Acta Cryst. (1969). A25, 223

Survey of Results in the Determination of X-ray Intensities and Structure Factors for Metals, Alloys and Covalent Compounds

By N. N. Sirota

Institute of Physics of Solids and Semiconductors, Belorussian Academy of Sciences, Minsk, USSR

The problem of the interatomic bond in molecules and crystals is first of all that of a fairly precise determination of the electron distribution. The electron density distribution in crystals can be considered as the distribution of the square of the wave function. Thus an experimental determination of structure factors is one of the most direct methods of experimental determination of wave functions. Calculations of physical and physical-chemical properties of crystals can be made by using quantum mechanical methods, making use of wave functions obtained experimentally. The question arises of the necessary limits of accuracy of experimental F^2 values for solving various quantum mechanical problems as well as for comparing them with theoretical values. It should be noted that the theoretical structure factors are approximate since the exact solution of the Schrödinger equation is possible for the hydrogen atom only. Experimental determination of F^2 values on powders poses very complicated problems including the measurement of absolute X-ray scattering intensities. Results of experimental determinations of F^2 values on powder of metals, alloys, and compounds with covalent character, including semiconductors, are analysed. Possible reasons for deviations, including the role of extinction, particle size of the powders under investigation, possibility of preferred orientation, change of state and composition of the surface, the role of polarization of the monochromated beam and lattice dynamics, are discussed. The difference between the data of different authors, which seems to be due to the degree of the accuracy of scaling to absolute intensity values, is also discussed. Different parts of the f-curves give different information on the electron density distribution of the crystal. The amount of information which F^2 values contain on the outer electron distribution depends to a great extent on the type and the parameters of the crystal lattice, and on the degree of anisotropy. There are some differences mainly in absolute values between the data of different authors. Some problems of reduction of the reflexion intensities are also discussed. The results of some measurements made on powders of the elements and on the semiconducting-type compounds with covalent bonds are analysed as well. A large number of measurements were made on $A^{\text{III}}B^{\text{V}}$ compounds. The results show the differences in F^2 values due to the change of the effective charge of ions. In conclusion some experimental determinations of f-curves are quoted and the necessary accuracy and possibilities of correction of the measured intensity of Debye reflexions are evaluated.

Introduction

The possibility of using Fourier series and their importance in lattice theory had already been shown in the first theoretical investigations of X-ray diffraction by crystal lattices carried out by Bragg (1915), and in the fundamental investigations by Ewald (1921). In subsequent papers by Epstein & Ehrenfest (1924), Duane (1925), Compton (1926) and others, methods of using Fourier series were developed with the aim of determining crystal structures and of obtaining the density distribution of scattering material in the crystal. The method of Fourier analysis developed by Bragg (1929), Robertson (1936), Patterson (1936), Belov (1947), and others formed the basis of modern structure analysis.

On the other hand, investigations showing the possibilities of a quantitative determination of the electron density distribution in crystals in terms of structure factors and atomic scattering factors determined experimentally, acquired great interest for solving the problem of the chemical bond in crystals (Brill, Grimm, Hermann & Peters, 1939; Laschkarov, 1935).

However, solving the problem of the precise determination of atomic coordinates and particularly that of finding the real electron density distribution in the crystal is limited to a great extent by the accuracy of structure factor determination; hence the importance to the problem of the absolute measurement accuracy of X-ray intensities and the precision of the experimental determination of structure factors and atomic scattering factors.

The distribution of the electron density in a crystal or a molecule can be considered to a close approximation as that of the squared electron wave function:

$$|\psi|^2\,(x,y,z)=\varrho(x,y,z)\;.$$

Calculation of the electron density distribution in crystals from experimental data is, in principle, an experimental determination of the squared wave eigenfunction distribution which can probably be assumed to satisfy the only stationary solution of the Schrödinger equation.

This, in principle, allows one to find various physical and physico-chemical properties of crystals in terms of the wave functions determined experimentally either by the very powerful quantum mechanical methods which have been developed or by approximate statistical methods.

One of the most important problems of physics, that of the interatomic bond in molecules and crystals, is one of sufficiently accurately determining the electron density distribution in these (Coulson, 1961; Slater, 1963).

Development of reliable methods of electron distribution determination in crystals creates an experimental basis of quantum chemistry and allows one to obtain extensive information about the properties of crystals from diffraction measurements.

In realizing the extremely attractive possibilities of using the wave functions found experimentally in various quantitative calculations, difficulties of two kinds arise: firstly, difficulties connected with the necessity for sufficiently precise experimental determinations of the structure factors, and with finding the needed degree of accuracy of determination of the experimental data; secondly, the difficulties connected with the development of the methods of finding sufficiently accurate values of the electron density distributions in crystals in terms of the structure factors and atomic scattering functions determined experimentally. Considerable progress has been achieved in this question, which we shall not touch upon here. Moreover, and this we emphasize particularly for quantum-mechanical considerations, the calculation of the electron density distribution is often not necessary: it is frequently sufficient to make use of the structure factors F or of the atomic scattering f-functions directly.

The atomic scattering functions of neutral atoms seem to be little sensitive to changes of the outer medium; however they change to a certain extent by formation of the crystal lattice. The changes in these scattering functions will depend on the crystal structure and on its anisotropy, on the energy and especially on the type of interatomic bond.

In the light of what has been said above, comparisons of experimentally determined F- and f-functions with theoretical ones are of great interest. The fundamental importance of precision determination of structure factors and atomic scattering functions (form factors) has become obvious for the development of the theory. The evaluation of the required and of the actually obtained accuracy of F and f-factors for solving these various problems and the elucidation of the reasons which limit the possibilities of increasing the measurement accuracy are very important.

Below, we shall consider the data available in the literature for metals with different types of crystal lattice, for elements with a covalent bonding character which form a diamond structure and then for some simple compounds mainly of the semiconducting type with a sphalerite structure. We should note that in many published papers there is a lack of the necessary minimum of information on the results of the initial experimental determinations before they are subjected to any subsequent treatment. Meanwhile, the I.U.Cr. project on accurate intensity measurements shows the advisability of publishing the original measurements

Table 1. *Experimental and theoretical values of atomic scattering functions of* Al

		f_{theor}	f_{exp} James, Brindley & Wood (1929)		f_{exp} Brindley (1936)			f_{exp} Ageev & Ageeva (1948)				f_{exp} Bensch, & Witte & Wölfel (1955)	f_{exp} Roof (1959)	f_{exp} Batterman Chipman & DeMarco (1961)
hkl	sin θ/λ	H.–F.	290°K	0°K	20°C	0°K	0°K	20°C	0°K	20°C	0°K	0°K	0°K	0°K
111	0·214	9·03	8·46	8·78	8·70	8·83	8·86	8·45	8·75	8·41	8·71	8·55	9·41	8·63
200	0·247	8·60	7·96	8·39	8·03	8·24	8·28	7·90	8·28	7·93	8·31	8·21	9·10	8·25
220	0·350	7·37		—	6·74	7·23	7·30	6·55	7·20	6·55	7·20	7·15	7·55	7·09
311	0·410	6·69		—	5·91	6·55	6·63	5·69	6·48	5·67	6·46	6·48	6·71	6·42
222	0·429	6·50	5·52	6·45	5·73	6·42	6·51	5·45	6·28		—	6·38	6·38	6·19
400	0·491	5·79	4·65	5·73	—	—							5·49	5·48
331	0·539	5·34		—	4·21	5·09	5·21	4·13	5·20		—		5·03	4·96
420	0·553	5·20		—	4·06	4·96	5·06	3·82	4·84		—		4·88	4·67
422	0·606	4·69		—	3·45	4·40	4·53	3·26	4·33		—		4·42	4·38
511, 333	0·632	4·38	2·99	4·25										4·00
B(Å^2)				0·774		0·744	0·8528*		0·774					0·8528
Particle size, μ			Single cryst. (111),(100)											5–10
X-ray			Mo $K\alpha$			Cu $K\alpha$		Cu $K\alpha$		Fe $K\alpha$			Mo $K\alpha$ Cu $K\alpha$ Cr $K\alpha$	Mo $K\alpha$ (LiF)
μ (cm^{-1})														13·5
$\Delta f'/\Delta f''$						−0·18/		−0·18/		−0·21/				0·1/
Absolute scale by			I_0			I_0		Al (Brindley)					I_0	I_0

in a certain standard form so as to allow comparisons of the results to be made independently of the state of the X-ray scattering theory at the moment of carrying out the work, and of the degree of reliability of the available subsidiary data used in the calculations.

The results of some investigations devoted to the absolute determination of F- and f-factors have been discussed by James (1950) and Weiss (1966). In the review by James relatively old papers were considered. The review of the latest papers by Weiss is, however, practically confined to an analysis of American investigations only. In the subsequent treatment we also deal partly with relatively old papers so as to give a sufficiently complete picture of the present state of the problem and of the progress achieved. It should be noted that some of the early work was carried out at a high experimental level and has not lost its importance now.

Below we shall consider the data available, in the literature, of structure amplitude and atomic scattering factor measurements of metals, elements and simple compounds, chiefly with covalent or semiconductor bonds.

We shall use the value of the disagreement factor as a basis for a comparison of the literature data with the theoretical data according to Hartree–Fock. In order to show the difference between the theoretical values of different theories, we also quote the values of the disagreement factor for the data calculated according to Slater–Dirac, Thomas–Fermi and Wakoh.

There is a possibility of obtaining the f-curves with an accuracy sufficient for testing and refining the theory and to elucidate the possibility and advisibility of using the experimental f- and F-functions for quantum mechanical and other calculations. Therefore, consideration of divergences between both experimental and theoretical values is of interest.

In the Tables given below we quote the results of the authors in the form in which they are given by them. In addition, to allow comparisons to be made, we have reduced the values to absolute zero using the temperature and other factors indicated by the authors.

In the case of compounds some reflexions are sensitive to changes of the effective charges of ions. This circumstance should be taken into account in analysing the values of the disagreement factors. We touch mainly upon work accomplished on powder samples. However, we also quote data obtained on monocrystals for comparison.

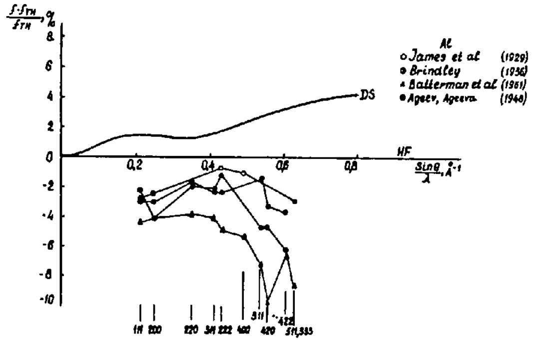

Fig. 1. Relative differences between various experimental and theoretical f-factors of Al.

Structure factors and atomic scattering functions of metals

Among the metals with face-centered cubic structures experimental measurements of atomic scattering factors were made for the metals Al, Ni, Cu, Ru, Cr, Fe, and with hexagonal structure for Mg, Zn.

Aluminum was investigated by Bearden (1927), James, Brindley & Wood (1929), Brindley (1936*a*), Ageev & Ageeva (1948*a*), Bensch, Witte & Wölfel (1955), Roof (1959), Batterman, Chipman & DeMarco (1961).

In Table 1 experimental and theoretical values of atomic scattering functions of aluminum and some data on the experimental conditions are given.

Fig. 1 shows the values of the disagreement factors, experimental and theoretical values for various *hkl* reflexions with the theoretical data according to Hartree–Fock.

Bearden (1927) made intensity measurements by three methods: on flat powder samples by reflexion and by transmission, and on a single-crystal sample by reflexion. As the author points out, the results on flat powder samples agreed fairly well with each other. However, the measurements on the single-crystal sample and the powder samples did not agree well, because extinction had not been fully taken into account.

James, Brindley & Wood (1929) measured the absolute value of the integrated intensity of reflexions and determined the temperature factors on two Al flat single crystals with planes 111 and 100. Scaling to absolute values was made by comparison with NaCl; the measurements were made at two temperatures: room temperature and that of liquid air. Investigations were carried out with Mo $K\alpha$ radiation without a monochromator. Correction was made for extinction.

Brindley (1936*a*) determined the Bragg reflexion intensity by a photographic method, scaling to the absolute values determined for finely ground KCl powder. X-ray measurements were made with Cu $K\alpha$ radiation. The aluminum samples were powders.

