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Electron Distributions in NaCl, LiF, CaF_2, and Al

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THOUGH Fourier methods have been well known since 1915, when William Henry Bragg used the Fourier series to investigate the structure of NaCl, comparatively little work has been done to study distributions of valency electrons in crystals. It was not until 1938, that Brill, Grimm, Hermann, and Peters published a series of papers concerning the features which appeared in density maps of substances belonging to various bonding types. In 1948 we continued this type of work and started a program of investigating electron distributions in simple lattice types. It was planned to study as many examples of each type as possible, since differences in bonding type might exist even between examples of the same lattice. There are several reasons why, nowadays, precise values of electron densities as well as absolute values of structure amplitudes are of interest.[1]

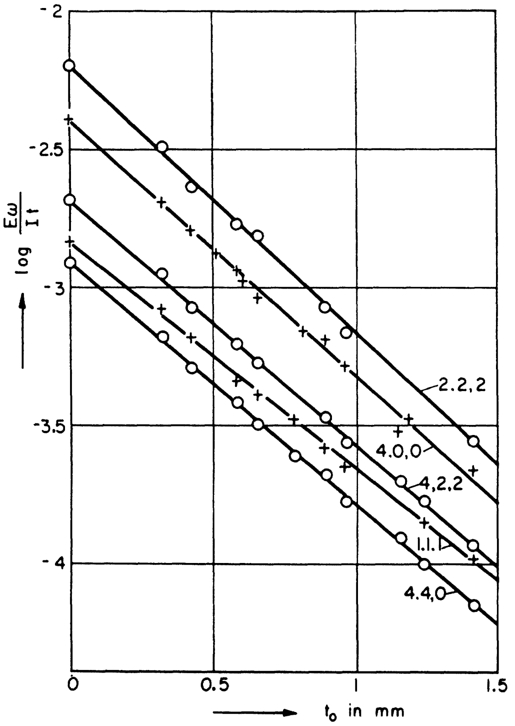

FIG. 1. Extinction measurements on NaCl single crystal slabs. t_0 = thickness of slabs; $E\omega/I$ = integrated reflection.

All measurements both on powder samples and single crystals were carried out on an absolute scale, i.e., in relation to the measured intensity of the primary beam, which was monochromatized Mo-Kα radiation. A Bragg-type spectrometer with an ionization chamber was used. The ionization chamber was kept in a fixed position while the crystal was rotated slowly through the Bragg angle. By varying the azimuthal angle on a full circle dial a large number of different reflections could be measured with one single adjustment. When using powder samples both the specimen and the ionization chamber were kept stationary. To make allowance for absorption and extinction the transmission technique was used, and slabs of different thicknesses were cut parallel to low-indexed planes and a number of the strongest structure amplitudes were measured as a function of the thickness.

When extinction effects were not too large, the absorption coefficients effective in reflection ($\mu_{\text{eff}} = \mu_0 + \epsilon$) could be derived directly by plotting $\log(E\omega/It)$ *vs* t, the thickness of the slabs (Fig. 1 for NaCl). The quantity ϵ can be expressed as a smooth function of Q, which is proportional to F^2. In this manner,

$$Q = \frac{1}{v^2}\frac{e^4\lambda^3}{m^2c^4}\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right)F^2.$$

(see Fig. 2 for NaCl). The largest structure factors, however, were also derived from a set of absolute measurements on powder specimens to check the results. In some cases when the extinction was appreciable weaker structure factors also were derived from powder data, using the Norelco spectrometer and Geiger counter tubes.

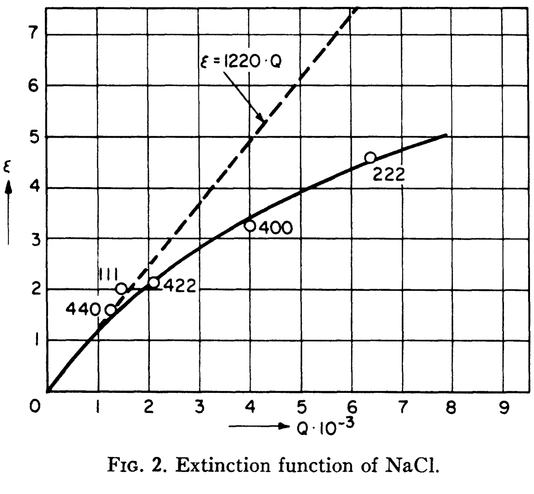

FIG. 2. Extinction function of NaCl.

