

Form factors of metallic aluminium from an atom-in-jellium-vacancy model

Tapio T Rantala

Department of Physics, University of Oulu, SF-90570 Oulu, Finland

Received 27 May 1986, in final form 15 August 1986

Abstract. Atomic form factors of metallic aluminium have been calculated within the spherical atom-in-jellium-vacancy model and using the local density approximation. The form factors obtained are in good agreement with those from x-ray diffraction experiments, and agree surprisingly well with those from other calculations where the full three-dimensional lattice structure of the metal crystal is taken into account. This leads to the conclusion that the non-spherical part of the conduction electron density plays only a minor role in determining the atomic form factors of aluminium metal. Furthermore, a self-consistent spherical-solid model is used to include spherically averaged potentials of neighbouring ions and the consequent effects on the form factors are examined.

1. Introduction

The electron distribution in a metal can be obtained from the atomic form factors of x-ray diffraction experiments, for example, and there are a number of methods available for evaluating it theoretically (Marcus *et al* 1971). The contributions to atomic form factors can be separated into those from core electron densities and those from conduction electron densities, but in order to calculate a total charge density of high quality, interactions between core and valence electrons have to be included self-consistently (the SCF technique). SCF first-principles calculations, where all electronic interactions are treated coherently, have proven to be the best methods available.

The jellium model of metals, where ion cores are smeared to a constant background charge and only conduction electrons are treated explicitly, provides a simple alternative to more sophisticated models in electron structure calculations. Lack of any crystal lattice structure limits the applicability of the jellium model here but, on the other hand, this can be of benefit in calculations, where the symmetry conditions now arise only from the problem considered and not from the crystal lattice. Hence spherical symmetry can often be used for bulk metal, making the model numerically attractive, but raising the question of to what extent using the spherical model is justified.

To treat core electrons an atom-in-jellium-vacancy model (Manninen *et al* 1981) is invoked, where the core structure of a metal atom subject to interactions with conduction electrons can be obtained by explicit treatment of the atom centred in a jellium vacancy. This makes it possible to apply the same local density approximation (LDA) to exchange and correlation (Kohn and Sham 1965) for all electrons in the system. This has been shown to be the best method for describing the conduction electron response to, for example, the

core-level electronic transitions of metal atoms (Nieminen and Puska 1982, Rantala 1983) and impurity atoms in metals (Nieminen and Puska 1980).

Some attempts have been made to improve the jellium model by including crystal lattice structure, but still preserving the spherical symmetry of infinite jellium. These spherical-solid models (SSM) (Almbladh and von Barth 1976, Manninen and Nieminen 1979, Bryant 1980, Jena *et al* 1984) have been obtained by taking a spherical average of the three-dimensional periodic potential of neighbouring metal ions as a correction to the one-electron effective potential of the jellium. Pseudopotentials of various forms have been used for the neighbouring metal ions, for example that of Ashcroft and Langreth (1967).

In this work we study the adequacy of the spherical representation of the charge density of metallic aluminium atoms. We do this by using atomic form factors and comparing them with results from calculations with full three-dimensional structure. Aluminium is a free-electron metal, where the degree of oriented bonding between atoms should be small; instead, the bonding should mainly arise from a rather uniform conduction electron distribution. However, in calculations using methods with full three-dimensional symmetry (Arlinghaus 1967, Walter *et al* 1973, Perrot 1974, Tawil 1975), appreciable deviations from spherical distribution have been found, offering a good testing ground for the problem mentioned above.

We first present briefly the models and calculational methods applied, and give results for the electron densities. Then we give results for the form factors, compare with experiment and other theoretical results and discuss the role of non-spherical contributions of the valence charge. Finally, conclusions are given. In addition, in the course of this work, we examine a new simple SSM approach to see what the effects are on the valence electron density.