Ageev & Ageeva (1948*a*) made their measurements of the Bragg reflexion intensity by a photographic method, using a flat sample with Fe $K\alpha$ ($\lambda = 1{\cdot}934$Å) and Cu $K\alpha$ ($\lambda = 1{\cdot}539$ Å) radiations. X-ray measurements of the samples were made at three different angles, 30°, 56° and 83° 30′ for copper radiation and 35° and 49° for the iron radiation. The absorption factor was determined by the Brindley & Spiers (1934) method. Scaling for the 002 surface was made to the values defined by James, Brindley & Wood (1929) with dispersion corrections according to Hönl (1933). Roof (1959) investigated flat powder samples with three radiations: Mo *Kα*, Cu *Kα* and Cr *Kα*, with the aim of accounting for extinction and for the surface roughness of the sample. The measurements were made on a diffractometer. Corrections were made for dispersion and temperature factors. Chipman & Paskin (1959) criticized these results, pointing out the error made by calculation and by the insufficiently correctly chosen absorption factor μ.

Batterman, Chipman & DeMarco (1961) investigated aluminum powders with particle sizes 5–10μ and purity 99·6%. The presence of preferred orientation at different pressures of powder compression was taken into account. X-ray measurements were made with Mo *Kα* radiation using a bent LiF crystal monochromator.

Some of the experimental conditions, the corrections, and the absorption coefficient values adopted in the papers of different authors are given in Table 1. As is seen from the quoted data, which are unfortunately not reported by all of the authors, a considerable discrepancy exists not only in the experimental conditions but also in the methods of treating the results.

Copper was investigated by Armstrong (1929), Wyckoff (1930), Rusterholz (1930), Brindley & Spiers (1935), Rovinskii (1937), Ageev & Ageeva (1948*b*), Batterman, Chipman & DeMarco (1961), Jennings, Chipman & DeMarco (1964), Hosoya & Yamagishi (1966) and others.

Table 2 gives the values of the atomic scattering functions of copper according to the data of the above papers as well as the theoretical data. Fig. 2 shows the relative deviation of the experimental and theoretical values from those according to Hartree–Fock.

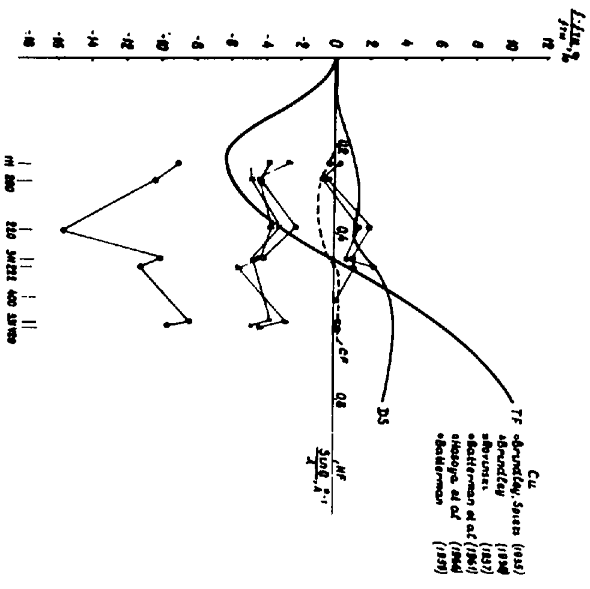

Fig. 2. Relative differences between various experimen al and theoretical *f*-factors of Cu.

Table 2. *Experimental and theoretical atomic scattering functions of* Cu,

		f_{theor}				f_{exp}											
hkl	sin θ/λ	H.–F.	D.–Sl. (1965)	T.–F.	H.–F. with crystal field	Brindley & Spiers (1935)	Brindley (1936)	Rovinski (1937)	Wyckoff (1930)	Armstrong (1929)	Ageev *et al.* (1948)	Jennings *et al.* (1964)	Batterman *et al.* (1961)	Batterman (1959)	Hosoya *et al.* (1966)	Hosoya *et al.* (1966)	Rusterholz (1930)
111	0·240	22·13	22·47	20·72	22·06	20·11	21·55	21·21	19·28	18·71	21·3	21·52	21·29	22·2	22·08	22·02	18·07
200	0·278	20·74	21·00	19·82	20·57	18·56	19·85	19·74	17·72	17·20	19·5		19·75	20·6	20·70	20·62	16·52
220	0·391	16·75	17·02	16·25	16·61	15·11	16·14	16·23	14·74	14·32	16·3		16·37	17·0	17·13	16·99	14·05
311	0·459	14·76	15·05	14·70	14·71	13·26	14·13	14·09	12·95	12·60	14·5		14·14	14·9	14·96	14·79	11·90
222	0·480	14·17	14·50	14·33	14·19	12·56	13·37					14·01		14·5	14·39	14·23	
400	0·556	12·40	12·85	12·85	12·43										12·48	12·28	
331	0·604	11·37	11·76	12·02	11·40	10·41	11·05	10·95			11·1				11·47	11·26	8·58
420	0·620	11·09	11·44	11·79	11·11	10·01	10·61	10·55			10·7				11·11	10·90	8·46
422													9·69				
511												9·41	8·37				
333																	
B(Å^2)						0·540	0·540	0·540	0·603*	0·603*	0·603*	0·550	0·543	0·555	0·603	0·543	0·603*
Particle size, μ						~5	~5	10–12	—	—	—	single crystal	~5	~5	~5	~5	—
X-ray						Cu *Kα*	Cu *Kα*	Cu *Kα*	—	—	Cu *Kα*	Mo *Kα*	Mo *Kα*	Fe *Kα*	Cu *Kα*	Cu *Kα*	—
μ (cm^{-1})						—	—	—	—	—	—	—	49·24	96·3	452	452	—
$\Delta f'/\Delta f''$						—	−2·6				−2·6	0·35/	0·35/	−1·51/ 0·93	−2·1/ 0·7	−2·1/ 0·7	—
Absolute scale by						KCl	Al . KCl	Al	NaCl	NaCl	Cu	I_0	I_0	NaCl	I_0	I_0	Al

In the detailed paper of Brindley & Spiers (1935) results were obtained which in the main confirmed the measurements of Wyckoff (1930) and Rusterholz (1930). The measurements were made with copper $K\alpha$ radiation on thin powders obtained by the method of chemical deposition. The particle sizes did not exceed 5μ. Transformation to an absolute scale was made by the reference sample method, with a KCl reference. In this work both the mixture method and that of separate X-ray measurements were used. Dispersion corrections were made according to Hönl. The characteristic temperature was assumed to be $\Theta = 315\,°\mathrm{K}$. Brindley (1936*a*) introduced the dispersion corrections which he determined as the difference between the theoretical values (according to Hartree–Fock) calculated in the paper of James & Brindley (1931) and the experimental ones.

Rovinskii (1937) made use of the photographic method for determining X-ray scattering intensities on powders with dimensions 10–12μ, finely ground by spraying, and annealed *in vacuo*. X-ray measurements were made on cylindrical samples consisting of a mixture of copper and aluminum powders bonded by Zapon varnish. The scaling was made against aluminum.

This author paid special attention to the role of the degree of dispersion of the powder and to the influence of lattice distortions on the absolute intensity determination.

Ageev & Ageeva (1948*b*) made their measurements by a photographic method on flat powder samples obtained by the condensation method in vacuum, according to Vekshinskii (1944). Annealing was carried out at 300 °C *in vacuo* to obtain powders of the needed degree of dispersion. X-ray measurements were performed with copper radiation without a monochromator. Dispersion corrections were made according to Hönl. Scaling to the absolute values was made according to Brindley, using the intensity of the copper (111) line, which was assumed equal to 18.3 at room temperature, taking into account the dispersion correction. Batterman, Chipman & DeMarco (1961) made absolute intensity measurements of Bragg reflexions on flat powder samples compressed at different powder pressures using Mo $K\alpha$ radiation. The particle size was 5μ. The purity of the copper was 99·2%. Attention was paid to the presence of preferred orientation, and the role of the cold treatment was taken into account. Dispersion corrections were also taken into account.

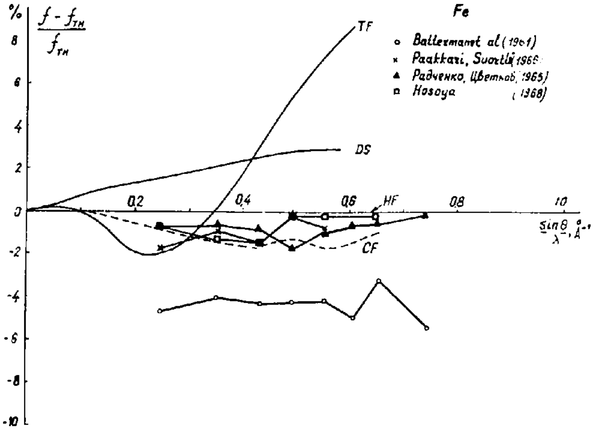

Fig. 3. Relative differences between various experimental and theoretical f-factors of Fe.

For comparison with the results of the previous authors we shall also quote the data obtained in the work by Jennings, Chipman & DeMarco (1964) on copper single crystals in a monochromated primary beam of Mo $K\alpha$ radiation. In calculating the f-factors these authors made corrections for thermal diffuse scattering, Debye–Waller factor and dispersion ($\Delta f^1 = 0{\cdot}55$). Single crystal samples with various etch pit densities were investigated. Three reflexions, 111, 222 and 333 were measured.

Hosoya & Yamagishi (1966) investigated four powder samples of copper with particle size 5μ. The powders were compressed at a pressure of $2 \cdot 10^3$ kg.cm^{-2}. No change of the reflexion intensity with compression was observed. One of the samples was prepared according to Batterman, Chipman & DeMarco (1961), the second was coated with an organic film, the third was the same as the second but without coating. The powder for the fourth sample was prepared by spark treatment; it was without coating. Similar results were obtained on all four samples. The Cu $K\alpha$ and Mo $K\alpha$ radiation was monochromated by quartz monochromators of two types. The temperature factor was determined as $\ln (F_{\text{theor}}/F_{\text{exp}})$ in the function of $\sin^2 \theta/\lambda^2$ ($B = 0{\cdot}584$ Å^2) for the Freeman–Watson and Wakoh curves. The transfer to an absolute scale was realized by direct measurements of the primary beam intensity I. The absorption coefficient μ was measured. Dispersion corrections for $\Delta f'$ and $\Delta f''$ were made. The measurements with copper and molybdenum radiation are in a good agreement. According to the authors, the samples under test were free of preferred orientation, effects of porosity and surface roughness.

Tsvetkov & Kravtsova (1963) made measurements of the Bragg reflexion intensities of copper. Scaling was carried out against the reflexion 220 of NaCl. In the published paper the tabulated values are not given.

Kritskaya & Rovinskii (1948) used the results obtained earlier to plot electron density distribution maps in copper.

Iron was investigated by Batterman (1959), Batterman, Chipman & DeMarco (1961), Radchenko & Tsvetkov (1965*a*), Paakkari & Suortti (1967) and by Hosoya (1968). Weiss & DeMarco (1958) made measurements on single crystal samples.

In Table 3 atomic scattering function values obtained in the papers of the above authors are given. In Fig. 3 the values of the disagreement factors are shown.

After the intriguing work of Weiss & DeMarco (1958), Batterman (1959) made measurements of the

Bragg reflexion intensities on samples prepared from compressed 30000 and 40000 p.s.i. powders in cylindrical pressforms. The particle size was 3μ. The purity of carbonyl iron was 99·5%. The powders were first subjected to cold work. In the paper the influence of compression pressure and preliminary cold work was investigated. X-ray measurements were made with monochromated (LiF bent monochromator) Fe $K\alpha$ and Mo $K\alpha$ radiation. The absorption coefficient was determined experimentally ($\mu = 70{\cdot}5$ cm^2.g^{-1}.). Scaling to absolute values was made against NaCl. Dispersion corrections were taken as $\Delta f' = 0{\cdot}4$, $\Delta f'' = 1$ for Mo $K\alpha$, and $\Delta f' = -2{\cdot}45$, $\Delta f'' = 0{\cdot}61$ for Fe $K\alpha$. $B_{293} = 0{\cdot}368$ according to Lonsdale ($\Theta = 420$°K).

Batterman, Chipman & DeMarco (1961) made absolute intensity measurements of Debye reflexions of iron and on the compressed powder samples on a diffractometer with Mo $K\alpha$ radiation. The choice of radiation had the purpose of decreasing the dispersion correction and the role of the surface roughness of the sample. The samples were prepared from carbonyl iron with particle diameters 3–5μ. Iron purity was 99·5%. For controlling and eliminating the texture the compression pressure was varied from 1 to 120000 p.s.i. The role of surface fluorescence was considered. Conversion of the relative measurements to the absolute ones was performed by determining I_0 and the ratio I/I_0.

For the absolute measurement of the primary beam three independent methods were used. They were: attenuation of the beam using a set of zirconium absorbers, a pinhole in a silver slit, and reflexion by a perfect silicon crystal. The difficulty consisted in decreasing the primary beam intensity by an exactly determined factor of the order of 10^4. All three methods gave similar results in which the discrepancy did not exceed 2%.

