential corresponds to the presence of about 0·85 electron in this hydrogen atom. Thus, the concept of a primarily ionic nature of the hydrogen bond, suggested by Pauling, has been experimentally confirmed in the course of this electron-diffraction study.

In a series of structure studies the N–H distance in the ammonium chloride structure has been determined. Since the first electron-diffraction study,[4] in which a value of 0·95 ± 0·07 Å was obtained (1933), the accuracy of determinations has increased: 0·98 ± 0·04 Å (1956),[28], 1·02 ± 0·02 Å (1959).[29] Neutron diffraction[30] yielded 1·03 ± 0·02 Å, and an X-ray study (cited in ref. 29, without any indication of accuracy) gave 0·93 Å.

During an electron-diffraction study of cryptohalite $(NH_4)_2SiF_6$ (electron-diffraction pattern II),[31] an interesting effect of reorientation of the NH_4 group was observed. It has been found that these tetrahedral groups, surrounded by twelve F atoms from the SiF_6 groups, occupy statistically six equally probable orientations, forming, in each of these, weak hydrogen bonds with four F atoms. One of these six orientations is presented in Fig. 6. The N–H distance is equal to 1·03; and H · · · F is 1·95 Å. It should be noted that, as a result of statistical reorientations on the Fourier map, only the peak of 1/3 atom is detected (of the six orientations, three are close in pairs), only 12 v in height (Fig. 7). This precision study, in which 1/3 H was detected in the presence of atoms of N ($Z = 7$), F ($Z = 9$), and Si ($Z = 14$), shows that one may hope to determine by electron-diffraction the positions of the "ordinary" hydrogen atoms in

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[28] Stasova and Vainshtein, *Trudy Inst. Krist. Akad. Nauk. S.S.S.R.*, 1956, **12**, 18.

[29] S. Kuwobara, Reports of Electron Diffraction Works in Japan: Symposium on Electron Diffraction in Leningrad, 1959.

[30] Levy and Peterson, *J. Amer. Chem. Soc.*, 1953, **75**, 1536.

[31] Vainshtein and Stasova, *Kristallografiya*, 1956, **1**, 311.

structures with a mean atomic number of the order of 30. As a matter of fact, the height of peaks, corresponding to statistically distributed hydrogen atoms (12 v) is but twice the value of the potential-measurement error ($\approx$ 6 v). Nevertheless, the positions of 1/3 H were ascertained, although the accuracy of determination of the N–H distance was inevitably lower (0·1 Å) than in the other cases. This study will be further discussed below.

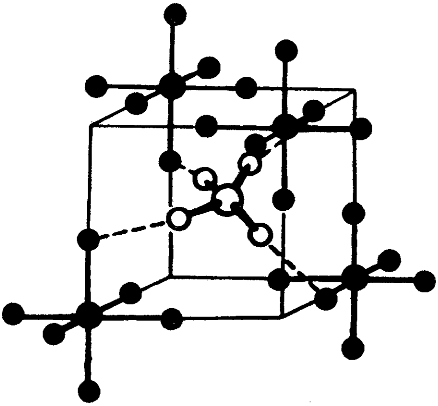

FIG. 6. *One of six equally probable orientations of the* NH_4 *tetrahedron in the crystal structure of* $(NH_4)_2SiF_6$.

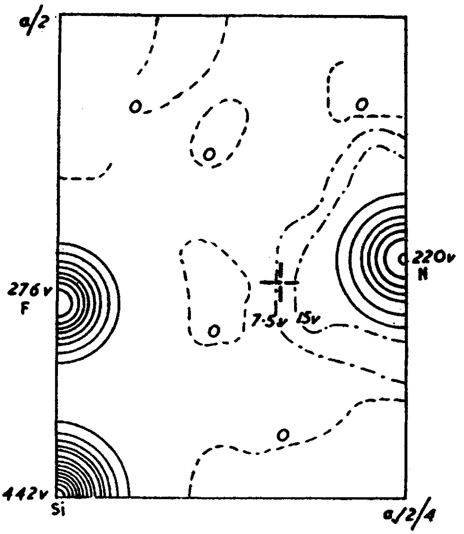

FIG. 7. *Section of three-dimensional synthesis of the potential of* $(NH_4)_2SiF_6$ *along the* (110) *plane.* Lines drawn at intervals of 30 volts. The cross indicates the position of 1/3H, as established from differential synthesis.

The O–H Distance.—The first example of an electron-diffraction determination of this distance was a study[32] of boric acid, $B(OH)_3$, in which a value of 1·00—1·05 Å was found.

Recently electron-diffraction was used for a study of the structure of cubic ice.[33] When electron-diffraction studies are carried out at low temperatures, ice is readily formed on the support from the water vapour remaining in the vacuum.[34] If the condensation temperature is below —80°c, the ice crystallises in the cubic "diamond" modification with $a = 3{\cdot}36$ Å and an O–O distance of 2·75 Å. Above —80°c the common hexagonal ice is formed. Analysis of the intensities and construction of the Fourier potential projection has proved that in the cubic as well as in the common hexagonal modification a statistical distribution of the hydrogen atoms occurs at two equally probable positions on the O–O line (Fig. 8). The O–H distance for each of these positions is 0·97 Å.