2. Models and calculations

The positive background charge of jellium is set to the average conduction electron density of the metal in question (for Al, $r_s = 2.07$). In jellium we take a spherical vacancy with a radius $R_{WS} = Z_h^{1/3} r_s$ (for Al, $Z_h = 3$) and place an aluminium atom with a point nucleus at the centre of it (for details see, e.g., Manninen *et al* 1981). In this atom-in-jellium-vacancy model we solve the one-electron equations

$$(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r))\psi_i = \epsilon_i\psi_i \quad (1)$$

for all electrons in the system, numerically, using a radial mesh in a sphere of radius 20 au and applying the LDA of Gunnarsson and Lundqvist (1976). This is done self-consistently for Al leading to ten core levels and continuum levels from zero to the Fermi energy ϵ_F . The resulting one-electron effective potential $V_{\text{eff}}^j(r)$ and electron density are shown in figures 1 and 2, respectively. Note that in these figures the potential and charge density at infinity are chosen as zero levels.

In figure 2 the core region is seen to range from the nucleus to about 1 to 2 au, the charge density showing the typical shell structure. Because of the core orthogonality, the conduction electron density shows oscillatory structure in the core region but the main structure is the strong screening charge, seen also to create a repulsive potential at about 3 au in figure 1. The screening is followed by a compensating depletion and decaying Friedel oscillations. The main features of our atom-in-jellium-vacancy results are the same as those found by Manninen *et al* (1981) and Jena *et al* (1984) with some differences in the screening and conduction electron oscillation in the core region.

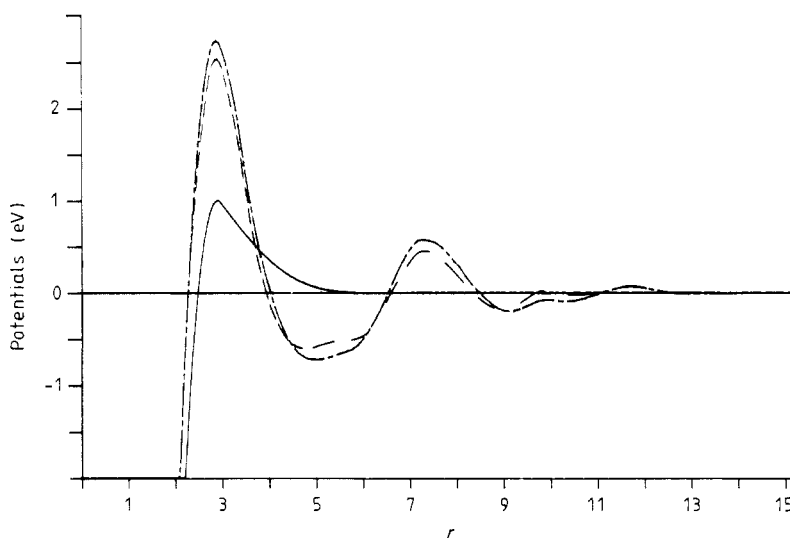


Figure 1. The one-electron effective potential $V_{\text{eff}}^j(r)$ of Al for the atom-in-jellium vacancy model (full curve), $V_{\text{eff}}^m(r)$ for the SSM (chain curve) and $V_{\text{eff}}^m(r)$ for the SCF SSM (broken curve). The constant background potential of jellium is chosen as the zero level.

We now introduce our simple approach to the SSM. We avoid the use of additional pseudopotentials by introducing the new idea of simply using the effective potential of the atom-in-jellium-vacancy, $V_{\text{eff}}^j(r)$, shown in figure 1. We define our 'pseudopotential' as

$$W_0(\rho) = \begin{cases} V_{\text{eff}}^j(r_c) & \text{if } \rho < r_c \\ V_{\text{eff}}^j(\rho) & \text{if } \rho \geq r_c \end{cases} \quad (2)$$