Tsvetkov & Kravtsova (1963) investigated the intensity of the Bragg reflexion of iron. The measurements were made with monochromated Mo $K\alpha$ radiation with a scintillation counter diffractometer, on samples prepared from iron powders with particle sizes 2–3μ. The sample density was 4·7–4·8 g.cm^{-3}. The plane 002 of pentaerythritol served as a monochromator. Texture effects and the state of the surface were neglected. Corrections were made for dispersion ($\Delta f' = 0{\cdot}4$ and $\Delta f'' = 1{\cdot}0$). The value of B was assumed to be 0·310 Å^2. Transfer to an absolute scale was carried out on the reflexions 220, 222, 400, 420, 422 of NaCl from which the scaling coefficients were determined.

Paakkari & Suortti (1967) made measurements of the absolute scattering factor of iron on samples from compressed powders of carbonyl iron with Mo $K\alpha$ radiation. The measurements were made on a diffractometer using a NaI(Tl) counter. The iron powder of purity 99·5% consisted of particles 3–5μ. The samples were prepared by compression at 400 kp.cm^{-2} and 2000 kp.cm^{2-}, and impregnated with a binding material (Tensol-cement no. 6). The surface of the sample was ground. Close values of the 110 reflexion intensities were obtained on all three samples. The absorption coefficient $\mu = 37{\cdot}90 \pm 0{\cdot}30$ cm^2/g was determined in agreement with the data of Cooper (1965*a*). A quartz monochromator was placed behind the reception slit to eliminate secondary radiation. The monochromator was considered to be ideally-mosaic. Absolute intensity measurements were made for the (110) line for which the absolute structure factor $F(110) = 36{\cdot}30 \pm 0{\cdot}40$ was found. Thermal diffuse scattering was taken into ac-

Table 3. *Experimental and theoretical atomic scattering functions of* Fe

hkl	sin θ/λ	f_{theor} H.–F.	f_{theor} Wakoh	f_{exp} Batterman (1959) 0°K	f_{exp} Batterman, Chipman & De Marco (1961) 0°K	f_{exp} Paakkari & Suortti (1966) 0°K	f_{exp} Radchenco & Tsvetkow (1965) 0°K	f_{exp} Hosoya (1968) 0°K
110	0·247	18·50	18·34	19·0	17·63 ± 0·20	18·19	18·33 ± 0·44	18·38
200	0·349	15·33	15·12	15·9 – 15·5	14·70 ± 0·23	15·19 ± 0·03	15·23 ± 0·15	15·13
211	0·427	13·20	12·98	14·0 – 13·8	12·62 ± 0·21	13·01 ± 0·03	13·09 ± 0·17	13·18
220	0·493	11·63	11·48	12·5 – 12·1	11·13 ± 0·20	11·60 ± 0·05	11·43 ± 0·17	11·60
310	0·551	10·55			10·10 ± 0·19	10·47 ± 0·05	10·45 ± 0·13	10·39
222	0·604	9·66			9·13 ± 0·25		9·60 ± 0·12	
321	0·653	9·05	10·36		8·75 ± 0·19		9·00 ± 0·14	8·97
411;330	0·740	8·12			7·68 ± 0·21		8·00 ± 0·10	
420	0·780						7·70 ± 0·10	
332	0·818						7·32 ± 0·10	
422	0·855						7·19 ± 0·14	
431;510	0·889						6·99 ± 0·12	
B(Å^2)				0·368	0·3589	0·36	0·310	
Particle size, μ				3	3 – 5	3 – 5	2 – 3	—
X-ray				Mo $K\alpha$, Fe $K\alpha$ (LiF)	Mo $K\alpha$ (LiF)	Mo $K\alpha$ SiO$_2$	Mo $K\alpha$	
μ (cm^{-1})				307·3; 556·9	295·9	299·4		
$\Delta f'/\Delta f''$				0·4/1; –2·45/0·61	0·35/	0·4/	0·4/	—
Abs. scale by				NaCl	I_0	I_0	NaCl	

count using the Chipman & Paskin formula (1959). The primary beam intensity was determined with the help of zirconium absorbers. The authors used the same dispersion correction $\Delta f' = 0{\cdot}35$ as Batterman *et al.* (1961) had used, and the temperature factor $B = 0{\cdot}36$ Å^2. As a result the value $f(110)\, f = 18{\cdot}19$ was obtained. The relative values obtained earlier by one of the authors were then transformed to absolute values.

Hosoya (1968) kindly informed us of the finished, but not yet published, results of the measurements by Hosoya & Fukomasha of the atomic scattering factor absolute values of iron, on the samples prepared from carbonyl iron powders. These data are also given in Table 3. Theoretical values according to Hartree–Fock (Watson & Freeman, 1961), Dirac–Slater (Cromer & Waber, 1965) and Thomas–Fermi (*International Tables for X-ray Crystallography,* 1962) as well as the data taking into account the crystal field, from the private communication of Hosoya, are given there. The relative discrepancy of the experimental values from the theoretical ones according to Hartree–Fock is shown in Fig. 3. As we pointed out, Hosoya quoted the f-factor values determined by way of the absolute reflexion measurements with copper and molybdenum radiations and converted them to absolute zero using various characteristic temperatures (Table 3). As can be seen from the given table, discrepancies, as a rule, are within the limits of one per cent.

The fact (which seems of no small importance to us) that the results obtained in the old work by photographic methods were not bad, is deserving of attention. Indeed, *vestigia semper adora.*

Nickel is at present the object of an I.U.Cr. project on making a standard. It was investigated earlier in the work of Brindley & Spiers (1935), Brindley (1936*a*), Ageev & Guseva (1948), Inkinen & Suortti (1964), Hosoya (1968). In Table 4 the main results of the above papers are quoted. Fig. 4 shows difference factors.

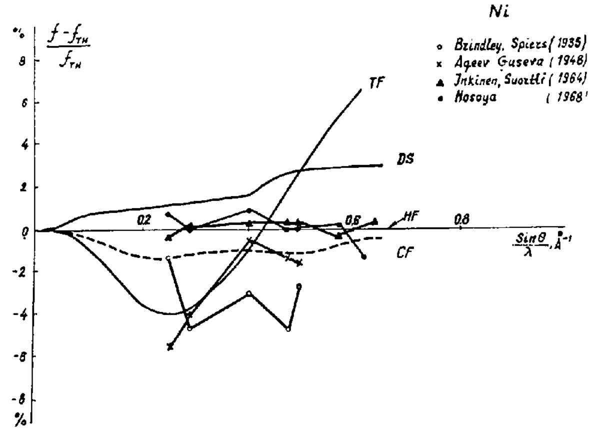

Fig. 4. Relative differences between various experimental and theoretical f-factors of Ni.

Table 4. *Experimental and theoretical atomic scattering functions of* Ni

hkl	sin θ/λ	f_{theor} H.–F.	f_{theor} Wakoh	f_{exp} Brindley & Spiers (1935)		f_{exp} Brindley (1936)		f_{exp} Ageev & Guseva (1948)			f_{exp} Inkinen & Suortti (1964)			f_{exp} Hosoya (1968)	
				20°C	0°K	20°C	0°K	20°C	0°K	20°C	20°C	0°K	0°K	0°K	0°K
111	0·2458	20·63	20·28	14·9	15·3	16·42	20·34	16·85	19·47		20·31	20·55	20·60	20·78	20·88
200	0·2838	19·30	19·05	13·1	13·55	14·40	18·39	15·74	18·48		19·04	19·30	19·38	19·29	19·41
220	0·4013	15·48	15·35	9·8	10·45	10·75	15·00	12·35	15·39		14·97	15·56	15·67	15·60	15·80
311	0·4706	13·63	13·47	7·95	8·7	8·73	13·07	10·27	13·45	9·08	12·91	13·68	13·81	13·63	13·88
222	0·4915	13·08	12·96	—	5·55	—		9·66	12·86		12·30	13·12	13·24	13·09	13·34
400	0·5676	11·47	11·35	—		—	—		—		10·46	11·44	11·59	(11·49)	11·78
331	0·6185	10·53	10·47	4·75		5·18	9·57		10·38	5·40	9·52	10·62	10·78	10·61	10·93
420	0·6346	10·27	10·21	—		—	—		9·82	4·88	9·18	10·31	10·48	10·38	10·71
B(Å^2)				0·410		0·410			0·408			0·37	0·410*	0·330	0·410*
Particle size, μ				3		3			3–5			3			
X-ray				Cu *Kα*		Cu *Kα*		Co *Kα*		Cu *Kα*		Mo *Kα*		Cu *Kα*	Mo *Kα*
μ (cm^{-1})				—		—		673·7				396·0			
$\Delta f'/\Delta f''$				—		3·53/			2·20/	3·50/		0·28/1·02			
Absolute scale by				KCl		KCl, Al			Al			NaCl			

Brindley & Spiers (1934) made their investigation by a photographic method with Cu *Kα* radiation on flat samples prepared from powder. The powder was obtained by spraying. The particle size was 3*μ*. Transfer from relative to absolute values was made against KCl. Brindley (1936*a*) found the dispersion correction value for Cu *Kα* radiation in terms of the difference between the theoretical and experimental values of the atomic scattering factor. This correction was, on average, in agreement with the correction according to Hönl.

Ageev & Guseva (1948) determined the relative intensities of the Bragg reflexions on flat samples prepared from nickel powder with particle sizes 3–5*μ*. Extinction was neglected. The angles between the sample surface and that of the primary beam were 16°, 25° and 34°. Transformation to absolute values was made using aluminum data as a standard. X-ray measurements were made with Co *Kα* and Cu *Kα* radiation. Dispersion correction was made according to Hönl.

Inkinen & Suortti (1964) used a cold worked powder with a particle size of 3 *μ*. A series of samples were prepared by compression at various pressures with differently treated surfaces. X-ray measurements were made with Mo *Kα* radiation with a zirconium filter (without monochromator) on a diffractometer with a NaI(Tl) counter. The roles of texture and surface roughness were negligibly small. The value of Θ_D was determined as 410°K (B=0·368 Å^2). Dispersion correction was made according to Hönl. Hosoya kindly informed us of the data of the completed but not yet published work which he performed together with Fukomeni. These data are also given in Table 4.

In Table 4 *f*-factors reduced to absolute zero temperature, experimental conditions and the data used in the calculations of the above papers are given.

Chromium was investigated by Cooper (1962) with two monochromated radiations: Ag *Kα* and Cu *Kα*. The sample was flat from a powder with particle size 5*μ*. The compression pressure was 10000–150000 p.s.i. The characteristic temperature was assumed to be 450°K (B=0·275 Å^2). Primary beam intensity measurements were used to obtain the absolute values of the atomic scattering factor. Corrections for dispersion and TDS were taken into account by the author.

Hosoya (1964) made measurements of the reflexion intensity on powder samples with Cu *Kα* radiation. He found a decrease with time of the 110 reflexion intensity. This change of the intensity ceased when the sample was placed in an atmosphere of nitrogen or into a vacuum. This phenomenon has not been confirmed by other authors, though indirect evidence shows the possibility.

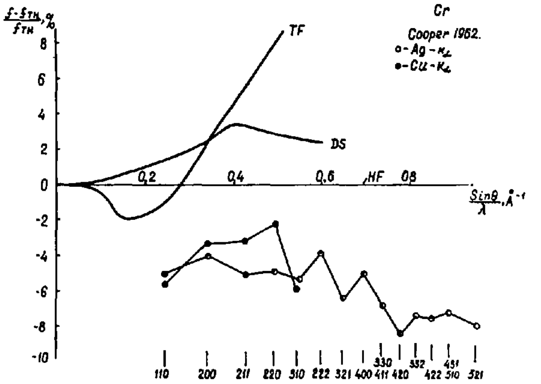

Fig. 5. Relative differences between various experimental and theoretical *f*-factors of Cr.

Table 5. *Theoretical and experimental atomic scattering factors of* Cr

hkl	sin θ/λ	f_{theor} H.-F.	f_{exp} Cooper (1962)	
110	0·2450	16·76	15·91	15·80
200	0·3466	13·62	13·08±0·11	13·15±0·32
211	0·4244	11·68	11·08±0·07	11·30±0·33
220	0·4901	10·30	9·80±0·07	10·06±0·50
310	0·5479	9·42	8·91±0·07	8·87±0·29
222	0·6003	8·72	8·38±0·16	—
321	0·6485	8·20	7·68±0·10	—
400	0·6932	7·80	7·42±0·24	—
330, 411	0·7353	7·50	6·97±0·09	—
420	0·7750	7·25	6·63±0·15	—
332	0·8128	7·02	6·50±0·19	—
422	0·8490	6·83	6·31±0·12	—
431, 510	0·8836	6·65	6·17±0·09	—
521	0·9492	6·35	5·84±0·11	—
B(Å^2)			0·2754	
Particle size, *μ*			5	
X-ray			Ag *Kα*	Cu *Kα*
μ (cm^{-1})			105·04	1799
$\Delta f'/\Delta f''$			0·43/	2·58/
Absolute scale by			I_0	

The values of the atomic scattering factors of the above papers are quoted in Table 5. Fig. 5 shows the comparison of the theoretical with the experimental data.