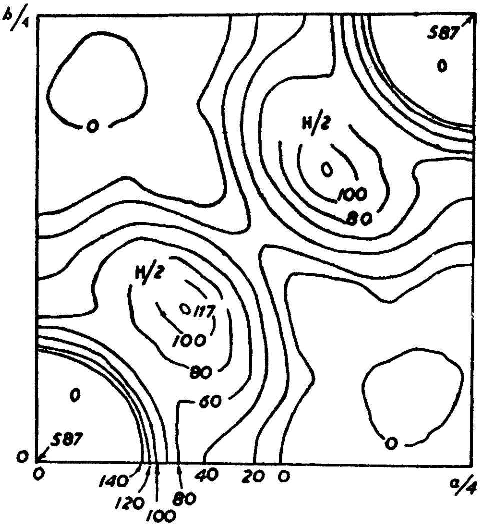

FIG. 8. *Fourier projection of the potential of cubic ice on the* (100) *plane.* (Units of scale: 0·37 volt Å).

The instances cited above show the possibilities of the electron-diffraction method for a study of hydrogen atoms, namely, the possibility of directly locating them in the lattice and of making an analysis of the thermal motion and of the degree of ionisation.

Study of the state of atoms in a crystal

The structure of the electron shell of a free atom changes when the atom is incorporated into the crystal lattice. As is known, the general

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[32] Cowley, *Acta Cryst.*, 1953, **6**, 516, 522, 846.

[33] Honjo and Shimaoka, *Acta Cryst.*, 1957, **10**, 710.

[34] For review of electron diffraction investigations at low temperatures, see Dvoriankin, *Kristallografiya*, **1959**, **4**, 441.

features of this change may be described as follows. In metals, a part of the electrons go to the conductivity zone; in ionic compounds, the electrons are redistributed from cations to anions; with a covalent bond, directed electron "bridges" are formed between valency-bound atoms. These changes affect the potential distribution, as has been shown above, and hence may be detected by means of electron-diffraction. Electron-diffraction work of this type is analogous to *X*-ray studies of electron-density distribution, initiated by the well-known work by Brill *et al.*[35] Some examples may be considered. In the first work of this type,[9] from experimental electron-diffraction data the potential distribution in the crystalline lattice of Al, Cu, and Ag was found. In Fig. 9 is shown the distribution of the potential along the body diagonal of the face-centred cubic unit cell of Ag. Some unevenness of the distribution obtained is due to errors in the measurement of *F*(*hkl*) and the so-called termination effect in the Fourier series, which may be artificially eliminated. In spite of this unevenness, however, some essential features of the distribution of the potential in metals may be seen in Fig. 9.

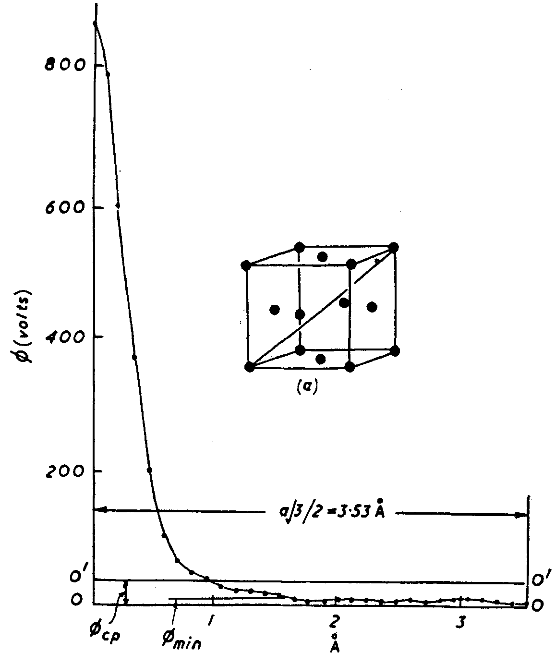

FIG. 9. *Potential of* Ag *along the diagonal of the unit cell.*

Analysis of the shape of peaks for all the three metals has shown them to be spherically symmetrical. This is in accord with the concept of an undirected metallic bond. The potential in the interatomic space is

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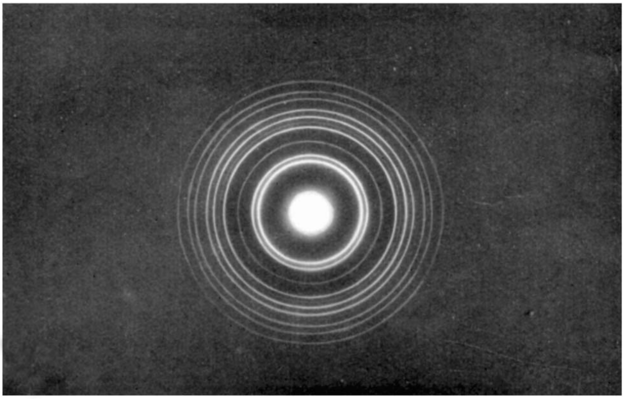
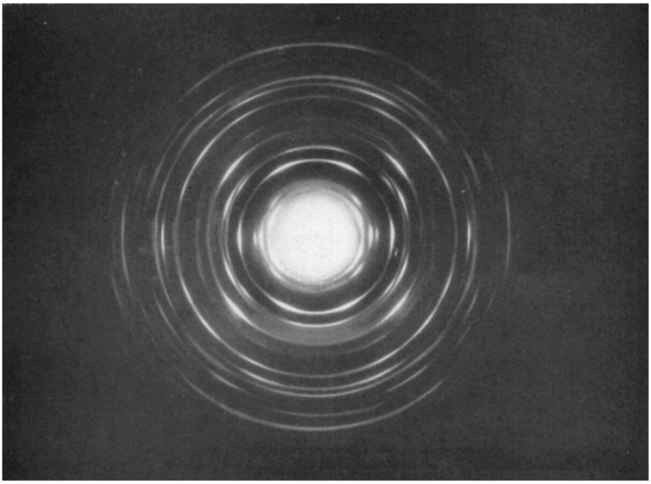
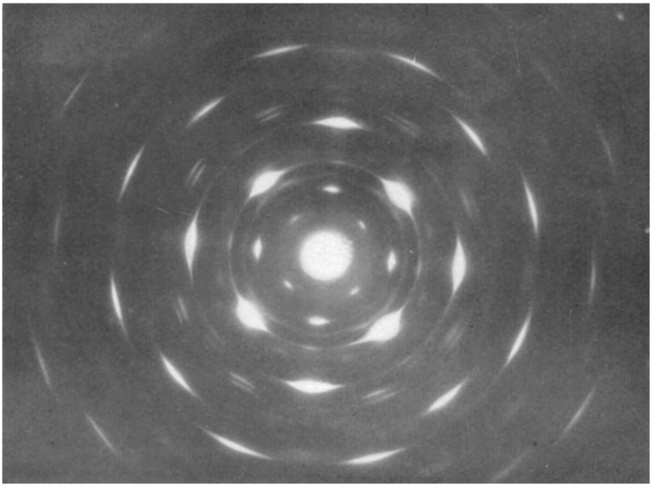
[35] Brill, Grimm, Hermann, and Peters, *Ann. Physik*, 1939, **34**, 393.