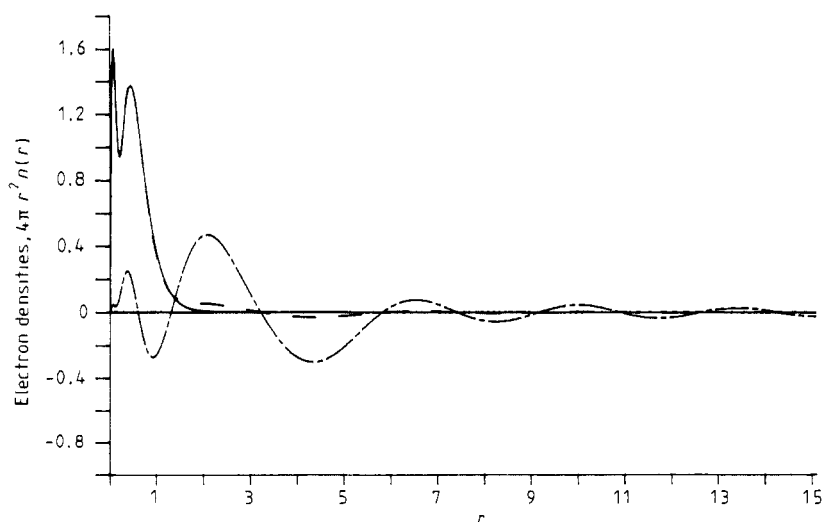


Figure 2. The electron density of Al for the atom-in-jellium-vacancy model (broken curve) and its core contribution (full curve), both reduced by a factor of ten, and the valence contribution (chain curve). The constant background charge density of jellium is chosen as the zero level.

where r_c is the smallest value for which the condition that the (integrated) net potential of $W_0(\rho)$ vanishes holds. Thus the parameter r_c is fixed so that the average of the resulting spherical-solid potential $V_{\text{SSM}}(r)$ vanishes. This leads to 'initial' values of $r_c = 2.0$ au and $W_0(r_c) = -4.2$ eV. The potential $V_{\text{SSM}}(r)$ is computed numerically in real space and added to the effective potential in (1), yielding the effective one-electron potential for the ssm

$$V_{\text{eff}}^{\text{m}}(r) = V_{\text{eff}}^{\text{j}}(r) + V_{\text{SSM}}(r) \quad (3)$$

shown in figure 1. Furthermore, we let $W_0(\rho)$ become self-consistent by repeating the procedure of equations (2)–(3) while performing the SCF iterations of $V_{\text{eff}}^{\text{j}}(r)$ given by (1), leading to self-consistent potentials $V_{\text{SSM}}(r)$ and $V_{\text{eff}}^{\text{m}}(r)$. The resulting one-electron effective potential $V_{\text{eff}}^{\text{m}}(r)$ of our self-consistent ssm (the SCF ssm) is shown in figure 1 and the corresponding electron densities in figure 3.

It is noteworthy that the self-consistency effect on the shape of $V_{\text{eff}}^{\text{m}}(r)$ seen in figure 1 is very small. However, the self-consistent 'pseudopotential' of (2) is defined by the parameters $r_c = 2.1$ au and $W_0(r_c) = -7.2$ eV, where the depth of W_0 is seen to have increased substantially from its initial value. In practice, in the calculations, the spherical-solid potential was cut off at about 10 au by multiplying with a cut-off function of Fermi–Dirac shape, effectively damping the spherical-solid potential to zero in a range of a few au.

Bryant (1980) had chosen to use the charge density of neighbouring metal ions, instead of a pseudopotential, in the calculation of the spherical-solid potential. For a Coulomb contribution this leads to the same result as ours and therefore our method is reminiscent of Bryant's. These two methods give charge oscillations that are relatively large compared with those obtained via pseudopotential approaches (Jena *et al* 1984); this difference can be traced back to the different core contributions in pseudopotentials. Our simple ssm approach is not refined enough for total-energy calculations but nevertheless we expect to find the correct trends in electron density.