For the completion of the review we should point out that the compounds Fe_3Al and Fe_3Si were studied by Komura, Tomiie & Nathans (1959) using single-crystal plates. The work is of interest in connection with the discussion on Fe which took place after the papers by Weiss & DeMarco.

The compound Fe_3Si was studied by Radchenko & Tsvetkov (1965*b*) and investigated in powder form with Mo $K\alpha$ radiation. Scaling to the absolute values was performed against NaCl. $\Theta_{Si} \simeq 660$ °K (numerical data of f are not given).

The metallic compounds NiAl, CoAl were investigated by Ageev & Guseva (1949), and by Cooper (1963). Investigations were carried out on flat powder samples with particle sizes 3–6μ (Ageev & Guseva) and 3–7μ (Cooper).

Ageev & Guseva made their measurements by a photographic method with Co $K\alpha$ radiation. Dispersion corrections $\Delta f'_{Al} = -0{\cdot}20$ and $\Delta f'_{Ni} = 2{\cdot}20$ were made according to Hönl. It was found that $\Theta = 450$ °K ($B = 0{\cdot}480$ Å^2). Cooper carried out investigations with monochromated Ag $K\alpha$ and Co $K\alpha$ radiations. The samples were compressed at 40000 p.s.i. Temperature corrections were made separately for the ions. Dispersion corrections were made according to Hönl. The measurements were made by the absolute method.

The main results of the NiAl investigation are given in Table 6. Large disagreements are observed between the results of Cooper obtained with different radiations.

Table 6. *Theoretical and experimental atomic scattering factors of* NiAl

		Ageev & Guseva (1949) $T=20$ °C	Cooper (1963) $T=20$ °C Ag $K\alpha$		Cooper (1963) $T=20$ °C Co $K\alpha$	
hkl	sin θ/λ	Cu $K\alpha$	Experimental	Theoretical	Experimental	Theoretical
100	0·174	13·89	13·08 ± 0·08	13·27	10·43 ± 0·08	11·08
110	0·245	29·72	28·83	28·81	26·12	26·99
111	0·301	11·27	10·80 ± 0·14	10·79		
200	0·347	23·42	22·80 ± 0·23	23·86	20·81 ± 0·27	22·08
210	0·388	8·97	8·79 ± 0·11	8·92	—	—
211	0·425	20·44	20·46 ± 0·16	20·34	18·10 ± 0·20	18·59
220	0·491	17·65	17·52 ± 0·25	17·64	15·21 ± 0·24	13·95
221, 300	0·521	7·10	6·85 ± 0·11	6·74	—	—
310	0·549	14·83	15·61 ± 0·20	15·64	—	—
222	0·601	—	14·15 ± 0·28	13·95	—	—
321	0·649	—	12·62 ± 0·18	12·65	—	—
				$B_{Ni} = 0{\cdot}34$ Å^2		$B_{Ni} = 0{\cdot}34$ Å^2
				$B_{Ni} = 0{\cdot}43$		$B_{Al} = 0{\cdot}43$
				$B_{NiAl} = 0{\cdot}37$		$B_{NiAl} = 0{\cdot}37$

Table 7. *Theoretical and experimental atomic scattering factors of* Zn *and* Mg

Zn

		Brindley (1936) f_{exp}		H.–F.
hikl	sin θ/λ	290 °K	0 °K	f_{theor}
0002	0·203	20·1	21·2	24·25
$10\bar{1}0$	0·218	22·4	22·9	23·7
$10\bar{1}1$	0·240	19·4	20·1	22·90
$10\bar{1}2$	0·298	16·8	18·2	20·90
$10\bar{1}3$	0·374	13·65	15·2	18·25
$11\bar{2}0$	0·378			
$11\bar{2}2$	0·428	12·0	13·5	16·55
$20\bar{2}1$	0·448	12·1	13·4	15·95
$20\bar{2}3$	0·532	8·0	9·9	13·70
$10\bar{1}5$	0·552	6·9	9·4	13·25
$11\bar{2}4$	0·554			
$21\bar{3}1$	0·585	7·6	9·0	12·5
0006	0·609	6·3	8·2	12·0
$21\bar{3}2$	0·611			
		$\sqrt{\bar{u}_{\parallel}^2} = 0{\cdot}1265$ Å $\sqrt{\bar{u}_{\perp}^2} = 0{\cdot}0791$ Å		
X-ray		Cu $K\alpha$		
Absolute scale by		Al		

Mg

		Brill, Chopra (1962) f_{exp}	H.–F. f_{theor}
hikl	sin θ/λ	296 °K	
$10\bar{1}0$	0·181	8·65	8·59
0002	0·193	8·35	8·38
$10\bar{1}1$	0·205	8·15	8·15
$10\bar{1}2$	0·264	7·00	7·04
$11\bar{2}0$	0·312	6·15	6·16
$10\bar{1}3$	0·340	5·70	5·66
$20\bar{2}0$	0·361	5·35	5·27
0004	0·385	5·05	4·88
$10\bar{1}4$	0·425	4·35	4·27
$21\bar{3}0$	0·479	3·55	3·55
$10\bar{1}5$	0·514	3·15	3·15
$30\bar{3}0$	0·541	2·85	2·85
0006	0·577	2·50	2·52
$10\bar{1}1$	0·605	2·25	2·29

Of the metals possessing a hexagonal structure only magnesium, zinc and ruthenium have been studied and absolute measurements of atomic scattering factors made.

Magnesium was investigated by Brill, Hermann & Peters (1942) on a single-crystal plate with Mo $K\alpha$ radiation. After this Brill & Chopra (1962) made measurements of the reflexion intensities on magnesium powder at the temperatures 296°, 90° and 5°K. Anisotropic temperature corrections were made, characteristic temperatures were determined according to the eigendata at 296°K ($\Theta = 315$°K), 90°K ($\Theta = 320$°K) and 5°K ($\Theta = 375$°K). Theoretical and experimental *f*-curves were compared.

The detailed determination of the absolute atomic scattering factors of *zinc* was carried out by Brindley & Spiers (1935) and by Brindley (1936*b*). Brindley & Spiers made the measurements of the zinc reflexion intensity on fine powders obtained by precipitation *in vacuo*. The samples were flat. The Cu $K\alpha$ radiation was not monochromated. The photographic method was used. Scaling to the absolute values was made against KCl as a standard. In the subsequent work by Brindley (1936*b*) the method of measurement remained the same as in the preceding investigation. However, aluminum was used as a standard, and special attention was concentrated upon the anisotropy of the zinc atom vibrations. The authors found the values of the absolute scattering factor at absolute zero which are given in Table 7. Calculating the anisotropic atomic scattering factor at absolute zero, the authors used approximate theories by Zener (1936) and a somewhat better approximation developed by themselves.

In Table 7 theoretical values of the atomic scattering factors of zinc calculated according to the Hartree–Fock theory (*International Tables*, 1962) are also given.

Diamond-type elements

Investigations of the fourth group of elements of the Periodic Table with the structure of diamond are of great interest.

Diamond was investigated by Brill, Grimm, Hermann & Peterson (1939), and by Göttlicher & Wölfel (1959). Transformation to an absolute scale was made against NaCl. X-ray measurements were made using Mo $K\alpha$ and Pd $K\alpha$ radiations on powder and single-crystal samples.

Silicon was studied by Wyckoff (1930), by Göttlicher, Kuphal, Nagorsen & Wölfel (1959), by Sheleg (1964), by Hattori, Kuriyama, Katogawa & Kato (1965), by DeMarco & Weiss (1965), and by Radchenko & Tsvetkov (1965*a*).

Germanium was investigated by Sirota & Sheleg (1960) and by Weiss & DeMarco (1965).

The main results of these investigations are given in Table 8. Fig. 6 shows the disagreement factor values.

The powder sample of silicon was investigated in the work of Göttlicher *et al.* using Mo $K\alpha$ radiation with a LiF monochromator. Characteristic temperatures were taken as equal to 543°K ($B = 0{\cdot}452$).

Sirota & Sheleg (Sheleg, 1964) investigated powder with particle sizes 3–6μ with Cu $K\alpha$ filtered radiation. The characteristic temperature was assumed to be equal to 680°K ($B = 0{\cdot}427$). Conversion to an absolute scale was made against NaCl.

Radchenko & Tsvetkov (1965*a*) investigated powder (2–3μ) with pentaerythritol monochromated Mo $K\alpha$ radiation. A dispersion correction was introduced according to Hönl. Conversion to an absolute scale was made against NaCl.

Sirota & Sheleg (1960) investigated germanium powder samples with particle sizes 5–7μ with filtered Cu $K\alpha$ radiation at two temperatures. Conversion to an ab-

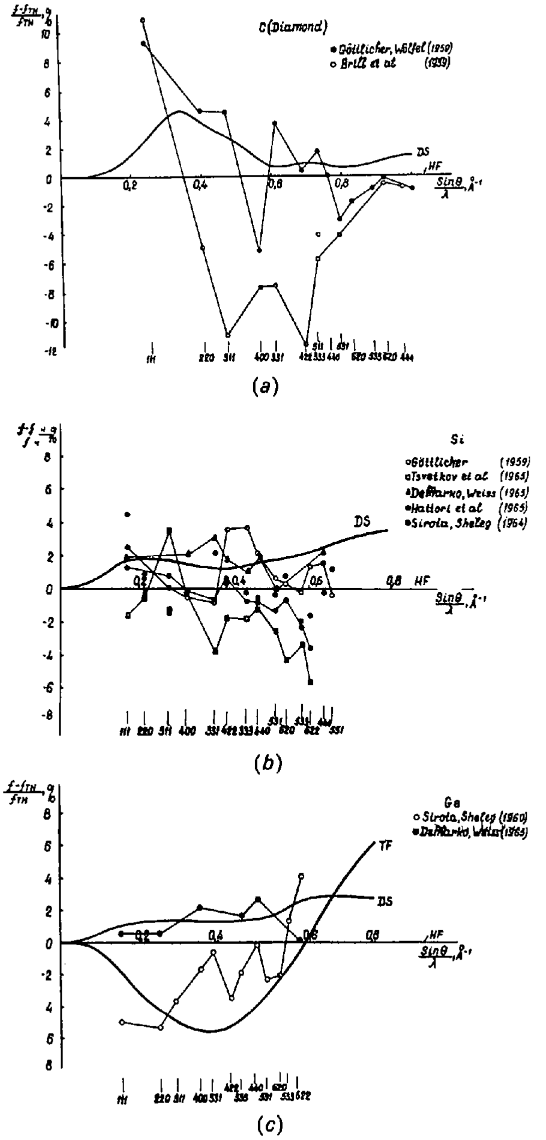

Fig. 6. Relative differences between various experimental and theoretical *f*-factors of (*a*) C; (*b*) Si; (*c*) Ge.