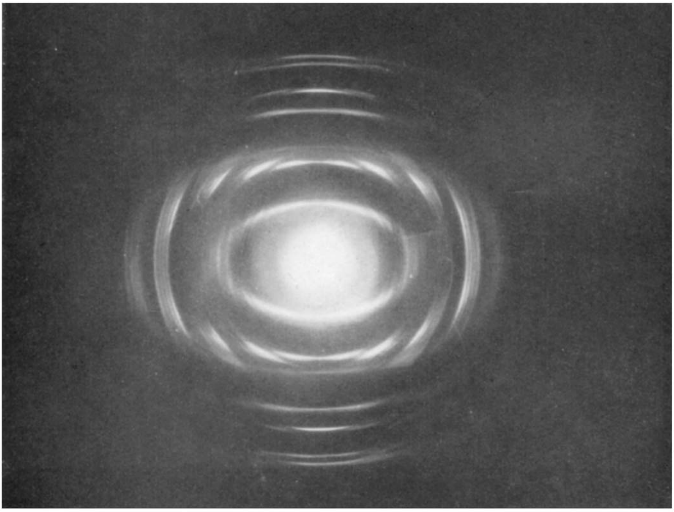
(I) *Structure of paraffin*, $C_{30}H_{62}$. Plane of the specimen is perpendicular to the electron beam.



(II) *Structure of* $(NH_4)_2SiF_6$. Angle of tilt of specimen is 55°.



(III) *Mosaic single crystal film of* γ-Mo_2N.



(IV) *Structure of kaolinite*. Angle of tilt is 60°.

determined by the experimental values of *F*(*hkl*) according to eqn. (3), its absolute value, however, being dependent also on the value of the zero coefficient *F*(000), determining the mean inner potential $\phi_m = F(000)/V$. Without the *F*(000) term, the beginning of the scale is the *O′–O′* line in Fig. 10(*a*); its introduction transfers the beginning to the *O–O* line. The Reviewer[9] assumed from theoretical calculations that ϕ_m(Ag) is 38·8 v. On averaging the background oscillations, a value of $\phi_{\min}$(Ag) = 17 ± 4 v was obtained as the minimum potential value in interatomic space. According to other, more precise, data,[14] however, ϕ_m(Ag) is equal to 23 v, from which it follows that $\phi_{\min}$(Ag) = 1 ± 4 v. Thus the potential in the interatomic space of metals is in practice very close to zero but still remains positive throughout, as would follow from general conceptions.

Most sharply pronounced in electron-diffraction is the ionic nature of the bond, since there occur a decrease in the potential of anions and an increase in that of cations, as compared with neutral free atoms [Fig. 10 (*b*)]. The value of the potential in neutral free atoms may be estimated theoretically, from the so-called atomic amplitude curves.[6,15,16] Thus, in the analysis of the structure of cryptohalite (above),[31] it was found that $\phi(0)_{\mathrm{Si}} = 428$ (420), and $\phi(0)_{\mathrm{F}} = 278$ v (290). A comparison of the theoretical values given in parentheses shows that in this lattice silicon is positively, and fluorine negatively, ionised, the bond thus having an ionic nature. It should be noted that the fluorine potential peak has proved to be also more "compressed", which may be accounted for by the above-mentioned effect of the electron shells' being drawn towards the nucleus,

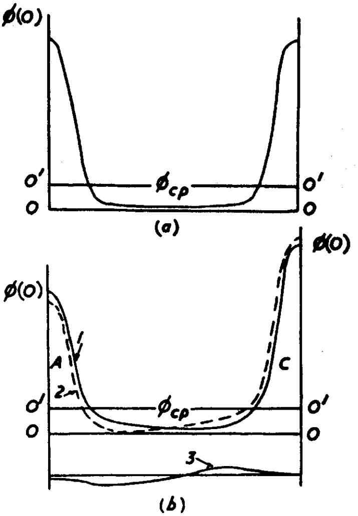


FIG. 10. *Schemes of potential distribution:* (*a*) in metal; (*b*) 1, in the crystal structure of neutral atoms; 2, in the same structure at ionisation (C=cation, A=anion); 3, the difference between curves 2 and 1.

a decrease of r^2 [formula (6′)], which is particularly marked for elements at the end of the second period of the Periodic Table.