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[1] This résumé is a short abstract of the following papers:
Wagner, Witte, und Wölfel, Z. physik. Chem. **3**, 273 (1955), (experimental method).
H. Witte and E. Wölfel, Z. physik. Chem. **3**, 296 (1955), (NaCl). Krug, H. Witte and E. Wölfel, Z. physik. Chem. **4**, 36 (1955) (LiF). Bensch, H. Witte and E. Wölfel, Z. physik. Chem. **4**, 65 (1955) (Al). Weiss, H. Witte and E. Wölfel, Z. physik. Chem. **10**, 98 (1957) (CaF_2). In these papers the reader will find all references to the literature.

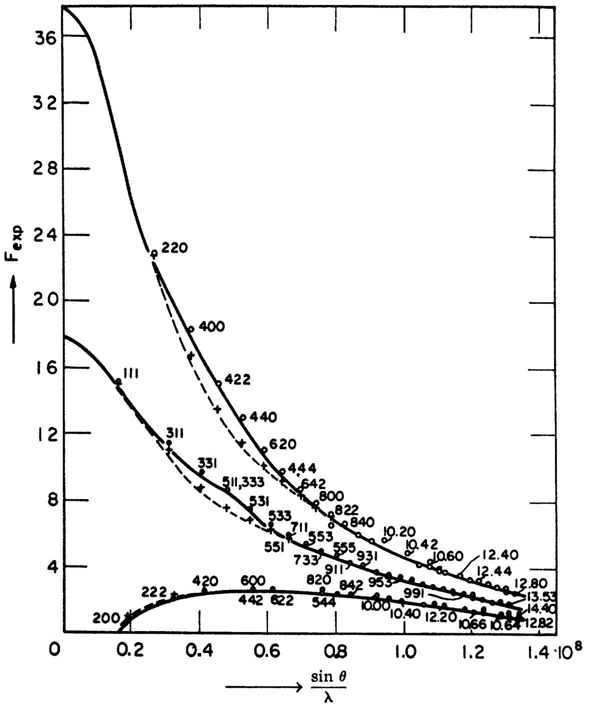

FIG. 3. Structure factors of CaF_2.

TABLE I. Structure amplitudes of NaCl, as measured by Renninger and Witte-Wölfel.

Reflexion	Structure amplitudes of: Witte-Wölfel	Renninger	Δ	Our s.d.
1,1,1	4.71	4.81	0.10	0.10
2,0,0	20.19	20.55	0.36	0.20
3,1,1	2.62	2.55	0.07	0.04
2,2,2	14.42	14.35	0.07	0.35
4,0,0	12.45	12.52	0.07	0.35
3,3,1	2.49	2.52	0.03	0.03
3,3,3	2.64	2.55	0.09	0.03
6,0,0	8.00	7.85	0.15	0.07
6,2,2	6.63	6.45	0.18	0.06
4,4,4	6.20	6.16	0.04	0.06
7,1,1	2.19	2.32	0.13	0.03
8,0,0	4.68	4.73	0.05	0.05
6,4,4	4.39	4.47	0.08	0.05
8,2,2	4.27	4.00	0.27	0.04
5,5,5	1.77	1.71	0.06	0.03
10,0,0	2.73	2.58	0.15	0.04
6,6,6	2.58	2.40	0.18	0.04

By far the greatest difficulty lies in the search for suitable single crystals or powder specimens. The behavior of the substances which have been investigated was quite different in respect to their mosaic structure. We found suitable rocksalt crystals which were nearly ideally mosaic, and we could make all measurements on single crystals with the exception of the 2 strongest reflections 200 and 220 which were derived from measurements on powder samples. In contrast to rocksalt, all crystals of LiF showed appreciable extinction effects and it was necessary to make measurements on the 10 strongest reflections on powder specimens. The primary extinction effects for the following weaker reflection were so small that only a small correction was necessary. With calcium fluoride we found crystals, which were nearly ideal, among others which showed only small extinction effects, and were suitable for single crystal work. Aluminum presented special problems, since the lattice of our single crystals was disturbed by the grinding process and a thermal treatment was necessary to remove lattice defects. By this thermal treatment, however, the extinction increased. It was quite difficult to prepare suitable fine-grained powder specimens which were free of texture.