Table 8. *Theoretical and experimental atomic scattering factors of diamond,* Si *and* Ge

	C (diamond)					Si											Ge				
		Brill *et al.* (1939)		Göttlicher (1959)				Göttlicher (1959)		Wyckoff (1930)		Sirota & Sheleg (1964)		Tsvet-kow *et al.* (1965)	De Marco *et al.* (1965)	Kato *et al.* (1965)			Sirota & Sheleg (1960)		De Marco *et al.* (1965)
hkl	H.–F.	20°C	0°K	20°C	0°K	H.–F.	D.–Sl.	20°C	0°K	20°C	0°K	20°C	0°K	0°K	0°K	0°K	H.–F.	T.–F.	20°C	0°K	0°K
111	3·038	3·300	3·339	3·282	3·321	10·60	10·73	10·75	10·87	10·12	10·23	10·84	10·95	10·42	10·80	11·09	27·4	26·9	25·65	25·83	27·55
220	1·961	1·805	1·863	1·911	1·972	8·73	8·88	10·48	8·74	7·86	8·09	8·55	8·80	8·69	8·70	8·81	23·76	22·75	22·05	22·47	23·90
311	1·760	1·498	1·565	1·592	1·663	8·18	8·30	7·80	8·13	6·86	7·14	7·86	8·17	8·47	8·07	8·07	22·31	21·22	20·93	21·48	
222	1·712														0·18						
400	1·595	1·381	1·471	1·389	1·479	7·52	7·61	7·02	7·46	6·08	6·44	7·04	7·46	7·49	7·69	7·41	20·43	19·25	19·31	20·08	20·9
331	1·522	1·375	1·482	1·465	1·579	7·19	7·28	6·94	7·45	6·17	6·61	6·75	7·23	6·90	7·41	7·35	19·43	18·30	18·43	19·30	
422	1·438	1·166	1·282	1·313	1·444	6·70	6·80	6·34	6·95	5·50	5·99	6·10	6·65	6·58	6·83	6·73	18·00	17·05	17·59	18·64	
333	1·395	1·181	1·314	1·275	1·419	6·43	6·55	5·93	6·57	5·17	5·70	5·79	6·38	6·31	6·50	6·42	17·23	16·42	16·45	17·56	17·52
511		1·202	1·338												6·56	6·38					
440	1·328	1·120	1·271	1·135	1·288	6·05	6·17	5·39	6·09	4·60	5·17	5·32	5·97	5·98	6·05	6·03	16·19	15·57	14·97	16·11	16·62
531	1·292			1·106	1·269	5·82	5·96	5·11	5·84	4·49	5·03	5·07	5·76	5·67		5·86	15·58	15·00	13·99	15·22	
620	1·233			1·044	1·222	5·50	5·64	4·71	5·49	4·15	4·80	4·65	5·37	5·26		5·39	14·61	14·29	13·57	14·92	
533	1·192	1·011	1·198	1·007	1·193	5·28	5·42	4·54	5·35				5·09	5·10		5·19	14·18	13·94	12·61	13·98	
622	1·181					4·97	5·10	4·21	5·06					4·69	5·10	4·97	13·48	13·40	11·50	12·91	13·50
444	1·135	0·891	1·077																		
551	1·087	0·906	1·109	0·896	1·096	4·83	4·96	3·96	4·81							4·87					
711		0·900	1·101																		
B(Å^2)			0·2007		0·2007				0·452		0·427*		0·427	0·310		0·401				0·308	
Particle size, μ			1		0·5–1; 2–5 5–10						—		5	2–3	single crystal	single crystal				5–8	single crystal
X-ray			Mo *Kα*		Mo *Kα*				Mo *Kα*		—		Cu *Kα*	Mo *Kα*		Ag *Kα* Mo *Kα*				Cu *Kα*	Mo *Kα*
μ (cm^{-1})			—		—						—		140	—	14·67	—				371	325·5
$\Delta f'/\Delta f''$			—		—						—		—	—	+0·10/	—				−1·3/	+0·2/
Absolute scale by			I_0		LiF NaCl				LiF NaCl				NaCl	NaCl	I_0					NaCl	I_0

solute scale was made against NaCl. Weiss & DeMarco (1965) investigated a single-crystal sample.

Grey tin was studied by Sirota & Sheleg (1962) on powder samples at two temperatures. The particle sizes were 3–5μ; X-ray measurements were made using Cu $K\alpha$ radiation. There were impurities of white Sn in the powder. The characteristic temperature was taken equal to 150°K ($B=1{\cdot}279$). Absolute f-values were obtained by comparison with NaCl.

$\mathrm{A^{III}B^{V}}$ Componds

Aluminum, gallium and *indium arsenides* were studied by Sirota & Olekhnovich (1961*a*; 1961*b*, 1962). X-ray measurements were made with filtered Cu $K\alpha$ radiation on flat samples. Conversion to an absolute scale was made against NaCl. In converting to the absolute scale temperature corrections were made separately for A and B ions.

Gallium arsenide was also studied by DeMarco & Weiss (1964) on two single crystals in monochromated Mo $K\alpha$ radiation.

Aluminum, gallium and *indium antimonides* were investigated by Sirota & Gololobov (1961, 1962*a*, 1962*b*, 1965) on flat powder samples with filtered Cu $K\alpha$ radiation. Conversion to an absolute scale was made against NaCl. Temperature correction was introduced separately for each type of ion.

Investigation on a spherical single crystal of 0·43 mm radius was carried out by Attard & Azaroff (1963) using filtered Mo $K\alpha$ radiation with a scintillation counter. Conversion to absolute values was realized by scaling against theoretical.

The phosphides, GaP *and* InP were investigated by Sirota & Sheleg (1968) and by Sirota & Gololobov (1968) on powder samples using Cu $K\alpha$ radiation with a bent germanium monochromator and a scintillation counter. Corrections for TDS and dispersion were introduced according to Dauben & Templeton. Conversion to an absolute scale was made by the absolute method and against Ni.

In all work of Sirota, Olekhnovich, Gololobov & Sheleg the powders were obtained by sedimentation (settling) in toluol.

The required degree of dispersion was determined by preliminary experiments (Fig. 7). The particle size did not exceed 5μ. Corrections for secondary extinction were not introduced. Preliminary experiments also decided the pressures necessary for powder compression. A check on the surface roughness and the presence of texture showed that they were negligibly small. The measurements, as a rule, were made at three temperatures including room, liquid nitrogen and some intermediate temperatures.

In Table 9 the main results obtained in the work on $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds are quoted. Figs. 8, 9 and 10 show the values of the disagreement factor with the theoretical values for neutral atoms. $A^{\mathrm{II}}B^{\mathrm{VI}}$ compounds have not yet been studied sufficiently.

Zinc sulphide was studied by Jumpertz (1955) using powders and single-crystal plates with Mo $K\alpha$, Fe $K\alpha$ and Cu $K\alpha$ radiations. $\Theta_{\mathrm{Zn}}=230°$, $\Theta_{\mathrm{S}}=334°$, $\Theta_{\mathrm{ZnS}}=$

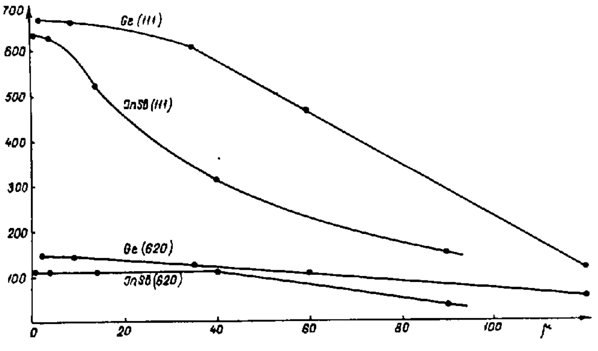

Fig. 7. Dependence of the measured reflexion intensity of InSb and Ge on the particle sizes.

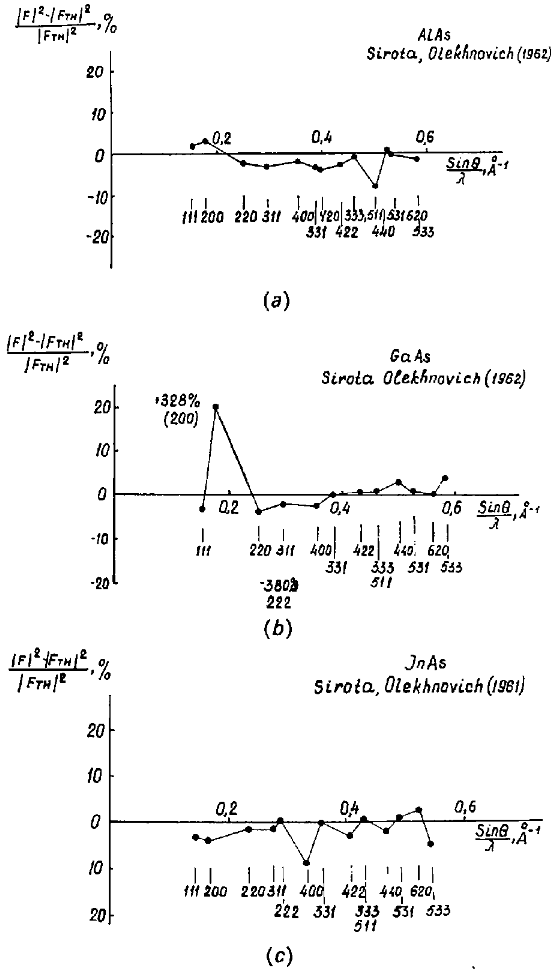

Fig. 8. Relative differences between various experimental and theoretical f-factors of (*a*) AlAs; (*b*) GaAs; (*c*) InAs.

Table 9. *Theoretical and experimental atomic scattering factors of some $A^{III}B^{V}$ compounds*

	AlAs			GaAs			InAs			AlSb		
		Sirota & Olekhnovich (1962)			Sirota & Olekhnovich (1961)			Sirota & Olekhnovich (1961)			Sirota & Gololobov (1962 *b*)	
hkl	exp 20°C	0°K	theor H–F	exp 20°C	0°K	theor H–F	exp 20°C	0°K	theor H–F	exp 20°C	0°K	theor H–F
111	828	900	884·0	1312	1437	1489	2403	2505	2693	2056	2172	2134
200	280	323	303·8	7·2	7·3	1·56	186	209	218	1056	1187	1128
220	972	1053	1076	1822	2153	2247	3318	3394	3961	2050	2343	2540
311	499	557	574·3	788	952	973	1505	1800	1823	1206	1418	1463
222	174	170	215·5	(2·8)	(4·8)	1·02	148	144	143·6	692	801	815
400	709	788	799	1288	1616	1656	2183	2777	2975	1400	1786	1756
331	392	437	451	590	754	755·7	1049	1423	1424	915	1195	1132
420	150	162	168	—	—	—	—	—	—	540	631	635
422	544	620	635	989	1310	1305	1675	2333	2405	1053	1507	1429
333, 511	325	359	362	441	599	594·5	773	1163	1162	634	990	939
440	452	535	513	777	1082	1050	1250	2043	2038	776	1240	1197
531	263	299	297	333	479	474	594	987	979	512	818	795
442	115	115	115	—	—	—	58	—	—	—	—	—
620	377	428	429	570	858	858·5	864	1772	1727	576	1024	1030
533	231	244	247	250	385	401	328	805	848	382	663	690
444	—	—	—	—			—			432	—	—
B(Å²)		$B_{\mathrm{Al}}=1·12$			$B_{\mathrm{Ga}}=0·20$			$B_{\mathrm{Jn}}=1·00$			$B_{\mathrm{Al}}=1·7$	
		$B_{\mathrm{As}}=0·36$			$B_{\mathrm{As}}=0·56$			$B_{\mathrm{As}}=1·00$			$B_{\mathrm{Sb}}=1·0$	
Particle size, μ		15–10			5–8			6–8			~5	
X-ray		Cu $K\alpha$			Cu $K\alpha$			Cu $K\alpha$			Cu $K\alpha$	
μ (cm^{-1})		259·3			374·6			940·9			1023	
$\Delta f'/\Delta f''$		0·2/0 – Al			−1·5/0·9 – Ga			−0·6/5·4 – In			0·2/0 – Al	
		−1·2/1·2 – As			−1·2/1·2 – As			−1·2/1·2 – As			−0·8/6·3 – Sb	
Absolute scale by		NaCl			NaCl			NaCl			NaCl	

(*a*) Sirota & Sheleg (1968).
(*b*) Sirota & Gololobov (1968).

GaSb			InSb			InSb	GaP			InP		
Sirota & Gololobov (1961)			Sirota & Gololobov (1962*a*)			Attard & Azaroff (1963)	(*a*)			(*b*)		
exp 20°C	0°K	theor H–F	exp 20°C	0°T	theor H–F	0°K	exp 20°C	0°K	theor H–F	exp 20°C	0°K	theor H–F
2493	2695	2765	3532	3684	3828	3682	731	821	830·7	1842	1976	1996
290	319	292·4	3·84	10·56	3·15	—	148	204	220·5	785	892	930
3474	3938	4019	5347	5892	5963	5660	1110	1023	1024	1893	2249	2250
1661	1889	1880	2362	2719	2699	2571	416	533	534·7	1050	1321	1329
209	209	203·0	—	—	—	—	948	153	156·6	492	659	668
2483	2980	3025	3758	4654	4624	4297	510	733	737·1	1195	1652	1648
1195	1430	1483	1639	2116	2096	2195	281	391	390·2	675	1024	1011
175	175	167·7	—	—	—	—	58	113	111·9	326	516	506
818	2372	2411	2755	3813	3752	3597	364	575	571·2	820	1329	1308
878	1210	1198	1246	1798	1762	1885; 1798	175	306	303·2	430	813	820
1342	1954	2008	2050	3158	3187	3215	326	450	454·9	575	1107	1096
640	982	1011	917	1475	1513	1525	126	245	245·6	333	696	687
—	—	—	—	—	—	—	21	60·5	61·6	—	—	—
994	1678	1708	1526	2652	2790	2663	186	378	375·6	422	929	945
478	799	855·5	663	1271	1336	1373	85	202	201·6	250	604	599
680	1410	1478	1107	2304	2475	2398	—			336	819	837
	$B_{\mathrm{Ga}}=0·85$			$B_{\mathrm{Jn}}=1·287$		$B=0·89$		$B_{\mathrm{Ga}}=0·91$			$B_{\mathrm{Jn}}=1·3$	
	$B_{\mathrm{Sb}}=0·72$			$B_{\mathrm{Sb}}=1·24$				$B_{\mathrm{p}}=0·89$			$B_{\mathrm{p}}=1·5$	
	~5			~5		Single crystal		~3			~1–2	
	Cu $K\alpha$			Cu $K\alpha$		Mo $K\alpha$		Cu $K\alpha$			Cu $K\alpha$	
	1140			1544				287·3			1016	
	−1·5/0·9 – Ga			−0·6/5·4 – In				−1·5/0·9 – Ga			−0·61/4·98 – In	
	−0·8/6·3 – Sb			−0·8/6·3 – Sb				0·27/0·46 – P			0·27/0·46 – P	
	NaCl			NaCl		theor		Ni			Ni, I_0	

248° were determined by comparison with the theoretical *f*-curves. The intensity measurements were made on the diffractometer.