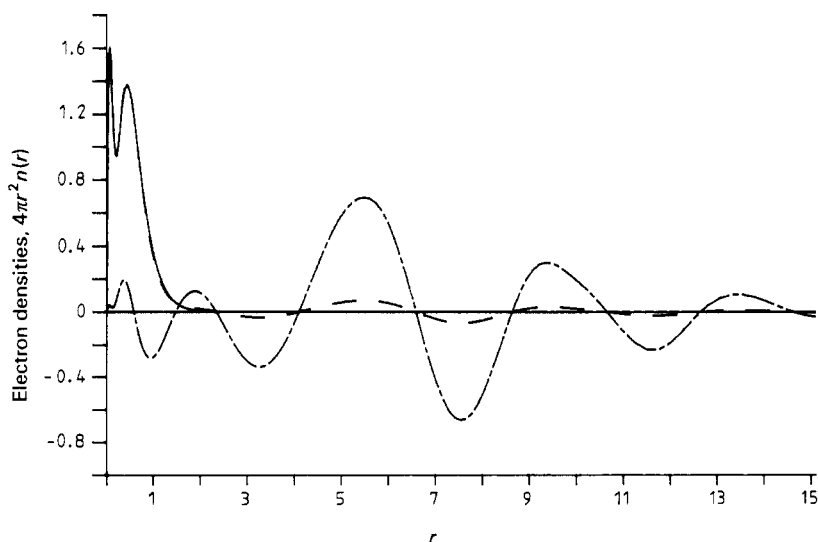


Figure 3. The electron density of Al for the SCF ssm; see the caption for figure 2.

3. Results

The atomic form factor, defined as a Fourier transform of the charge density $n(\mathbf{r})$ of the atom:

$$f(\mathbf{G}) = \int n(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}} d\mathbf{r} \quad (4)$$

gives the elastic x-ray scattering intensity of the atomic charge for a reflection $\mathbf{G}$. The form factor is a measure for the centralisation and shape of the charge distribution.

In table 1 we give our numerical results from the atom-in-jellium-vacancy model. The core contributions are about 0.5% smaller than those from free-atom calculations due to the conduction electron screening in metals, in good agreement with the results of Perrot (1974). The scf ssm core contributions are also essentially the same, but are larger by about 0.05%.

We also make a comparison with the experimental data of Raccah and Henrich (1969) given in table 1. These data are quite similar to those of Rantavuori and Tanninen (1977), whereas other experimental data available (Batterman *et al* 1961, De Marco 1967, Järvinen *et al* 1969, Takama *et al* 1982) are more scattered. With regard to valence electrons only, the experimental uncertainty turns out to mask the contributions to form factors as seen in table 1, and it is difficult to reach any firm conclusions, as also found by Perrot (1974) and von Barth and Pedroza (1985). However, our form factors agree well with the measured ones within the experimental uncertainty, but only if the valence contributions are included. For a discussion comparing theoretical and experimental form factors we refer the reader to Soininen (1983).

We next compare our theoretical valence charge density with other calculated results and show graphically the contributions to form factors from the atom-in-jellium-vacancy and scf ssm calculations in figure 4. The APW results of Perrot (1974) and the tight-binding band-structure results of Tawil (1975) are also shown, whereas the results of Walter *et al* (1973) are too scattered and therefore are not displayed. Cooper and Williams (1972) were not able to describe valence electrons properly with free-atom Hartree–Fock calculations, so their results cannot be used for comparison.

We see that the overall agreement with the other calculations is good. In particular, the jellium curve follows the results from Perrot's Kohn–Sham (ks) calculation, which being

Table 1. Atom-in-jellium-vacancy form factors of Al metal. The experimental results are from Raccah and Henrich (1969), with the experimental uncertainty of the last digit given in parentheses.

h	k	l	Core	Valence	Total	Experimental
1	1	1	8.837	0.020	8.857	8.80 (6)
2	0	0	8.498	−0.081	8.417	8.38 (6)
2	2	0	7.334	−0.036	7.298	7.27 (6)
3	1	1	6.625	0.013	6.639	6.66 (6)
2	2	2	6.414	0.025	6.440	6.48 (6)
4	0	0	5.676	0.057	5.733	5.78 (6)
3	3	1	5.214	0.068	5.282	5.33 (6)
4	2	0	5.074	0.070	5.144	5.20 (5)
4	2	2	4.579	0.072	4.651	4.66 (5)

of $X\alpha$ (or LDA) type are obviously the appropriate ones for comparing with ours. The agreement between these two sets of results is better than the agreement between Perrot's KS and mixed Hartree-Fock results or between Perrot's and Tawil's results. Furthermore, Perrot's KS results are consistent with the experimental data of Raccach and Henrich (1969) as also pointed out by Soininen (1983).

Perrot (1974) argued that the non-spherical valence density is of central importance and should be taken into account. In some cases the non-spherical contribution is even opposite to the spherical muffin-tin (MT) part in his calculations. He separated the valence contribution of the form factors into a contribution to the spherical MT part, which is treated self-consistently, and one to the non-spherical part, which is included after the last iteration only. If Perrot's bare MT and our jellium-vacancy values are compared, the agreement is not as good as that seen in figure 4, suggesting that his non-MT part is included in our spherical jellium-vacancy model to some extent.