In the course of a study of the chemical bond in the LiH structure,[36] the following values have been obtained: $\phi(0)_{Li} = 142$ (138), $\phi(0)_H = 43$ (55), all values being in volts, and in parentheses the theoretical values for neutral atoms being cited. In this way, in this hydride occurs a marked ionic bond Li^+H^-.

When studying NaF Japanese investigators[37] used the procedure of a difference synthesis or subtracting of peaks, already referred to in the description of the study of paraffins (cf. Fig. 4). The (3) series is constructed in this case according to the coefficients ($\Phi_{exp.}-\Phi_{calc.}$), where the experimental coefficients $\Phi_{exp.}$ carry the effect of ionisation and, in general, of electron redistribution, while the values of $\Phi_{calc.}$ have been calculated for neutral atoms. In Fig. 11 is shown the picture of distribution of such a difference potential in the plane passing through Na and F atoms [see the non-dimensional scheme, Fig. 10(*b*)]. The difference distribution in Fig. 11 shows that there occurs a shift of the negative charge from the periphery of the Na^+ cation to that of the F^- anion, especially along the line connecting these two atoms. $\phi(0)_F$ is diminished (by about 13 v) and $\phi(0)_{Na}$ is slightly raised (by about 2 v).

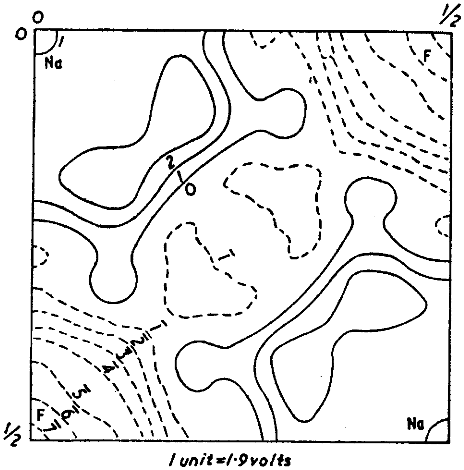


FIG. 11. *Difference synthesis of potential of* NaF *along the* (100) *plane.*

Some details of the picture obtained may be due to errors in the determination of *F*(000), but the general nature of the potential redistribution (and hence of the charge) is not subject to doubt.

The lattice consisting of anions and cations is on the whole neutral; the external negative shell of the potential of anions enters into the lattice

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[36] Pinsker and Kurdyumova, *Kristallografiya*, 1958, **3**, 501.
[37] Kitamura and Honjo, see ref. 29.

potential in a superposition with the excess of positive potential of cations [cf. Figs. 3(*b*) and 10(*b*)]. It is not clear *a priori* whether, in the ionic lattice at the boundary of anions, there might be sites with a negative potential (in metals and lattices of "neutral" atoms this is altogether impossible). In the synthesis shown in Fig. 11, owing to its different nature, the $F(000)$ value does not enter, and according to other data[5] it is equal to +8·3 v for NaF. This is larger than the value of —4 v on the periphery of the atom, according to Fig. 11, and hence the potential of this lattice is positive everywhere, as has been also found in the investigations of LiH and cryptohalite referred to above. Thus the view as to the non-negative values of the potential in "interatomic" space of crystal structures seems to be of general validity.

A qualitative deduction as to the nature of the bond may be made without reference to the potential maps, by direct consideration of the course of $F(000)$ amplitudes depending on the θ scattering angle which is characterised by the value $\sin\theta/\lambda$. From the values of $F(000)$ amplitudes one may pass to the atomic amplitude $f_e(\sin\theta/\lambda)$, characterising the scattering by a particular atom, and hence its electron structure, f_e being equal to $f_e(0)$ at $\sin\theta/\lambda = 0$ according to eqn. (6′).

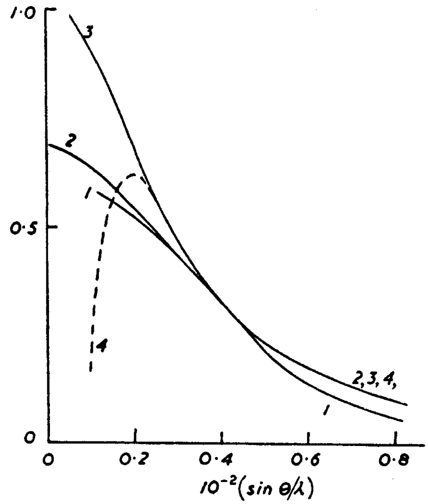

FIG. 12. f_e *Curves of oxygen in* Li_2O. (1) Experimental; (2), (3), (4) theoretical (see text for explanation).

In Fig. 12 is shown the fe curve (1) for oxygen, found in the course of a study of Li_2O;[38] theoretical curves are also drawn, corresponding to the free oxygen atom with a distribution after Hartree–Fock (2), to a bonded oxygen atom (3), and to the O^{2-} anion (4). From this Figure it is seen that

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[38] Vainshtein and Dvoriankin, *Kristallografiya*, 1956, **1**, 626.

the f_e curves at small angles are very sensitive to the nature of the bond. A qualitative inference from a comparison of curves 1—4 is that the bond in Li_2O is basically of a covalent nature, but has also a very small contribution from the ionic state, since at low angles curve 1 is somewhat below curve 3. The lowering of curve 1 as compared with the theoretical curves at large angles is due to the thermal motion of atoms in the lattice and is not related to the state of the atom.

