

*Acta Cryst.* (1980). A36, 155–156

**The accuracy of the one-term Gaussian representation for core electrons in calculating the experimental valence charge density of KCl.** By M. V. H. LINKOAHO, *Laboratory of Physics, Helsinki University of Technology, Otakaari 1, SF-02150 Espoo 15, Finland*

(Received 18 May 1979; accepted 1 September 1979)

**Abstract**

The scattering factors of the  $1s^2 2s^2 2p^6$  core for  $K^+$  and  $Cl^-$  have been calculated from analytical wave functions and also with one-term Gaussian representations. These scattering factors, together with the experimental structure factors, have been used to obtain, by difference Fourier inversion, the valence-electron charge distributions of KCl in the [100], [110] and [111] directions. By comparison, a very simple one-term Gaussian representation has been shown to yield reliable results.

I have already demonstrated (Linkoaho, 1972, 1979), the merits of the one-term Gaussian representation (De Ranter & Van Dijk, 1971) for core electrons in calculating valence-electron charge distribution. De Ranter & Van Dijk (1971) have also discussed the limits of their approximation. They have not, however, given any detailed estimates of the influence of their approximation upon the accuracy of the final valence charge densities. I present here one such estimate for the calculation of the valence charge density of KCl.

In the one-term Gaussian representation, the spherically symmetric atomic scattering factor of core electrons is expressed in the form

$$f(r^*) = G \exp(-\pi^2 g^2 r^{*2}), \quad (1)$$

where  $r^* = 2 \sin \theta / \lambda$  is the magnitude of the reciprocal vector,  $G$  is the number of core electrons and  $g$  is the half-width of the assumed Gaussian charge distribution of the core electrons. The applicability of (1) is restricted to a range from  $r^* = 0$  to  $r^* = r_c^*$ . The critical value  $r_c^*$ , which depends both on the electron configuration and on the atom considered, gives, fortunately, also the point where the contribution of the outer (valence) electrons is reduced to about zero (De Ranter & Van Dijk, 1971). Thus for  $r^* > r_c^*$ , the total theoretical atomic scattering factors represent the core electrons alone.

I have calculated the scattering factors of the  $1s^2 2s^2 2p^6$  core for both the  $K^+$  and  $Cl^-$  ions with one-term Gaussian representations. The parameters (KCl, 300 K)  $G$ ,  $g$  and  $r_c^*$ , together with the Debye–Waller coefficients  $B$  (Patomäki &

Linkoaho, 1969) and the number of Bragg reflections in the range  $0 \leq r^* \leq r_c^*$ , have been shown in Table 1. To get an idea of the accuracy of the one-term Gaussian approximation, I have also calculated the  $1s^2 2s^2 2p^6$  scattering factors for  $K^+$  and  $Cl^-$  from analytical wave functions of Bagus (1965). To perform this Fourier inversion, an Algol program was constructed in our laboratory. This program has been used previously (Patomäki & Linkoaho, 1969). By using the Debye–Waller factors from Table 1, I thus obtained the core structure factors of KCl at 300 K, both for Gaussian cores and for cores based on analytical wave functions. The differences between these structure factors were very small ( $< 0.2$ ) except at higher values ( $\geq 0.9 \text{ \AA}^{-1}$ ) of the reciprocal vector. At most this difference between the ‘approximated’ and the ‘true’ structure factor of core electrons was about 0.6. The Gaussian scattering factors for both K and Cl deviated from the analytical ones almost equally in the same direction. Thus, this discrepancy seemed not to be due to the use of atomic (given by De Ranter & Van Dijk, 1971) instead of ionic values for  $g$  and  $r_c^*$ . To be sure, however, I repeated my calculations using the ionic values (based on the wavefunctions of Bagus, 1965) of these parameters (*cf.* Table 1). The discrepancy appeared to be somewhat larger and, therefore, the following results have been calculated with the original values of these parameters

Table 1. Values of the constants for KCl at 300 K;  $a = 6.292 \text{ \AA}$

	K	Cl	$K^+$	$Cl^-$
$G$	10	10	10	10
$g$ ( $\text{\AA}$ )	0.154	0.176	0.156	0.181
$r_c^*$ ( $\text{\AA}^{-1}$ )	1.09	0.95	1.05	0.87
$B$ ( $\text{\AA}^2$ )	2.08	2.06	2.08	2.06
No. of reflexions	18	13	17	11