The sources of errors influencing our results were studied in detail. Although for the strongest reflections the accuracy of the measured structure amplitudes depends primarily on the nature of the powder specimen and on the recording method used for the small ionization currents, the extinction is predominant for structure factors of medium magnitude. Finally the error of the weak structure factors is given by the uncertainty of drawing the base line to the reflection curves. The standard deviation (s.d.) of a particular structure amplitude was obtained from a set of different measurements of the same structure amplitude using different specimens under different conditions as intensity of the primary beam etc. Although the standard deviations differ from substance to substance we can roughly say that the strongest structure factors that were obtained from powder measurements have a s.d. of ±1%, those of the medium and weak structure factors are ±2-3%, while the s.d. of the weakest structure factors are still higher. It is of interest to compare our results

TABLE II. Error function for aluminum in 1/24 steps. x, y, 0 plane. $\Delta\rho$ in el/A³.

	0	1	2	3	4	5	6	7	8	9	10	11	$\longrightarrow \frac{x}{24}$ 12
0	0.28	0.19	0.12	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.12	0.19	0.28
1	0.19	0.14	0.09	0.07	0.06	0.06	0.06	0.06	0.06	0.07	0.09	0.14	0.19
2	0.12	0.09	0.08	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.08	0.09	0.12
3	0.09	0.07	0.05	0.06	0.05	0.05	0.06	0.05	0.05	0.06	0.05	0.07	0.09
4	0.09	0.06	0.05	0.05	0.08	0.06	0.05	0.06	0.08	0.05	0.05	0.06	0.09
5	0.09	0.06	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.06	0.09
6	0.09	0.06	0.05	0.06	0.05	0.06	0.09	0.06	0.05	0.06	0.05	0.06	0.09
$\downarrow \frac{y}{24}$													

with those of other investigators. As an example a comparison of our values on NaCl with Renninger's data is given in Table I. Most of the differences are within the range of our s.d.

Most of the measured structure amplitudes deviate slightly from smooth curves and the deviations are generally within the s.d. as shown by Fig. 3 for CaF$_2$. The full lines are smooth curves through the measured values of the structure amplitudes; the dotted lines are drawn through the calculated structure amplitudes (see below). Occasionally two reflections occur at the same $(\lambda^{-1}\sin\theta)$, and we found them to have a difference more than the s.d. As an example the LiF reflections 600 and 442 afford a direct proof of the deviation of the electron density from spherical symmetry.

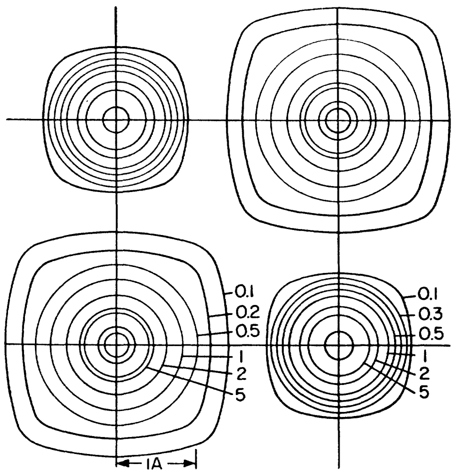

FIG. 4. Electron densities of NaCl in $xy0$ plane. Densities in el/A^3.

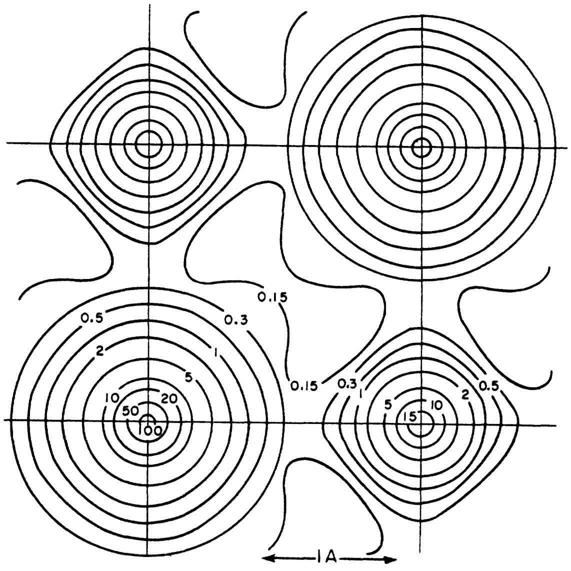

FIG. 5. Electron densities of LiF in $xy0$ plane.