It should be noted that there is a possibility of finding the structure amplitudes $F(hkl)$, not from intensities, but from the fine structure of the interference spots of electron-diffraction patterns, arising from the so-called dynamic birefringence, if the microcrystals studied have a regular habit. This possibility has been realised, and the Fourier potential series has been constructed for the MgO structure.[39]

The statements made above may now be summarised. Electron-diffraction data make it possible quantitatively to characterise the distribution of the electrostatic potential of atoms in the crystal lattice and to make a number of inferences regarding the chemical bond. These investigations require a high accuracy of experimentation and have as yet been carried out only on crystals of fairly simple structure. From the examples cited it is seen that it is easiest to establish the presence or absence of ionisation of the atom. The identification of a covalent bond, in which there is no passage of electrons from one atom to another, is more complicated, but nevertheless also possible, particularly if difference syntheses are used.

We may note that in principle (with the aid of the Poisson equation) it is possible to find from the potential distribution that of the charges, and to obtain the map of electron-density directly from electron-diffraction and not from *X*-ray data.

Study of the structure of nitrides and carbides of metals

Electron-diffraction has been applied to this problem for a number of reasons. One of these is the comparative simplicity of preparing one-phase specimens of metals in thin layers in the gas phase. By sublimation of pure metals onto a heated orienting support [*e.g.*, the (100) face of rock-salt] the metal film may be made a single-crystal one, which facilitates some stages of the study and allows, in particular, the orientational relations between the phases to be established. *X*-Ray studies of this kind are carried out on polycrystals by the Debye method, which makes it difficult to carry out structure determinations. Moreover, not one but several phases are as a rule contained in polycrystalline macro-specimens making it difficult to carry out an *X*-ray analysis.

Another advantage of electron-diffraction lies in the possibility of locating light atoms (carbon and nitrogen in this particular case) in the presence of heavy-metal atoms.

[39] Cowley, Goodman, and Rees, *Acta Cryst.*, 1957, **10**, 19.

At the same time, in analysing such specimens one encounters some specific difficulties, in particular, in the determination of the composition of the films. Nitrides and carbides, forming interstitial structures, are generally represented on the equilibrium diagram by several phases, these being in most cases phases of variable composition. Chemical analysis of the thin films, studied by electron-diffraction methods, is very difficult. So an electron-diffraction study of structure is in this case also a determination of composition; *i.e.*, here is an example of chemical analysis by the diffraction method. Nitridation of the films is carried out at temperatures of 300—500°C in a stream of ammonia, which at the metal surface dissociates into nitrogen and hydrogen: $2x\text{M} + 2\text{NH}_3 \rightarrow 2\text{M}_x\text{N} + 3\text{H}_2$. Gas-cementation of films is made in a stream of carbon monoxide.

An electron-diffraction study of the systems Fe–C, Fe–N, Cr–N, Mo–N, W–N has been systematically conducted by Z. G. Pinsker and his colleagues.[40–43] Recently, the Ni–C system has been studied by Japanese authors.[44] Here only a selection of results will be cited.

The structure of cubic iron nitride, Fe_4N, has been repeatedly subjected to *X*-ray analysis; but owing to the fact that the scattering of *X*-rays is primarily determined by the presence of four iron atoms, it was not possible to obtain direct information on the arrangement of nitrogen atoms in this structure. An idea of their position could be obtained only on the basis of geometrical analysis, *i.e.*, by considering the crystal chemical radii of Fe and N atoms.

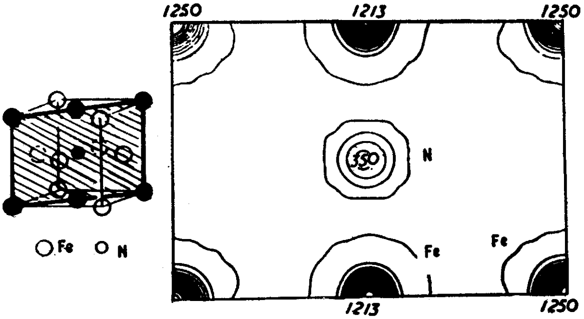

FIG. 13. *Potential of* Fe_4N *in plane* (110) (volts).

By employing precision electron-diffraction methods and introducing, in particular, the dynamic correction *Q* when trying to find the structure amplitudes *F*(*hkl*), Dvoriankina *et al.*[41] calculated the potential distribution in the (111) plane of this structure (Fig. 13). In this map

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[40] Pinsker and Kaverin, *Kristallografiya*, 1957, **2**, 386.

[41] Dvoriankina and Pinsker, *Kristallografiya*, 1958, **3**, 438.

[41a] Pinsker and Abrosimova, *Kristallografiya*, 1958, **3**, 281.

[42] Troizkaija and Pinsker, *Kristallografiya*, 1959, **4**, 38.

[43] Hitrova and Pinsker, *Kristallografiya*, 1958, **3**, 545.

[44] Nagakura, *J. Phys. Soc. Japan*, 1957, **12**, 484; 1958, **13**, 1005.

the peak of the nitrogen atom potential is distinctively revealed. In viewing this pattern a small difference may be noted in the heights of the potential maxima of iron atoms lying at the origin of co-ordinates (1250 v) and in the centres of faces (1213 v). If a difference in the ionic state exists, the profiles of maxima should be different. They were found, however, to be similar, from which fact it was inferred that the difference in heights reflects a small disturbance of the stoicheiometric composition of the phase, which corresponds here to the subtraction structure. The positions in centres of faces are occupied by approximately (1213/1250) $\times$ 100 $=$ 97% atoms of Fe, and the formula of this nitride may be written as $Fe_2Fe_{2(1-x)}N$ ($x = 0{\cdot}03$). Probably, it is the vicinity of the nitrogen atom, to which the distance from the second atom of iron, 1·90 Å, is less than from the first (3·29 Å), that explains the partial non-occupation of the positions referred to.