Finally, we consider the SCF SSM curve in figure 4. It follows the other data reasonably well only for wavevector magnitudes greater than 2.5. This indicates that the long-wave oscillations in the charge density are not properly described by the present SCF SSM. For wavevectors of magnitude greater than 2.5 we find, however, that Perrot's KS results and the SCF SSM curve in figure 4 tend to deviate in the same direction with respect to the jellium-vacancy curve. This suggests that the SCF SSM may be an improvement on the jellium model as regards describing the short-wavelength oscillations of the charge density. Therefore we may conclude that using the present SSM to describe the lattice structure at

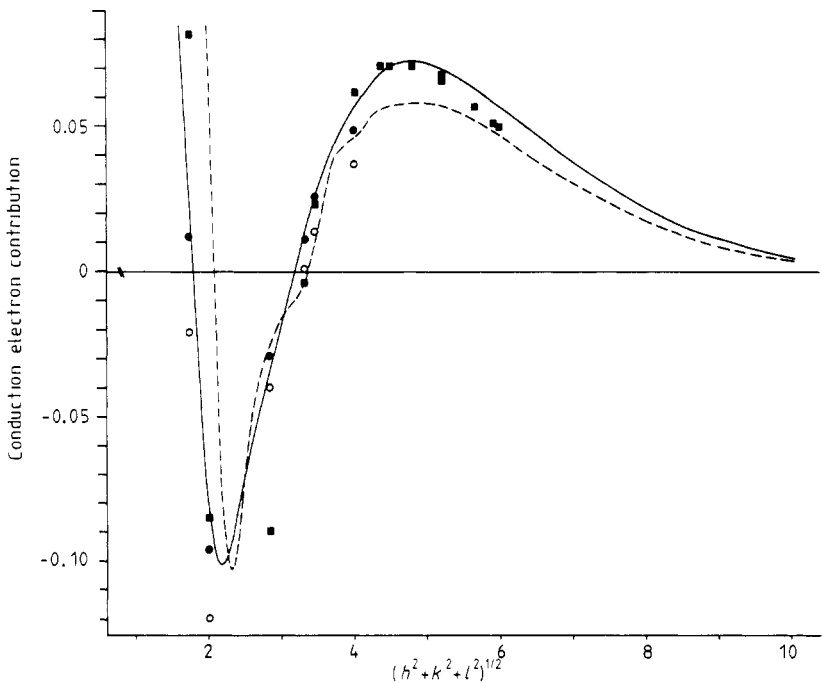


Figure 4. The conduction electron contribution to the atomic form factors of Al, for the atom-in-jellium-vacancy model (full curve) and the SCF SSM (broken curve). The APW KS or $X\alpha$ results (full circles) and APW HF results (open circles) of Perrot (1974) as well as the results of Tawil (1975) (squares) are shown where available.

the nearest neighbours is justified but that this is obviously not the case for sites further away.

4. Conclusions

Our calculated atomic form factors for aluminium metal agree with experiment within the experimental uncertainty. This is due to a large core contribution, which is theoretically well established, and a small valence contribution, which is almost negligible in comparison with the experimental uncertainty.

We find a surprisingly good agreement between our results and those of Perrot (1974) and Tawil (1975) for both core and valence contributions. Hence we conclude that, in contrast with what was asserted by Perrot, the non-spherical contribution of the valence charge density is not important but that, instead, the spherically averaged charge density of the atom-in-jellium-vacancy model is adequate for the evaluation of atomic form factors, at least for aluminium. We note however that Perrot's different definition of spherical charge using the muffin-tin sphere may be the origin of the difference between his conclusion and ours.

Although the lattice structure does not play a central role, its inclusion in a spherically averaged form may lead to an improvement for large wavevectors, as shown with our SCF SSM. However, this model does not appear to be appropriate for describing other than the nearest neighbours.

Acknowledgments

The author wishes to thank Professor E E Lähteenkorva for numerous discussions during the course of this work, and Professor R M Nieminen for reading the manuscript.

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