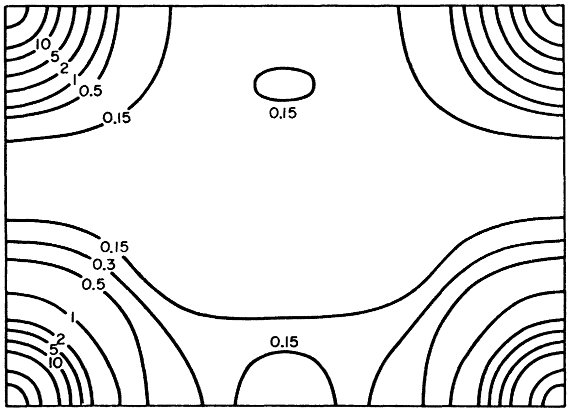

FIG. 6. Electron densities of NaCl in xxz plane.

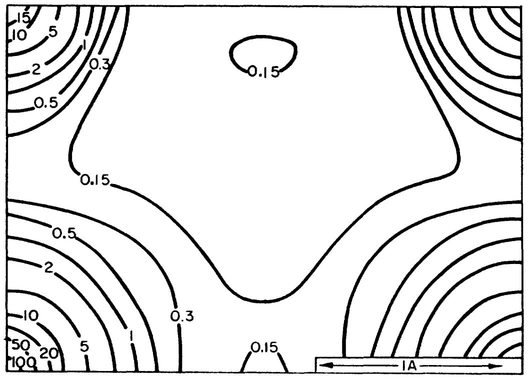

FIG. 7. Electron densities of LiF in xxz plane.

It is interesting to compare the smooth curves through the measured structure amplitudes with the theoretical ones. For calculation of the theoretical structure factors we used the atomic scattering factors of MacGillavry *et al.* Since we have to take into account the temperature factors $\exp(-B\lambda^{-2}\sin^2\theta)$ the B values were determined in the range $\lambda^{-1}\sin\theta=0.8-1.2$, where the influence of the special bonding type is to be neglected. We obtained the following B values for room temperature (a.u.^{2})

NaCl:	$B_{\text{Na}}=1.25$	$B_{\text{Cl}}=1.00$
LiF:	$B_{\text{Li}}=1.10$	$B_{\text{F}}=0.67$
Al:	$B_{\text{Al}}=0.78$	
CaF$_2$:	$B_{\text{Ca}}=0.47$	$B_{\text{F}}=0.67$

Using these values for B, the theoretical structure amplitudes at room temperature were calculated.

The greatest differences between the theoretical F curves and the smooth curves through the measured amplitudes are shown in Fig. 3 for CaF$_2$. There are appreciable differences in the range from $\lambda^{-1}\sin\theta=0.2$ to 0.7.

From the set of structure amplitudes on an absolute scale and the s.d. of these figures, electron densities and their standard deviations in important sections of the three-dimensional density-function $\rho(x,y,z)$ were calculated. The electron densities of NaCl, LiF, and Al were calculated with the measured values of the structure amplitudes, whereas the electron density of

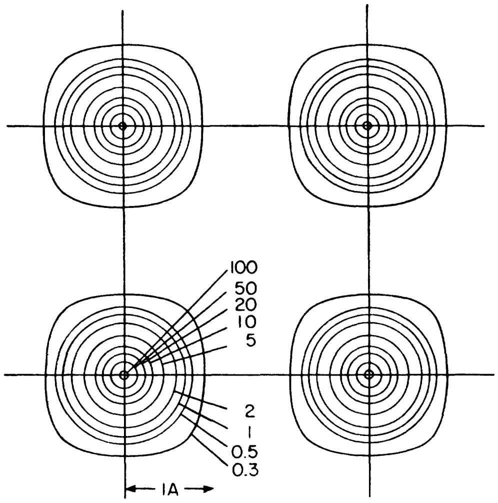

FIG. 8. Electron densities of CaF_2 in $xy\frac{1}{4}$ plane, which cuts through the F ions.