A comparison of the heights of maxima with theoretical values indicates a certain diminishing of the potential $\phi(0)_N$, which may be accounted for by an excess of electrons in nitrogen atoms. It should be noted that, owing to a smaller amplitude of thermal oscillations of atoms, the peak heights of carbon and nitrogen in carbides and nitrides are always greater than those in ionic or organic compounds. Therefore, comparison with theory is made with a proper choice of the B parameter of the thermal motion, which in this particular case was equal to unity. The inference as to the anionic state of nitrogen was made by constructing f_e curves (cf. Fig. 12) in the analysis of the CrN structure also.[41a]

Deviation from the stoicheiometric composition, as well as the distribution of nitrogen atoms over several equally probable positions, which are characteristic of interstitial phases, has been revealed also when analysing the structure[42] of γ-Mo_2N (electron-diffraction pattern III). This structure is represented in Fig. 14.

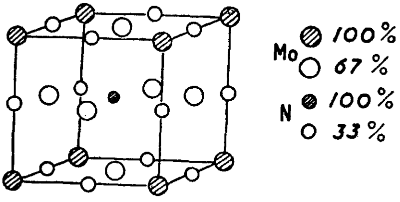

FIG. 14. *Structure of* γ-Mo_2N.

X-Ray structure data on nitride phases of tungsten are both indistinct and incomplete. It is altogether hopeless to attempt—even if *X*-ray photographs be obtained— to reveal the arrangement of nitrogen atoms ($Z = 7$) in the presence of tungsten atoms ($Z = 74$).

In studying films of tungsten nitrides,[43] prepared under different conditions of nitridation, in addition to electron-diffraction patterns from the well-known cubic phase of β-W_2N with a period $a = 4{\cdot}12$ Å, electron-diffraction patterns have been obtained from four hexagonal phases, not described previously, with $a = 2{\cdot}89$ Å and $c = 15{\cdot}3$ (i), 22·8 (ii), 23·4 (iii) 32·8 (iv) Å. The hexagonal δ-phase, known from *X*-ray data, with the same *a* period = 2·89 Å, but a short *c* period = 2·82 Å, was not observed. A complete structure study of phase (i) was carried out. This phase was found to be built up of three-layer sheets of tungsten atoms, the nitrogen, atoms entering into the packing holes–trigonal prisms. The sheets are superimposed upon each other according to the principles of close packing (Fig. 15). The positions in the centre are occupied by tungsten atoms to 100%, and the external "defective" positions only to 65%, which leads to a formula $W_2W_{4(1-x)}N_4$ ($x = 0{\cdot}35$), as against the "ideal" formula W_6N_4. It is noteworthy that for the distances W–W along the vertical we have a normal value of 2·80 Å, and for the "defective" W atoms a diminished one, 2·56 Å (the positions are occupied statistically). The W–N distance has been found to be 2·23 Å.

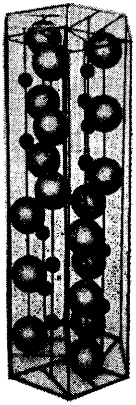

FIG. 15. *Model of structure of* W_6N_4.

An electron-diffraction study[44] of the structure of nickel carbide, Ni_3C, has revealed the conditions of the most rapid formation, as well as of the decomposition, of this carbide. The electron-diffraction patterns have been treated after introduction of the dynamic correction. Construction of the Fourier potential projection on the basal plane (Fig. 16) has revealed both nickel and carbon atoms. The unit cell has a large period, $c = 12{\cdot}92$ Å. Nickel atoms are arranged within it in closest hexagonal packing, while carbon atoms are distributed in one-third of the octahedral holes of this packing according to a rhombohedral law. By evaluation of the width of certain diffraction lines, the degree of ordering in this structure could be established. It was found that the mean size of the regions in which carbon atoms are regularly positioned is 28 Å, which corresponds to about 13 layers of packing.

Thus, in electron-diffraction studies of interstitial phases it is feasible fully to establish their structure, including the position of light atoms (which is difficult by *X*-ray methods), to reveal the composition of these phases, to give a quantitative characteristic of the statistics of arrangement of certain atoms, to estimate in some cases the chemical state of the atoms, and to analyse the orientational correspondence in a mutual phase transition.

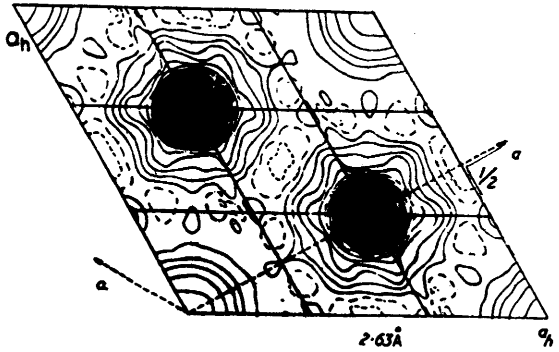

FIG. 16. *Projection of potential of* Ni_3C *on the basal plane.*

Some other applications of structure analysis by electron-diffraction. Conclusion

In a number of electron-diffraction studies use was made of the possibility of determining the structure of crystals in a highly disperse state. In these studies no qualitatively new relations have been established as compared with data of *X*-ray analysis. However, the crystal chemistry of this kind of substance, as a consequence of the specific features of *X*-ray structure analysis, requiring the availability of single-crystal specimens, presents a sort of "white spot" against the background of a huge number of other compounds studied by *X*-ray methods. Each new structure determination is, therefore, of essential importance.