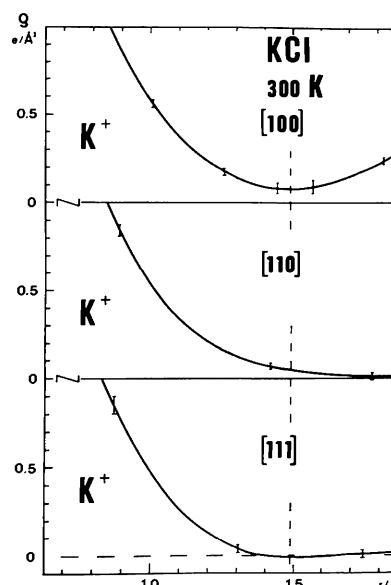


Fig. 1. The valence-electron charge density in the vicinity of the  $K^+$  ion along the [100], [110] and [111] directions for KCl at 300 K. The distance where the density between nearest neighbours reaches its minimum is indicated by vertical broken lines. This minimum value appears to be  $0.08 \pm 0.05 \text{ e \AA}^{-3}$ .

(De Ranter & Van Dijk, 1971). The essence of the following conclusions is independent of the choice of the parameters in Table 1.

The experimental valence ( $3s^23p^6$ ) charge densities of KCl at 300 K along the three principal directions are shown in Figs. 1 and 2. The experimental structure factors and Debye–Waller coefficients are from Patomäki & Linkoaho (1969). Figs. 1 and 2 clearly demonstrate the differences between the electron densities around the positive and

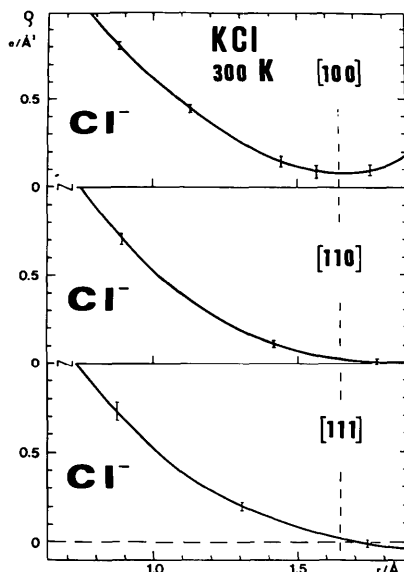


Fig. 2. The valence-electron charge density in the vicinity of the  $\text{Cl}^-$  ion along the [100], [110] and [111] directions for KCl at 300 K. The distance where the density between nearest neighbours reaches its minimum value is indicated by vertical broken lines.

negative isoelectronic ions; the latter are more diffuse. Some very slight aspherical deformations seen in Figs. 1 and 2 are probably insignificant. The effect on the charge densities from the one-term Gaussian approximation has been estimated by the differences between the core structure factors mentioned above. This effect appeared to be of the same order or smaller than the influence of experimental errors ( $\leq 0.04 \text{ e } \text{\AA}^{-3}$  in Figs. 1 and 2). The error estimates shown by vertical bars in Figs. 1 and 2 roughly indicate both the effect of experimental errors and the effect due to the Gaussian approximation. (Possible error from inaccuracy of the scale factor is omitted.)

In the light of the preceding considerations, the one-term Gaussian method which is used to subtract the core-electron contribution and to obtain the experimental valence charge densities seems satisfactory. The calculations are simple and the accuracy good enough compared with the effect of experimental errors. It is possible to attain still better accuracy by decreasing the limiting value  $r_c^*$  somewhat, say about 10%. By making this small reduction, one does not lose information on the valence charge distribution. The thermal smearing function is needed only for core electrons, where the use of isotropic approximation (Debye–Waller coefficients) is better justified. The refinement of the method by including symmetry-adapted aspherical thermal vibrations of core electrons is, however, quite straightforward.

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*Acta Cryst.* (1980). **A36**, 156

**The qualitative and quantitative analysis of renal stones by X-ray diffraction and electron-probe techniques.** By MONTE MODLIN, *Research Project Supervisor, Department of Urology, Medical School, Observatory 7925, Cape Town, Republic of South Africa*

(Received 7 August 1979; accepted 1 September 1979)

#### Abstract

The *Abstract* by Modlin & Rodgers [*Acta Cryst.* (1978), **A34**, S4, 381] was submitted without the knowledge of the present author, who was not aware of its content. Only preliminary discussions and work on certain aspects of a

research programme had taken place at the time that the *Abstract* was submitted. The conclusions claimed in the last sentence had not been arrived at.

All relevant information is contained in the *Abstract*.