Table 10. *Theoretical and experimental atomic scattering factors of* ZnS

hkl	sin θ/λ	$\lvert F\rvert_{\text{exp}}$ Jumpertz (1955)	$\lvert F\rvert_{\text{theor}}$ H.–F.
111	0·1605	93·13	102·8
002	0·1845	23·49	45·2
220	0·2682	107·29	111·6
113	0·3074	67·22	74·0
004	0·3707	87·83	86·0
331	0·4039	54·36	58·4
224	0·4540	69·06	72·0
115	0·4816	46·18	49·1
333	0·4816	45·40	49·1
440	0·5243	57·10	60·2
006	0·5561	13·40	17·6
442	0·5561	14·06	17·6
335	0·6077	33·65	35·4
226	0·6147	11·94	14·4
444	0·6421	42·61	43·6

Zinc selenide was investigated by Raccah, Arnott & Wood (1966) with monochromated Cu $K\alpha$ radiation. Extinction was negligibly small, values of $B_{\text{Zn}} = 1{\cdot}34$ Å^2, $B_{\text{Se}} = 0{\cdot}68$ Å^2, $R = 2{\cdot}5$% being determined.

In analysing the data attention should be paid to the possibility of the influence of polytypism on the results of the absolute intensity determination.

Discussion

A detailed discussion of the results of the investigations of each author taken separately on each of the elements or compounds investigated is seemingly of no particular importance. The above diagrams and the Tables show the present state clearly enough. Although the factor of disagreement with the theoretical data according to Hartree–Fock for neutral atoms cannot be an unequivocal criterion of the accuracy of an experiment, the considerable discrepancies from the theoretical values which occurred are due rather to the defects in the experimental technique than to an inaccuracy of the theory. At present the mean discrepancy from the theoretical values of the atomic scattering factors for metals and elements is about 1–2% and for the simplest semiconductor $A^{\text{III}}B^{\text{V}}$ compounds it is no more than 3–5%. At the same time discrepancies between different theories reach large values, and therefore it is obviously necessary to choose with sufficient justification certain theoretical values as some basis for comparison of experimental data.

Let us consider the most important factors which determine the accuracy of the measurements and of the absolute values of the atomic scattering and structure amplitude function. The difficult problem of extinction is practically removed by using sufficiently fine powders. However, in using disperse powders one meets with new obstacles. For each of the materials investigated some dispersity threshold exists. For example, the role of extinction becomes, as follows from Fig. 7, negligibly small for InSb with the particle size less than 3–4μ and for Ge, beginning with 8–10μ. On the other hand, some critical degree of dispersity exists above which the use of powders serves no purpose. By further increasing the degree of dispersity the value of the inner surface rises, its absorption ability increases and the chemical activity grows. The change in the chemical composition of the surface and its cer-

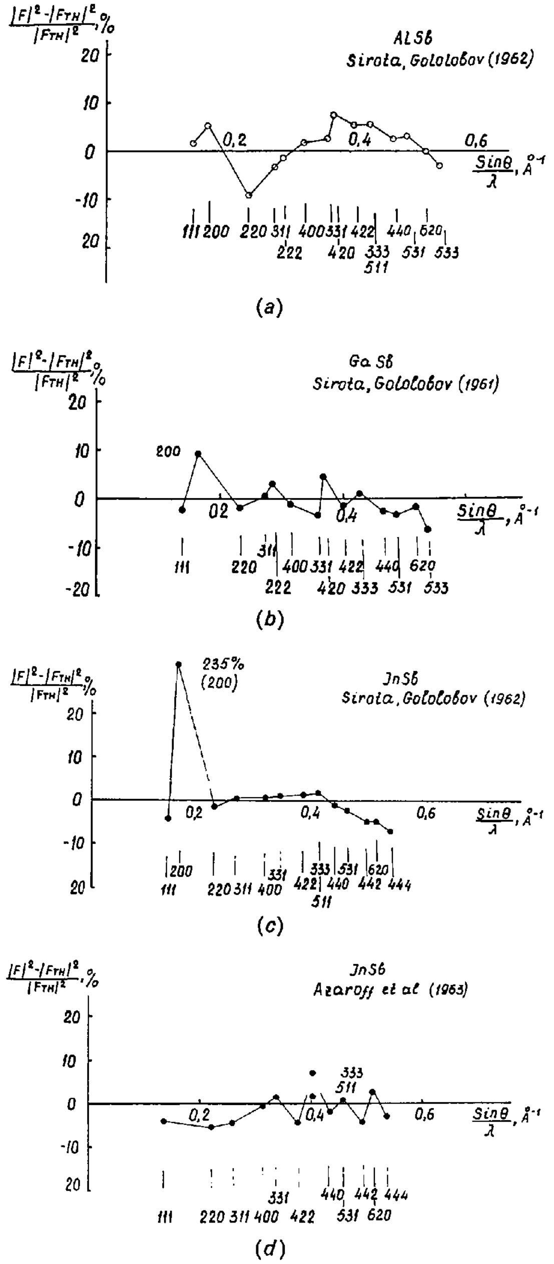

Fig. 9. Relative differences between various experimental and theoretical *f*-factors of (*a*) AlSb; (*b*) GaSb; (*c*) (*d*) InSb.

tain amorphization leading to a rise in the background is a consequence of this. The optimal degree of powder dispersion is different for different materials and for different surrounding media. This problem has not been analysed in detail at present. The use of powders is to some extent accompanied by an increase of the porosity of the sample under investigation. The analysis of the role of porosity was given by Cooper (1965*b*). As his measurements showed, the role of porosity can be eliminated by the correct choice of the compression pressure. Nevertheless, an insufficiently accurate estimate of the porosity can give rise to an error of several per cent in determining the reflexion intensity value. Texture arises by the compression of powders. In a number of cases the texture is eliminated in the sample plane but remains along the sample length. For example, an investigation of the nickel samples of the I.U.Cr. project has shown that the texture is absent in the sample plane; however it is marked in the direction normal to the plane, *i.e.* in the direction of compression (Olekhnovich, Sheleg). The presence of such a texture can lead to an inaccuracy in the intensity of up to 3–4%.

Undoubtedly, one of the defects of the powder samples is that overlapping reflexions cannot be measured separately. This makes it difficult to estimate the asphericity of the electron distribution; this asphericity is of special importance in covalent and ferromagnetic crystals.

In Table 11 relative discrepancies in the reflexion intensity values due to the difference in B values used by different authors in converting to absolute zero are given. Inaccuracies in the characteristic temperature values taken can lead to errors of up to 3 % in estimating the reflexion intensities at absolute zero. Insufficient accuracy in the determination of the temperature at which the X-ray measurements are made leads to

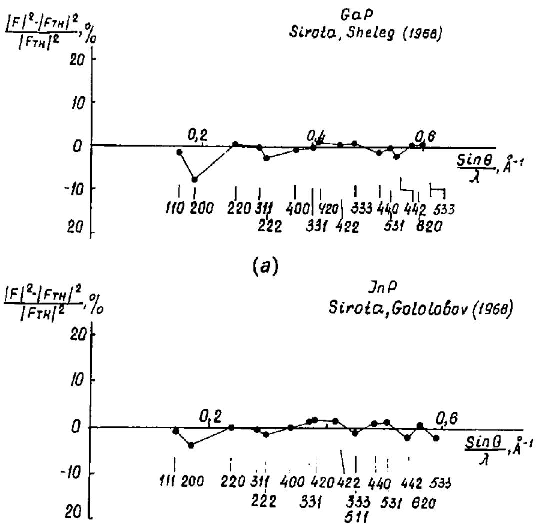

Fig. 10. Relative differences between various experimental and theoretical f-factors of (*a*) GaP; (*b*) InP.

Table 11. *Relative discrepancies between intensities due to the difference of values used by various authors*

Al					Ni					Fe					Cu				
B(Å^2)	Author	θ,°K	I_{111}	I_{422}	B(Å)^2	Author	θ,°K	I_{111}	I_{400}	B(Å)^2	Author	θ,°K	I_{110}	I_{310}	B(Å)^2	Author	θ,°K	I_{111}	I_{420}
0·774	James *et al.* (1929)	403	100·0	100·0	0·330	Hosoya *et al.* (1968)	430	100·0	100·0	0·310	Radchenko & Tsvetkov (1965)	450	100·0	100·0	0·543	Batterman *et al.* (1961)	320	100·0	100·0
0·8528	Batterman *et al.* (1961)	395	100·4	102·9	0·370	Inkinen & Suortti (1964)	410	100·2	101·3	0·360	Batterman *et al.* (1961)	425	100·3	101·5	0·550	Jennings *et al.* (1964)	315	100·0	100·3
					0·408	Ageev *et al.* (1948)	390	100·3	102·5	0·368	Batterman (1959)	420	100·4	101·8	0·584	Hosoya & Yamagishi (1966)	300	100·2	101·6
					0·410	Brindley *et al.* (1935)	380	100·3	102·6						0·603		290	100·3	102·3

The I_{hkl} intensities corresponding to the maximal values of characteristic temperatures were taken for 100%.

errors in the values reduced to absolute zero. For example, at the characteristic temperature for Al, $\Theta = 395\,^{\circ}\mathrm{K}$, an inaccuracy of 5 °C in determining the X-ray measurement temperature leads to an error in the reflexion intensity estimation at 0 °K, as can be seen from Table 12. Incorrect use of the temperature factor seems to be one of the error sources in treating the experimental results. In the review of Herbstein (1961) the spread of characteristic temperature values is shown for the same materials determined by different methods and at various temperatures. X-ray characteristic Θ-values differ from the thermal ones both in magnitude and in temperature dependence. This is particularly displayed in the elements and compounds with covalent bonds, as is convincingly shown by Herbstein (1961) and by other authors (Piesbergen, 1963; Sirota & Pashintsev, 1959; Gololobov & Sirota, 1959; Sirota & Sheleg, 1959).

Table 12

Al, $\theta = 395$

T °C	I_{111}	I_{422}
15	100·0	100·0
20	100·0	100·6
25	100·1	101·1

In the papers of Sirota & Sokolovskii (1967) the total phonon spectrum of the diamond, germanium and silicon crystals was divided into separate vibration spectra of acoustic and optical branches respectively, and the surfaces of equal frequency in reciprocal space for these crystals have been calculated. In accordance with these calculations characteristic temperatures are different in different directions in the cubic lattice of diamond. Accordingly, characteristic temperatures for reflexions with different indices can be different. The attractive method of determining Θ on the 'tails', in the comparison of experimental f-curves with theoretical ones, widely used by a number of authors, is open to criticism. The tensor character of the mean square dynamic displacements of ions, and hence, the difference of characteristic temperatures in different directions should be taken into account. It should be taken into account especially in the case of elements and compounds with cubic lattices. In particular, as was shown by Brindley (1936*b*) for zinc, and by Sirota, Olekhnovich & Olekhnovich (1968) for AlN, mean square displacements differ two and more times in different crystallographic directions.

In the present review we show that comparatively small differences in the temperature factor do not lead to a considerable change of the given reduced reflexion intensity. Nevertheless, the errors arising in precision measurements should be taken into account. At the same time there is no general criterion for the choice of the point of the characteristic temperature.

Undoubtedly, the difficult problem of accounting for thermal and statistical diffuse scattering as well as for scattering by air has not yet been solved. The an-

Table 13. *Relative discrepancies between intensities due to the difference of absorption coefficients used by various authors*

Al			Fe			Ni			Cu		
μ cm^{-1} Mo $K\alpha$	Authors	I_{hkl}	μ cm^{-1} Mo $K\alpha$	Authors	I_{hkl}	μ cm^{-1} Mo $K\alpha$	Authors	I_{hkl}	μ cm^{-1} Mo $K\alpha$	Authors	I_{hkl}
13·77	Cooper, 1965	98·8	296·37	Cooper, 1965	97·7	413·51	Cooper, 1964	99·6	436·50	Cooper, 1964	96·0
13·93	*Inter. Tables*	100·0	303·38	*Inter. Tables*	100·0	415·21	*Inter. Tables*	100·0	454·53	*Inter. Tables*	100·0
13·55	Batterman *et al.* 1961	97·3	306·53	Batterman, 1959	101·0	396·0	Inkinen & Suortti, 1964	95·4	455·43	Batterman, 1959	100·2
			298·65	Paakkari & Suortti, 1966	98·4				439·71	Batterman *et al.* 1961	96·7
			295·18	Batterman *et al.* 1961	97·3						

alysis carried out by Chipman & Paskin (1959) of TDS in crystals does not take into account the influence of the scattering of air, the role of which is not negligibly small for weak reflexions.