A good example of such a work is furnished by the study of basic lead carbonate.[45] The crystals of this basic salt represent minute hexagonal plates about 5μ across. This compound is formed in aqueous suspensions of lead oxide by interaction with the carbon dioxide of the air. It has been found that $Pb(OH)_2,2PbCO_3$ has a hexagonal unit cell with $a = 9{\cdot}06$ Å, $c = 24{\cdot}8$ Å. The structure is built up of three-layer sheets 8·24 Å thick, in which the layer of $Pb(OH)_2$ is surrounded by a layer of $PbCO_3$ on each side.

Fig. 17 shows a difference Fourier potential projection of one sheet of this structure, from which atoms of Pb have been subtracted. The light

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[45] Cowley, *Acta Cryst.*, 1955, **9**, 397, 399.

atoms of C and O are well revealed. The interatomic Pb–O distances vary over the range 2·5—2·8 Å; the C–O distance in the CO_3 group is 1·45 Å.

The structure of an individual sheet is comparatively stable, and the interaction between sheets is determined by weak residual forces. In this structure, therefore, as well as in many other layered structures, particularly in clay minerals, errors in the sheet positions have been revealed.

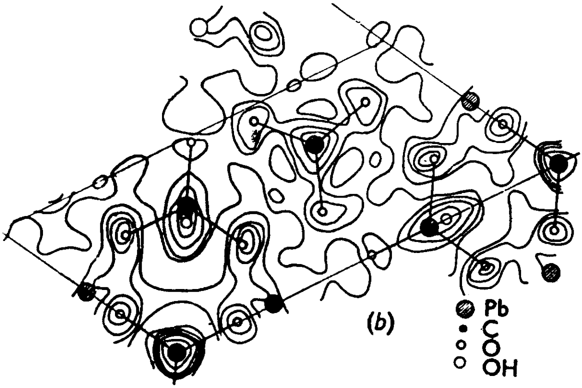

FIG. 17. *Projection of potential of basic lead carbonate.* Contributions of Pb atoms in the indicated positions have been subtracted.

The statistics of these positions may be described by a certain distribution function, being directly determined from the electron-diffraction pattern.

In another example of structure study[46] of a basic salt, $CuCl_2,Cu(OH)_2$, a characteristic tendency of the copper atom to form square complexes has been revealed. Four hydroxyl group of the six anions surrounding Cu are spaced at distances of 1·86—1·97 Å, which points to a covalent nature of these bonds. The other OH groups (or Cl ions) are situated at considerably greater distances, *viz.*, 2·37 and 2·86 Å, respectively.

An important field of application of electron diffraction is in the study of clay minerals.[47] The specific features of the latter are: highly dispersed state; disturbances of structure perfection; variations in composition, related to isomorphous replacements of cations; and laminated, or less frequently fibrous, form of particles. Specimens for study are prepared from aqueous suspensions. Most favourable for structure analysis are diffraction patterns from laminated textures of clay minerals. The formation of such textures is related to the layer nature of their atomic structure, built up of octahedron networks, populated by cations of the Mg, Al, Fe type, and tetrahedron networks of SiO_4. It should be noted that electron-diffraction data concerning the structure of the swelling clay minerals of the montmorillonite group, obtained in conditions of high vacuum, refer only to a fully dehydrated state.

[46] Voronova and Vainshtein, *Kristallografiya*, 1958, **3**, 444.

[47] Pinsker, Works of the Institute of Geochemistry, Acad. Sci. U.S.S.R., 1954, p. 116.

In every clay mineral there are specific characteristics due to their being built up, in the ideal scheme, of networks of octahedra and tetrahedra. Among these features are: nature of linkage of the networks and their mutual orientation; specific configuration of the networks and the interatomic spaces inside them; structure of interlayer spaces; and, finally, the mutual arrangement of layer sheets.

Already, in addition to numerous studies on the electron-diffraction determination of the unit cells of clay minerals, some examples of full structure determinations are also available. Zvyaghin[48] has studied the atomic structure of seladonite—a ferromagnesium mica, which is representative of "three-storey" clay minerals, the layer of which is built up of an octahedron network with networks of tetrahedra on each side. The same author[49] has determined the structure of kaolinite, the most important representative of clay minerals, built up of "two-storey" layers (one network of octahedra and one of tetrahedra) (electron-diffraction pattern IV). This structure has no centre of symmetry, and its layers are polar. The unit cell is triclinic: $a = 5{\cdot}13$, $b = 8{\cdot}89$, $c = 7{\cdot}25$ Å, $\alpha = 91°40'$, $\beta = 104°40'$, $\gamma = 90°$. The construction of the Fourier potential projections (Fig. 18) and the determination of structure, because of the absence of a centre of symmetry, were considerably more complicated than if a centre of symmetry had existed. In particular, the structure factors $F(hkl)$ have in this case complex numbers. A unique result in calculating a non-centrosymmetrical structure is achieved by a series of successive approximations. The accuracy of determination of the atom co-ordinates is about 0·03—0·04 Å.

