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The Experimental Determination of the Distribution of the Valence Electrons in Crystals

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In six recent publications Ageev and co-authors have attempted to obtain the detailed outer (valence) electron distributions, by means of Fourier summations along various lines in the unit cell, for aluminum (Ageev & Ageeva, 1948*a*; Ageev & Guseva, 1945), copper (Ageev & Ageeva, 1948*b*), nickel (Ageev & Guseva, 1948*a, b*) and the compound NiAl (Ageev & Guseva, 1949). They conclude that metallic aluminum has a valence between 2 and 3, and that in metallic nickel and copper the electron density midway between neighbors is greater than that in the octahedral holes, so that bridge electrons which correspond to directed bonds are present. Bridge electrons are also found for NiAl but not for aluminum. If the author's conclusions are valid, they are of importance to the theory of the bonding of solids, since they would support the Pauling (1938, 1947) covalent model of the bonding in copper and nickel, as opposed to that of Mott & Jones (1936), wherein these metals would be expected to have essentially non-directional bonding.

Ageev and co-authors used radiation of comparatively high wave-length (Fe, Co, Cu$K\alpha$) to obtain intensity data. Consequently the Fourier coefficients (structure factors) of even the highest-order reflections observed were of large enough magnitude that when used unaltered in the Fourier series no information could be obtained about the distribution of outer electrons because diffraction ripples (James, 1948), due to non-termination of the series, obscured the true distributions. Termination of the series was, therefore, effected by multiplying each structure factor by an artificial temperature factor of the form $\exp[-(K\sin^2\theta)/\lambda^2]$. The values of K were in the vicinity of 11 A.^{2}, which is exceptionally large. On the basis of the Debye–Waller theory, values of the root-mean-square amplitude of vibration of the atoms, corresponding to the K values, are in the vicinity of 0·38 A., and the corresponding calculation temperatures are Al (4000° C.), Cu (6000°), Ni (8000°) and NiAl (10,000°). In view of the extremely large artificial temperature factors used by Ageev & Ageeva, it is quite possible that the electron densities of the outermost electrons are increased somewhat and, therefore, at the point midway between nearest neighbors, even for truly spherically symmetrical atoms, there will appear an increase in electron density which may seem to be due to bridge bonds but which will actually be caused by the summation of the overlapping density distributions of the outer electrons of the spherical atoms.

It is possible semi-quantitatively to check the possibility of the high bridge electron density being due to artificial overlap effects. In NiAl, which has the cesium chloride structure, let us imagine the unit cell drawn with the nickel atoms at the corners. The authors give electron-density values along the [100] line, the [110] line and the line parallel to [100] but drawn through the aluminum atom. The electron density at the point $(\frac{1}{2}, \frac{1}{2}, 0)\,a$ is 0·2 e.A.$^{-3}$. From simple geometrical considerations it may be seen that the electron density along the [110] line through a nickel atom in this crystal may be taken as a good measure of the electron density the atom of nickel would have if it were really spherically symmetrical, and that likewise the electron density parallel to the [100] line through the aluminum atom is a good representation of its electron density, since in these directions overlapping of electron distributions by other atoms can be safely ignored. If the electron densities obtained in this manner are used to calculate what the bridge-bond electron density will be, on the basis of simple superposition of overlapping electron densities for the Ni–Al bridge, one obtains values of 0·9 and 1·1 e.A.$^{-3}$ for the electron densities at distances of 1·25 and 1·5 A., respectively, along the [111] line. These calculated values are identical with those obtained by Fourier summation along [111] by Ageev & Guseva (1949). The 'bridges' found may, therefore, be entirely due to the method of calculation used by Ageev.