The problems of accounting for dispersion, absorption coefficient, and primary beam polarization remain in principle unsolved. All these problems, except the purely experimental ones, need to be considered theoretically as well.

In the above references to absolute intensity measurements a large discrepancy is apparent between the values of the absorption coefficient as used by different authors. Table 13 lists the absorption coefficient values adopted by some authors and the resulting relative discrepancies in the reflexion intensity values at absolute zero.

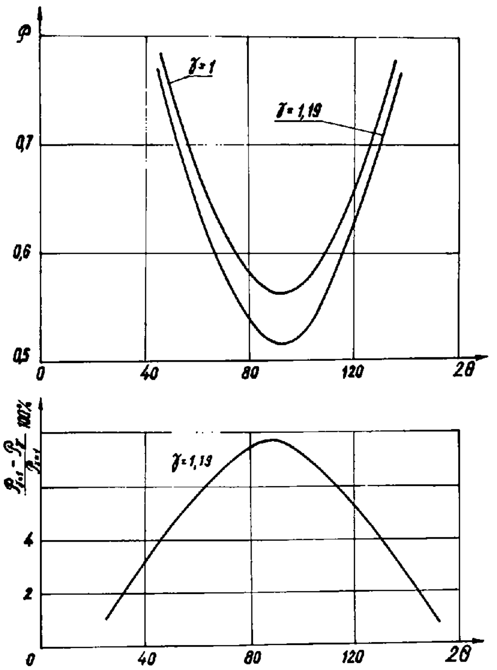

Fig. 11. Dependence of the polarization factor on the degree of monochromator mosaicity.

While using monochromators the value of the polarization factor is usually estimated with the help of the following expression:

$$P=\frac{1+K\cos^2 2\theta}{1+K},$$

where $K=\gamma\cos^2 2\theta_M$, and where the γ-coefficient takes into account the degree of mosaicity of the monochromator crystal. As Jennings (1968) has pointed out, in the case of real crystals the value of K may not fall between the values for a perfect and for an ideally mosaic crystal. Measurements made by Olekhnovich and Sheleg for a bent germanium crystal monochromator showed that with Cu $K\alpha$ radiation the value of $K=0{\cdot}94$, *i.e.* $\gamma=1{\cdot}19$.

As is well known, $\gamma=1$ for an ideally mosaic crystal, *i.e.* $K=\cos^2\theta_M$, while $\gamma=1/\cos\theta_M$ for a perfect crystal. In the case of the bent germanium crystal $\gamma=1{\cdot}125$ at $\cos\theta_M=0{\cdot}888$. The change of the polarization factor value in terms of the angle of reflexion is shown in Fig. 11 for a monochromator with a perfect, an ideally mosaic and a real bent germanium crystal.

Table 14 gives the percentage changes in the intensities of different nickel lines using bent germanium crystal monochromators with different degrees of deviation from an ideally mosaic state. Fig. 11 shows the corresponding changes of the polarization factor as well as the relative differences between these factors. The problem of the monochromator is a very real one. Determination of the value of γ, which is a part of the polarization factor expression, is in many respects subjective and has not, in the main, been analysed. Compton scattering by the monochromator is usually not allowed for. Dispersion corrections are made according to Hönl and Dauben & Templeton. However, discrepancies between them, as calculations show, amount to 2–3% (Table 15).

Table 14. % *Variation of intensities of nickel lines with mosaicity of the monochromator*

hkl	2θ	$\frac{P_{\gamma=1}}{\sin^2\theta\cos\theta}$	$\frac{P_{\gamma}}{\sin^2\theta\cos\theta}$	$\frac{P_{\gamma=1}-P_{\gamma}}{P_{\gamma}}\,.\,100\%$
111	44°32′	5·893	5·722	2·9
200	51 54	4·226	4·063	3·9
220	76 20	1·944	1·805	7·1
311	93 02	1·547	1·426	7·8
222	98 32	1·515	1·400	7·6
400	122 08	1·846	1·761	4·6

Table 15. *Relative discrepancies between intensities due to the dispersion correction values*

Ni			Cu			
$\Delta f'$ Cu $K\alpha$	I_{111}	I_{400}	$\Delta f'$ Cu $K\alpha$	I_{111}	I_{420}	Authors
$-3{\cdot}50$	100	100	$-2{\cdot}5$	100	100	Hönl
$-3{\cdot}10$	98·1	96·5	$-2{\cdot}1$	98·2	96·4	Dauben & Templeton

The methods used to put the measurements on an absolute scale are open to criticism. Developments of new methods of direct absolute measurements of primary and secondary beams are needed and the creation of international standards acquires great importance.

An important way of increasing the measurement accuracy could be the making of measurements *in vacuo*, over a wide range of temperatures, including liquid helium temperature, and with different radiations.

The development of monochromatic sources of radiation using radioisotopes may offer great advantages. In general, an analysis of present experimental techniques shows that there are as yet unrealized possibilities of eliminating a number of sources of errors and of increasing the absolute measuring accuracy.

Undoubtedly, statistical methods of treatment of results can assist in increasing the accuracy. However, these methods are effective only when full allowance is made for all the factors which cause measurement and calculation errors. Otherwise, they only allow the scatter to be narrowed a little and lead to incorrect values.

According to the above estimates, at present the measurement errors in the absolute reflexion intensities, for example of nickel, are of the order of 3–4%. The error is determined by the following principal items: absorption coefficient; dispersion coefficient; polarization factor; precision of the sample composition; X-ray measurement temperature; porosity; extinction; diffuse scattering; Compton effect; fluorescence; preferred orientation; conversion to an absolute scale.

The errors connected with fluctuations, irregularities and noise in electronic equipment and of counters, insufficient stabilization of the X-ray tube current, voltage and wave-form, as well as of the measuring device temperature should also be considered as contributing to the overall error. The importance of these factors increases when the individual X-ray reflexions are measured sequentially. In this respect photographic methods possess some advantages since measurements of reflexions are made simultaneously. In the light of these considerations, the problem of combining measurements on powders and single crystal samples deserves attention. X-ray measurements *in vacuo* at different temperatures including low temperatures, acquire considerable interest. Special attention should be concentrated upon the conversion of the relative values to the absolute ones and upon the technique used for the experimental measurement of the primary beam intensity. Scanning the primary beam cross section with a small slit followed by integration seems to be the best method.

Comparison with theoretical data

In comparing experimental values of structure amplitudes we take as a basis the values calculated according to Hartree–Fock. A summary of these with an indication of the authors is given in *International Tables* (1962). These values can probably be considered to be the most accurate at present available. However, it is obvious that the self-consistent field method is not above criticism. In addition, so far atomic scattering factors have been calculated only for isolated neutral atoms or ions according to Hartree–Fock, Thomas–Fermi, Dirac–Slater and others. The work of Wakoh in which the crystal field is taken into account is seen to be an exception. However, as can be seen from the above figures, discrepancies between the data of all the theoretical calculations are rather large. At $\sin\theta/\lambda = 0{\cdot}5$, for example, for Ni the atomic scattering factor calculated according to Hartree–Fock differs from that calculated according to Thomas–Fermi and Dirac–Slater by 2% and by 1·5% from the values of the crystal field theory. Neither of these theoretical data can be assumed as a perfect basis.

At the same time, the scatter between experimental data is so large that, as a rule, they are not sufficiently accurate to be used for checks and refinements of the theory. For some compounds (*e.g.* $A^{\mathrm{III}}B^{\mathrm{V}}$) the disagreement factors are different for different reflexions.

Reflexions the structure amplitudes of which are determined by the sum of the atomic scattering factors have intensities closer to the theoretical ones. The intensity of reflexions the structure amplitudes of which are proportional to the difference of the atomic scattering factor [in the case of sphalerite, for example, $|F|_{200} = 4/(f_A - f_B)$] will depend on the effective charges of ions. Therefore, the disagreement factors with theoretical values for neutral atoms can reach large values, which are larger than the experimental errors. In particular, from Fig. 9 the disagreement factor for the 200 reflexion of InSb reaches 235%, for GaSb 10% *etc.*, while the divergence factor, for example of the 400 reflexion is only of the order of 0·5% for InSb and 1% for GaSb.

In the sphalerite lattice those reflexions with even Miller indices whose sum is divisible by four have structure amplitudes proportional to the sum of the atomic scattering factors; the reflexions with Miller indices with an even sum which is not divisible by four have structure amplitudes proportional to the difference of the atomic scattering factors.

An accuracy of 1–2% in the absolute values of the atomic scattering and structure factors may be considered in some cases as sufficient for solving a number of quantum-chemical and quantum-mechanical problems. Quantitative calculation of certain properties of crystals is already possible from the atomic scattering or structure factor values with an accuracy comparable with a direct experimental determination. We shall enumerate some opportunities which are now open in terms of the experimentally determined structure factors. They are as follows: qualitative classification of crystals according to the type of the chemical bond, including a calculation of the number of quasi-free electrons in metals; determination of dia- and paramagnetic components (Langevin and van Vleck part) of magnetic susceptibility in semiconductor crystals of elements and the simplest compounds, for example with a sphalerite structure; definition of the effective ionic charges in ionic and covalent crystals; semi-quantitative estimation of the energy of the chemical bond in crystals; calculation of the zone structure in semiconductors; calculation of the elastic constants and phonon spectra in crystals, using maps of the electron density distribution or directly using structure and atomic scattering factors.

For example, Table 16 gives the values of the experimentally determined structure amplitudes of the 200 reflexion for some $A^{III}B^{V}$ compounds; the errors $(\Delta F_{200}/F_{200}) \times 100$ are also given, as well as the disagreement factors and the values and the signs of the calculated effective ion charges. These data are in agreement with those for some compounds of other authors. However, the signs of the charges are specified for the first time (Sirota & Gololobov, 1964; Sirota, Gololobov, Oleknovich & Sheleg, 1966). The values for dia- and paramagnetic components given in Table 17 have been calculated directly from the data of the structure amplitudes. Separation of these components into Langevin and van Vleck terms of magnetic susceptibility appeared to be possible (Sirota & Sheleg, 1963; Sirota & Oleknovich, 1963; Bush & Kern, 1959).

It should be emphasized that in a number of similar quantitative calculations it is not necessary to draw the electron density distribution maps; it is enough to know the atomic scattering factor or structure factor for some calculations.

Sufficiently precise experimental determinations of structure factors and quantitative calculations of different physical properties of crystals from these experimental values will open a new chapter in quantum chemistry.

Conclusion

There is no doubt of the great importance of discussing the accuracy of absolute measurements of X-ray reflexion intensities. It follows from the present review that there exists the possibility of a substantial increase in the measurement accuracy. To realize this possibility, improvements in experimental techniques and further developments of the theory of X-ray scattering by real crystals are necessary. The measurement accuracy of reflexions with small Miller indices plays a particularly important role for the purposes of investigating the electron density distribution.

In many cases the accuracy is sufficient to allow the use of the structure factors F in solving different problems connected with the direct calculation of physical properties of crystals from the experimental values of F-factors. Further improvements in making absolute measurements of the atomic scattering and structure factors are needed.

Table 16. *Structure amplitudes of some $A^{III}B^{V}$ compounds*

$A^{III}B^{V}$	AlP	GaP	InP	AlAs	AlAs	InAs	AlSb	GaSb	InSb
$\lvert F_{\text{exp}}\rvert$ (200) Sirota & Gololobov (1964)	1·96	11·62	28·42	17·10	2·68	14·03	33·11	19·17	1·96
$\dfrac{\Delta F\,(200)}{\lvert F_{\text{exp}}\,(200)\rvert}$	±5%	±1-2%	±1%	±1%	±4%	±1%	±1%	±1%	±5%
$\dfrac{\lvert F_{\text{exp}}\rvert-\lvert F_{\text{theor}}\rvert}{\lvert F_{\text{theor}}\rvert}$	−70%	−2·5%	−2·4%	+6%	+26%	−4·5%	−2·8%	+4%	+18%
Effective charge*	0·80±0·20	0·75±0·20	0·58±0·15	0·60±0·15	0·51±0·10	0·35±0·07	0·45±0·08	0·43±0·07	0·18±0·05

* A^{III} ions have a positive sign of the effective charge and B^{V} ions have a negative one.