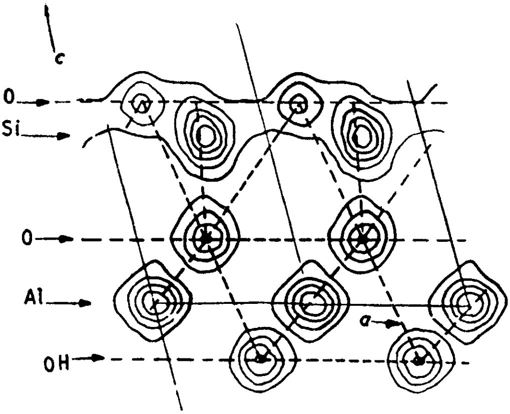

FIG. 18. *Side projection of kaolinite* $Al_2Si_2O_5(OH)_4$. The structure of the sheet built up of Si tetrahedra and Al octahedra is clearly seen. (Broken lines represent the edges of polyhedra.)

As a result of this study, a number of peculiar features in the structure of

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[48] Zvyaghin, *Kristallografiya*, 1957, **2**, 393.
[49] Zvyaghin, *Kristollografiya*, 1959, **4**, 5.

kaolinite have been revealed, concerning the structure and combination of the tetrahedral and octahedral networks. The O–O distances in the common edges of the octahedra are reduced, and the octahedra as a whole are somewhat flattened. The Al atoms are shifted to the lower sides of the octahedra (towards the OH groups), and the Si atoms in the SiO_4 tetrahedra towards the upper bases of tetrahedra. The atoms of the two external sides of the sheet do not lie in one plane but form a goffered network. The contact between the adjacent layers takes place between the atoms of oxygen and the hydroxyl groups, and hydrogen bonds are perhaps formed between them.

It should be noted that in recent years additional possibilities of studying the atomic structure of matter (and of clay minerals in particular) have been offered by the use of the microdiffraction method,[50] allowing a diffraction pattern to be obtained from an individual microcrystal, as well as by the use of superhigh (400 kv) voltages for electron acceleration.[51]

In conclusion, the author would like to stress that the present Review does not in any way pretend to give a survey of all the work on electron-diffraction, in which problems of the atomic structure of matter and the chemical bond in crystals are attacked in varying detail. The number of papers on the electron-diffraction of solids exceeds 2000, and those on electron-diffraction structure analysis number over 300.

The object of the present Review has been a much more limited one, namely, to give the reader an idea of the principles and possibilties of electron-diffraction structure analysis of crystals and to show some instances of its application to the study of the chemical bond. Many of these examples represent work carried out at the Electron Diffraction Laboratory of the Institute of Crystallography of the Academy of Sciences of the U.S.S.R.

At the same time, owing to lack of space, this presentation has omitted a number of trends of electron-diffraction structure analysis which are of interest for the theory of the chemical bond. Among these are, in the first place, experimental and theoretical work on the structure and nature of interaction in simple layer lattices.[5] There is, in addition, work on the structure of crystal hydrates and the crystal chemical functions of water molecules in them.[6] In the series of studies on the crystal chemistry of transition metals—Co, Ni, Mn—peculiar features of octahedral co-ordination and the conditions of a passage to tetrahedral co-ordination have been revealed;[6,52,53] in the work[54] on the structure of $KPtCl_3,NH_3$, the effect of the influence of the NH_3 group on the lengths of the bonds Pt–Cl in the square complex of the Pt atom has been observed. Great

[50] Honjo and Mihama, *Acta Cryst.*, 1954, **7**, 511.

[51] Popov and Zwjagin, *Kristallografiya*, 1958, **3**, 706.

[52] Vainshtein, *J. Phys. Chim.* (U.S.S.R.), 1952, **26**, 1774.

[53] Tishenko and Pinsker, *Doklady Akad. Nank S.S.S.R.*, 1955, **100**, 913.

[54] Bokii, Vainshtein, and Babureko, *Izvest. Akad. Nank S.S.S.R., Otdel. Khim. Nauk*, 1951, **6**, 667.

interest attaches to work on the oxidation of metals,[5,32,55,56] and on the structure of metals and alloys.[5,57,58] A long series[59–61] of electron-diffraction investigations has been conducted on the atomic structure of semiconducting materials. (References 47–62 are only individual examples or reviews.)

Finally, we wish to draw attention to the following points. Electron-diffraction analysis may be regarded as an independent method for atomic structure analysis, furnishing, in particular, much valuable information on the chemical bond. But it would be a serious mistake to consider it as a universal method which may be substituted for *X*-ray structure analysis. A comprehensive study of the nature and properties of matter requires the use of the most diverse methods, including diffraction methods—the *X*-ray, electron-diffraction, and neutron-diffraction analyses. Each of them has its own advantages and limitations, and there is for each a special field of application.

The Reviewer thanks Prof. Z. G. Pinsker for reading the manuscript and making valuable suggestions.

[55] Dankov, Ignatov, and Shishakov, "Electronographicheskie issledovania okisnich i gidrookisnich plenok na metallah" (Electron diffraction investigations of oxide and hydroxide films on metals), Moscow, 1953.

[56] Ignatov, *Kristallografiya*, 1957, **2**, 4.

[57] Trillat and Takahashi, *Compt. rend.*, 1953, **236**, 2245.

[58] Fujiwara, Hirabayashi, Watanabe, and Ogava, *J. Phys. Soc. Japau*, 1958, **13**, 167.

[59] Semiletov, *Trudy Inst. Krist., Akad. Nank S.S.S.R.*, 1954, **10**, 189.

[60] Vainshtein, *Nuovo Cim.*, 1956, Suppl. V, **3**, 773.

[61] Semiletov, *J. Sci. Ind. Res.*, 1956, **16**, *A*, 377.

[62] Pinsker, *Adv. Electronics and El. Physics*, 1959, XI.