The calculation of electron density in the bridge bonds for the face-centered cubic metals by the method outlined is more difficult owing to multiple overlaps by neighboring atoms, but some conclusions may be drawn since it is possible to set upper and lower limits on the electron density to be expected in the bridge bonds on the basis of simple overlap of spherical atoms. In this calculation the reasonable assumption is made that at the distances concerned the electron density, as one goes out radially from the center of an atom, will be continuously decreasing or at least will not increase. The authors list calculated electron densities along the lines [100], [110] and [111]. The limits that may be set are given in equation (1), where ρ designates the electron density at the bridge position at $(\frac{1}{4}, \frac{1}{4}, 0)\,a$, which is at 0·35 a from the center of the atom, where a is the lattice constant of the cubic cell. If ρ_A is the electron density at 0·35a from the center of the atom in the [111] direction, and if ρ_0 is the electron density at $(\frac{1}{2}, 0, 0)\,a$ and ρ_T, is the electron density at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\,a$,* then

$$(2\rho_A - \tfrac{3}{2}\rho_T) \leqslant \rho \leqslant (2\rho_A - \tfrac{1}{3}\rho_0). \qquad (1)$$

The values listed in Table 1 show that the presence of 'bridge' bonds in nickel and copper and the lack of such bridges in aluminum found by Ageev and co-authors are consistent with their being caused by effects due to calculation temperature rather than to the true electron distribution, since even the lower limits for copper and nickel in the third column correspond to bridge bonds, whereas the very low lower limit for aluminum shows that it is quite possible for this metal to have a spherically symmetrical electron distribution and not enough overlap at the calculation temperature used to lead to the appearance of bridge bonds.

Table 1. *Electron densities in face-centered cubic metals*

Metal	Electron density calculated by Ageev and co-authors by Fourier summation		Electron density at $(0, \frac{1}{4}, \frac{1}{4})\,a$ calculated by equation (1)
	At $(\frac{1}{2}, 0, 0)\,a$	At $(0, \frac{1}{4}, \frac{1}{4})\,a$	
Al	0·20 e.A.$^{-3}$	0·25 e.A.$^{-3}$	0·18–0·43 e.A.$^{-3}$
Cu	0·0	0·9	0·8 –1·4
Ni	0·5	1·0	0·8 –1·4

A more fundamental question might be asked concerning the results for aluminum. Comparing calculated values of 0·08, 0·16 and 0·24 e.A.$^{-3}$ for mono-, di- and trivalent aluminum, respectively, with the observed value of around 0·20 e.A.$^{-3}$ in the octahedral hole, the authors conclude that aluminum has a valence between 2 and 3. As James (1948) has pointed out, the atomic-scattering-factor curves for mono-, di- and trivalent aluminum are essentially identical in the range of obtainable diffraction maxima. Examination of the values obtained by James & Brindley (1931) for the atomic scattering factors of the various valence possibilities shows that only one reflection [111] will have its intensity affected by the valence of aluminum. The difference caused by a change in assumed valence for this reflection will be close to the limits of accuracy in f values, ±0·05, claimed by Ageev & Ageeva (1948*a*). Since the whole accuracy of the electron-density determination, in the absence of all other perturbing effects, will depend on this reflection, it seems overly optimistic to place any reliance on an electron-density difference of 0·04 e.A.$^{-3}$ as being meaningful, or to suppose that anything very valid can be said about the valence of metallic aluminum no matter how the data are mathematically treated.

Ageev and co-authors' choice of radiation for the work on copper, nickel and AlNi is particularly unfortunate, since the dispersion corrections are large for the long-wave-length radiations used, and the uncertainties in these corrections are large enough easily to mask the small differences in intensity of low-order reflections due to the outer electron distribution. For example, Ageev & Ageeva (1948*b*) use the Hönl (1931) calculated value of 2·6 for copper, but Brindley & Ridley (1938) experimentally determined the dispersion correction to be around 3·1. Ageev & Ageeva's uncorrected data check extremely well with those of Brindley & Ridley, so that an uncertainty of around 0·5 in the f value of each reflection is introduced solely from uncertainties in the dispersion correction.

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* For the lower limit the assumption is made that the contributions of the three neighbors to the position at 0·35a in the [111] direction, which are 0·45a distant, will be less than or equal to their contribution to the tetrahedral hole (0·43a distant), and the contributions of the four neighbors to $(\frac{1}{4}, \frac{1}{4}, 0)a$ which are 0·61a distant are ignored. For the upper limit the same principle is used, with octahedral-hole electron densities substituted for the tetrahedral-hole densities used above, and the contributions of the four neighbors to $(\frac{1}{4}, \frac{1}{4}, 0)a$ at 0·61a distant are approximated by the use of the octahedral-hole values.