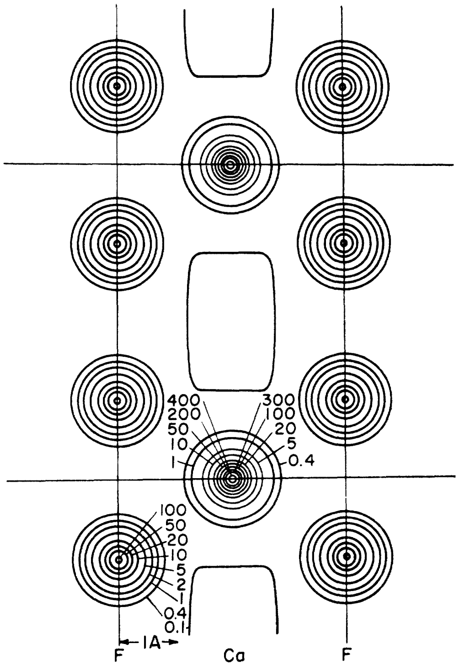

FIG. 9. Electron densities of CaF_2 in the xxz plane.

CaF_2 was calculated using the structure amplitudes on the smooth curves because of the great s.d., which are due to the large absorption coefficient of CaF_2.

Generally the s.d. were found to be in the range of 0.05–0.08 el/A^3 for points in general positions and in the range of 0.08–0.15 el/A^3 for points in special positions as $\frac{1}{4},0,0$; $\frac{1}{4},\frac{1}{4},0$; $\frac{1}{6},\frac{1}{6},0$ etc.

In the simple f.c.c. lattice, the octahedral hole $\frac{1}{2},0,0$ is not occupied by an atom and here the standard deviation reaches high values (0.3 el/A^3 in the case of Al). However, it is only high in the immediate vicinity of this point and drops down quickly.

The error function (Fehlerortsfunktion) is of great importance in the discussion of the electron density maps. The error function for Al is presented in Table II. Termination effects were avoided completely by extrapolation using Fourier integrals and a folding method as published by Hosemann and Bagchi (Nature, 1953), based on ideas of P. P. Ewald.

RESULTS

We first compare our results for NaCl with those for LiF, both of which belong to type $B1$. At room temperature in the sections $xy0$ and xxz (Figs. 4–7) the density distributions on lines between ions of opposite charge are different. The density along the line Na–Cl drops to zero, and there is a region of zero density between the ions, whereas the minimum density on the line Li—F is 0.19 el/A^3. Within the circular region of radius 0.6 A around this point of minimum density perpendic-

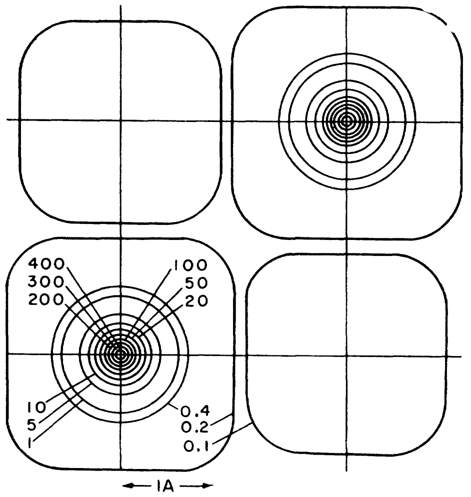

FIG. 10. Electron densities of CaF_2 in the $xy0$ plane (through the Ca ions).

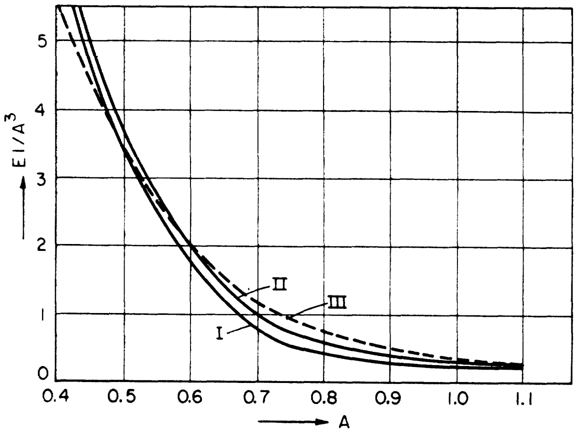

FIG. 11. Theoretical and experimental electron densities within the F ion in CaF_2. I. experimental curve along [1,0,0] and [1,1,0]. II. experimental curve along [1,1,1]. III. (dotted): theoretical curve.