The author wishes to express his thanks to Drs N. M. Olekhnovich, E. M. Gololobov and A. U. Sheleg for help in preparing this paper and to Professor Hosoya for supplying unpublished data on iron and nickel and for important comments.

References

Ageev, N. V. & Ageeva, D. L. (1948*a*). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* No. 1, 17.
Ageev, N. V. & Ageeva, D. L. (1948*b*). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* No. 3, 273.
Ageev, N. V. & Guseva, L. N. (1948). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* No. 5, 470.
Ageev, N. V. & Guseva, L. N. (1949). *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* No. 3, 225.
Armstrong, A. H. (1929). *Phys. Rev.* **34**, 931.
Attard, A. E. & Azaroff, L. V. (1963). *J. Appl. Phys.* **34**, 774.
Batterman, B. W. (1959). *Phys. Rev.* **115**, 81.
Batterman, B. W., Chipman, D. R. & DeMarco, J. J. (1961). *Phys. Rev.* **122**, No. 1, 68.
Bearden, J. A. (1927). *Phys. Rev.* **29**, 20.
Belov, N. V. (1947). *Структура ионных кристаллов и металлических фаз.* Издательство Акад. Наук СССР.
Bensch, H., Witte, H. & Wölfel, E. (1955). *Z. phys. Chem.* **4**, 65.
Bragg, W. H. (1915). *Phil. Trans.* A**215**, 253.
Bragg, W. L. (1929). *Proc. Roy. Soc.* A**123**, 537.
Brill, R. & Chopra, K. L. (1962). *Z. Kristallogr.* **117**, 321.
Brill, R., Grimm, H. G., Hermann, C. & Peters, C. (1939). *Ann. Phys. Lpz.* 5 Folge, **34**, 393.
Brill, R., Hermann, C. & Peters, C. (1942). *Ann. Phys. Lpz.* 5 Folge, **41**, 37.
Brindley, G. W. (1936*a*). *Phil. Mag.* **21**, No. 142, 778.
Brindley, G. W. (1936*b*). *Phil. Mag.* **21**, No. 142, 790.
Brindley, G. W. & Spiers, F. W. (1934). *Proc. Phys. Soc.* **46**, 841.
Brindley, G. W. & Spiers, F. W. (1935). *Phys. Rev. Letters,* **3**, No. 6, 268.
Bush, G. & Kern, R. (1959). *Helv. Phys. Acta,* **32**, 24.
Chipman, D. R. & Paskin, A. (1959). *J. Appl. Phys.* **30**, No. 12, 1992.
Compton, A. H. (1926). *X-Rays and Electrons.* New York.
Cooper, M. J. (1962). *Phil. Mag.* 7, No. 84, 2059.
Cooper, M. J. (1963). *Phil. Mag.* **8**, No. 89, 811.
Cooper, M. J. (1965*a*). *Acta Cryst.* **18**, 813.
Cooper, M. J. (1965*b*). *Phil. Mag.* **11**, 969.
Coulson, C. A. (1961). *Valence,* 2nd edition. Oxford Univ. Press.
Cromer, D. T. & Waber, J. (1965). *Acta Cryst.* **18**, 104.
DeMarco, J. J. & Weiss, R. (1964). *Phys. Letters,* **13**, No. 3, 209.
DeMarco, J. J. & Weiss, R. (1965). *Phys. Rev.* **137**, A1869.
Duane, W. (1925). *Proc. Nat. Acad. Sci. Wash.* **11**, 489.
Epstein, P. & Ehrenfest, P. S. (1924). *Proc. Nat. Acad. Sci. Wash.* **10**, 133.
Ewald, P. P. (1921). *Z. Kristallogr.* **56**, 129.
Gololobov, E. M. & Sirota, N. N. (1959). *Dokl. Akad. Nauk BSSR,* **3**, 368.
Göttlicher, S., Kuphal, R. Nagorsen, G. & Wölfel, E. (1959). *Z. Phys. Chem.* **21**, 133.
Göttlicher, S. & Wölfel, E. (1959). *Z. Elektrochem.* **63**, No. 8, 891.
Hattori, H., Kuriyama, H., Katogawa, T. & Kato, N. (1965). *J. Phys. Soc. Japan,* **20**, 988.
Herbstein, F. H. (1961). *Advanc. Phys.* **10**, 313.
Hönl, H. (1933). *Ann. Phys. Lpz.* **18**, 625.
Hosoya, S. (1964). *J. Phys. Soc. Japan,* **19**, 235.
Hosoya, S. (1968). Private communication: to be published.
Hosoya, S. & Yamagishi, T. (1966). *J. Phys. Soc. Japan,* **21**, 2638.
Inkinen, O. & Suortti, P. (1964). *Ann. Acad. Sci. Fenn.* AVI, No. 147.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
James, R. W. (1950). *The Optical Principles of the Diffraction of X-rays.* London: Bell.
James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* **12**, 81.
James, R. W., Brindley, G. W. & Wood, R. G. (1929). *Proc. Roy. Soc.* A**125**, 401.
Jennings, L. D. (1968). Private communication: to be published.
Jennings, L. D., Chipman, D. R. & DeMarco, J. J. (1964). *Phys. Rev.* **135**, A1612.
Jumpertz, K. (1955). *Z. Elektrochem.* **59**, 419.
Komura, Y., Tomiie, Y. & Nathans, R. (1959). *Phys. Rev. Letters,* **3**, No. 6, 268.
Kritskaya, V. K. & Rovinsky, B. M. (1948). *Zh. Eksperim. i Teor. Fiz.* **18**, No. 9, 785.
Laschkarov, V. E. (1935). *Phys. Zeitschr. Sovjet Union,* **8**, 227.
Paakkari, T. & Suortti, P. (1967). *Acta Cryst.* **22**, 755.

Table 17. *Dia- and paramagnetic components calculated from the structure amplitudes*

	$-\chi_d \cdot 10^6$	$\chi_p \cdot 10^6$	$-\chi = -(\chi_d+\chi_p) \cdot 10^6$	$-\chi_{\text{exp}} \cdot 10^6$
	a, b	*a, b*	*b, c*	*d*
C_2	14·4	0·7	13·7	11·8
Si_2	35·6	30·2	5·4	6·2
Ge_2	61·6	47·7	13·9	15·2
α–Sn_2	82·2	52·5	29·7	(63)
AlAs	47·4	15·5	32·0	—
GaAs	51·2	24·6	26·6	32·4
InAs	71·9	25·8	46·1	55·3
AlSb	58·6	24·5	34·1	—
GaSb	65·9	26·4	39·5	38·4
InSb	80·1	8·1	72·0	65·9

a Sirota & Sheleg (1963).
b Sirota & Olekhnovich (1963).
c Sirota, Gololobov, Olekhnovich & Sheleg (1966).
d Bush & Kern (1959).

Patterson, A. L. (1936). *Phil. Mag.* **22**, 753.

Piesbergen, U. (1963). *Z. Naturforschung,* **18**a, 141.

Raccah, P. M., Arnott, R. J. & Wood, A. (1966). *Phys. Rev.* **148**, No. 2, 904.

Radchenko, M. E. & Tsvetkov, V. P. (1965*a*). *Химическая связь полупроводниках и твердых телах.* Minsk.

Radchenko, M. E. & Tsvetkov, V. P. (1965*b*). *Ukr. fiz. Zh.* **10**, 99.

Robertson, J. M. (1936). *Phil. Mag.* **21**, 176.

Roof, R. B. (1959). *J. Appl. Phys.* **30**, No. 10, 1599.

Rovinsky, B. M. (1937). *Zh. Eksperim. i Teor. Fiz.* **7**, No. 8, 971.

Rusterholz, A. A. (1930). *Z. Phys.* **65**, 226.

Sheleg, A. U. (1964). *Izv. Akad. Nauk BSSR, ser. Fiz. Mat. Nauk,* No. 2, 51.

Sirota, N. N. & Gololobov, E. M. (1961). *Dokl. Akad. Nauk SSSR,* **138**, 162.

Sirota, N. N. & Gololobov, E. M. (1962*a*). *Dokl. Akad. Nauk SSSR,* **143**, 156.

Sirota, N. N. & Gololobov, E. M. (1962*b*). *Dokl. Akad. Nauk SSSR,* **144**, 398.

Sirota, N. N. & Gololobov, E. M. (1964). *Dokl. Akad. Nauk SSSR,* **156**, 1075.

Sirota, N. N. & Gololobov, E. M. (1965). *Izv. Akad. Nauk BSSR, ser. Fiz.-Mat. Nauk,* No. 4, 132.

Sirota, N. N. & Gololobov, E. M. (1968). In the press.

Sirota, N. N., Gololobov, E. M., Olekhnovich, N. M. & Sheleg, A. U. (1966). *Kristall und Technik,* **1**, 546.

Sirota, N. N., Olekhnovich, A. E. & Olekhnovich, N. M. (1968). *Acta Cryst.* A**24**, 000.

Sirota, N. N. & Olekhnovich, N. M. (1961*a*). *Dokl. Akad. Nauk SSSR,* **136**, 660.

Sirota, N. N. & Olekhnovich, N. M. (1961*b*). *Dokl. Akad. Nauk SSSR,* **136**, 879.

Sirota, N. N. & Olekhnovich, N. M. (1962). *Dokl. Akad. Nauk SSSR,* **143**, 370.

Sirota, N. N. & Olekhnovich, N. M. (1963). *Dokl. Akad. Nauk SSSR,* **151**, 1079.

Sirota, N. N. & Pashintsev, Yu. I. (1959). *Dokl. Akad. Nauk SSSR,* **127**, 609.

Sirota, N. N. & Sheleg, A. U. (1959). *Dokl. Akad. Nauk BSSR,* **3**, No. 10.

Sirota, N. N. & Sheleg, A. U. (1960). *Dokl. Akad. Nauk SSSR,* **135**, 1176.

Sirota, N. N. & Sheleg, A. U. (1962). *Dokl. Akad. Nauk SSSR,* **147**, 1344.

Sirota, N. N. & Sheleg, A. U. (1963). *Dokl. Akad. Nauk SSSR,* **152**, 81.

Sirota, N. N. & Sheleg, A. U. (1968). In the press.

Sirota, N. N. & Sokolovsky, T. D. (1967). *Dokl. Akad. Nauk SSSR,* **174**, 797.

Slater, I. C. (1963). *Electronic Structure of Molecules.* New York.

Tsvetkov, V. P. & Kravtsova, N. F. (1963). *Ukr. Fiz. Zh.* **8**, 469.

Vekshinsky, S. A. (1944). *Новый метод металлографического исследования сплавов.* Moscow.

Wakoh, S. quoted by Hosoya, S. & Yamagishi, T. (1966). *J. Phy. Soc. Japan,* **21**, 2638.

Watson, R. & Freeman, A. (1961). *Acta Cryst.* **14**, 27.

Weiss, R. J. (1966). *X-ray Determination of Electron Distributions.* Amsterdam: North Holland Publishing Co.

Weiss, R. J. & DeMarco, J. J. (1958). *Rev. Mod. Phys.* **30**, 59.

Wyckoff, R. W. G. (1930). *Phys. Rev.* **36**, 1116.

Zener, C. (1936). *Phys. Rev.* **49**, 122.

Acta Cryst. (1969). A**25**, 243 G2·3

Survey of Results for Ionic Crystals and Metallic Oxides, Carbides and Nitrides

By Sukeaki Hosoya

Institute for Solid State Physics, University of Tokyo, 22-1, *Roppongi* 7 *chome, Minato-ku, Tokyo, Japan.*

A survey is made of X-ray powder work which has been done since 1960 to obtain information on electron states and electron charge distributions. The investigations are classified into three groups, depending upon their aims. Then the following three subjects are described: electron state of metallic nitrides, especially of Fe_4N, deformation of charge cloud in ionic crystals and comparison of measurements on MgO.

Introduction

A considerable number of investigations have been made on the compounds to be surveyed in the present paper. Much of the older work is cited in the paper by Witte & Wölfel (1958) and in a review article recently written by Brill (1967). Therefore, only the work done since 1960 will be mentioned. Although every investigation was carried out for various purposes more or less of its own, it may not be unreasonable to classify these investigations into the following three groups.

In group 1, shown in Table 1, the main concern is to determine the ionicity, or the number of electrons transferred to or from an individual atom, by careful intensity measurements of reflexions in a small angle region. Among them, six compounds from Cu_2O to Mo_2C in Table 1 have reflexions, especially in the small angle region, which are contributed mostly by light atoms alone. Such compounds are especially suitable for this kind of study. In this group, some electron diffraction work is also quoted.

It is perhaps worth while to mention here that the inner reflexions are apt to be reduced because of various effects due to extinction, preferred orientation, porosity, surface roughness, incident beam divergence and other possible phenomena. Therefore, deliberate care has been taken in measuring the intensity of these reflexions.