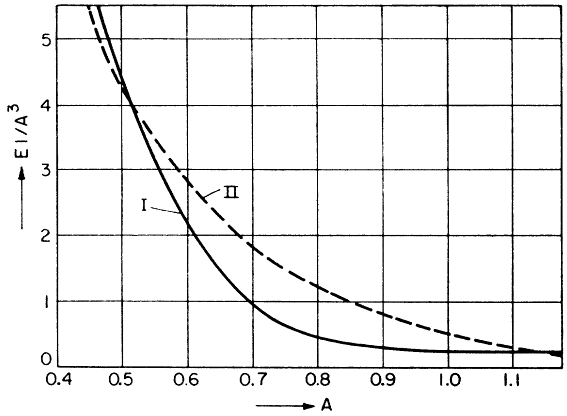

FIG. 12. Theoretical and experimental electron densities within the Ca ion in CaF_2. I. experimental curve. II. (dotted) theoretical curve.

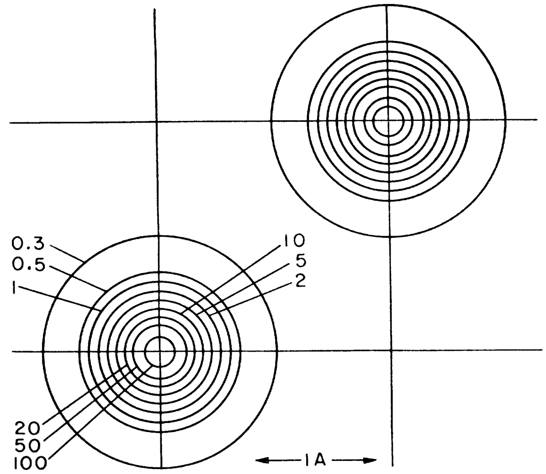

FIG. 13. Electron densities of Al in the *xy*0 plane.

ular to the line Li—F, the electron density is 0.17 el/A^3 (see *xxz* section).

Although the electron densities differ in lines joining different ions, they show similar features along lines joining equal ions. In central regions of Cl—Cl and F—F lines the average densities are 0.08 el/A^3 and 0.13 el/A^3 resp. The low densities in the $\frac{1}{4},\frac{1}{4},0$ region are connected with high values of their s.d. (0.14 and 0.11 el/A^3, respectively).

The investigation of CaF_2 showed as a main feature the appreciable average electron density of 0.20 el/A^3 in a plane between four F ions (Fig. 8), along the direction [1,0,0] or [1,1,0]. In the direction [1,1,1], (Fig. 9), however, the density drops to zero. The miminum density between Ca ions (along the direction [1,1,0], Fig. 10) was found to be 0.20 el/A^3. The deviations of the experimental structure factors from the theoretical curve as shown in Fig. 3 made it worthwhile to calculate densities using theoretical structure amplitudes and to compare the drops of both electron densities within the region of the ions. The results are shown in Fig. 11 for the F ion and in Fig. 12 for the Ca ion.

As a typical metal, aluminum was investigated. We found a spherical electron distribution (Fig. 13). The average density between the ions was 0.208 el/A^3.

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Attempt to Determine Electron Configurations in Aluminum-Rich Alloys of Transition Metals

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I. INTRODUCTION

A CONTRIBUTION to the study of the outer electron distribution in the atoms of transition metals in a number of complex Al-rich phases is described. We discuss only those features of the crystal structures which appear to be specially relevant to the topics of the Conference. We are greatly indebted to our colleagues in the Crystallographic Laboratory for unpublished information on their recent researches.

These investigations were undertaken in the first place in order to test ideas on electron transfer between atoms in alloys which arose in part from the theoretical treatments of Mott and of Pauling, in part from the extension and application of these treatments, by Raynor, to groups of alloy phase systems. The first structures to be examined gave some indication of a possible transfer of 1 or 2 electrons to the transition-metal atom, though in every case the conclusions were presented very tentatively. The structure analyses also showed that there were inconsistencies between these conclusions (if valid) and the deductions about "effective valency" from a naive application of Brillouin zone

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