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1992 J. Phys.: Condens. Matter 4 5173

(http://iopscience.iop.org/0953-8984/4/22/015)

J. Phys.: Condens. Matter 4 (1992) 5173–5180. Printed in the UK

X-ray form factors and Compton profiles for some solids derived using an atom-in-jellium-vacancy model

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Received 2 December 1991

Abstract. X-ray form factors $f(k)$, Compton profiles $J(q)$ and momentum expectation values $\langle p^n \rangle$ are calculated for Mg, Al, Si, Ge and Ag using the local-density approximation with the spherical atom-in-jellium-vacancy model. These theoretical results show satisfactory agreement with experiment, thus indicating the success of the present method for these solids in the position (r) as well as the momentum (p) space.

1. Introduction

Among the different electronic properties of solids, the electron charge density (ECD) $\rho(r)$ and the electron momentum density (EMD) $\gamma(p)$ provide valuable information about their electronic structure. Experimentally the ECD can be studied from the x-ray form factors $f(k)$, measured in an x-ray diffraction experiment, while the EMD $\gamma(p)$ can be investigated by measuring the Compton profiles (CPs) in a Compton scattering experiment (Williams 1977, Cooper 1985). Both these densities can be calculated theoretically using different sophisticated band-structure methods (Marcus *et al* 1971, Williams 1977, Cooper 1985) and a comparison of the experiment with theory provides valuable information about the electronic properties of the solids being studied. Although several such band-structure calculations of the ECD and EMD exist in the literature, very few of these studies have aimed to calculate *both* the ECD and the EMD. As a simple alternative to these elaborate band-structure methods the atom-in-jellium-vacancy (AIJV) model (Manninen *et al* 1981, Puska *et al* 1981) offers some advantages. In the AIJV model the positive ions are smeared out as a jellium background (uniform positive background) and the conduction electrons are treated as a uniform interacting electron gas. The atom under investigation is embedded in an electron gas of appropriate density and the responses of the electron gas as well as the core states are calculated self-consistently. Such calculations in the AIJV model are usually carried out within spherical symmetry and, although they offer computational ease and simplicity, the validity of the spherical model (and lack of crystal lattice structure) has to be examined carefully. Such a study has been reported by Rantala (1987) who has calculated the x-ray form factors of metallic aluminium using the AIJV model and has shown that his results agree well with experiment as well as with those from calculations with a full three-dimensional structure. It was, therefore, concluded by Rantala (1987) that the spherically averaged ECD of the AIJV model is adequate for the calculation of x-ray form factors of metallic Al, with the non-spherical

0953-8984/92/225173+08$04.50

contribution of the valence ECD playing a minor role. In view of these results we found it interesting to calculate the ECD and x-ray form factors in some other solids such as Mg, Si, Ge and Ag. The ECD so obtained was also used to compute the EMD in these solids using previously reported methods to transform from the ECD to the EMD (Singru and Mishra 1989). The aim of the present work is, therefore, to examine whether the AIJV model is simultaneously successful in predicting electronic properties in the position (r) as well as in the momentum (p) space. To this end we have calculated the x-ray form factors, CPs and momentum expectation values $\langle p^n \rangle$ for the solids Mg, Al, Si, Ge and Ag using the AIJV model and have compared them with experiment. We have also investigated the effect of different density functionals obtained by various treatments of the exchange–correlation effects on the values of $f(k)$ and $\langle p^n \rangle$ in Al. Some of these results were presented at the 9th Sagamore Conference by Mali *et al* (1988). We present here our results for Al in greater detail and extend the method to other solids.

2. Model and calculations

The AIJV model has been used extensively for calculating a number of electronic properties yielding satisfactory results and the working details of the model used by us have been described elsewhere (Manninen *et al* 1981, Puska *et al* 1981, Mali 1987). We outline below the relevant equations and provide the numerical details of our calculations.

For a point charge Z immersed in jellium the equations to be solved self-consistently (using atomic units throughout) are

$$[-\nabla^2/2 + V_{\text{eff}}(r)]\psi_i(r) = \epsilon_i \psi_i(r) \tag{1}$$

where the effective potential $V_{\text{eff}}(r)$ is given by

$$V_{\text{eff}}(r) = \phi(r) + \partial E_{\text{XC}}[\rho(r)]/\partial \rho(r) \tag{2}$$

with

$$\phi(r) = -\frac{Z}{r} + \int \frac{\rho(r')}{|r - r'|}\, dr' \tag{3}$$

and

$$\rho(r) = \sum_i n_i |\psi_i(r)|^2. \tag{4}$$

In the above, $\phi(r)$ is the total electrostatic potential of the system, ϵ_i, n_i and $\psi_i(r)$ are the eigenvalues, occupancy and eigenfunction, respectively, of the ith state. The second term in (2) is the exchange–correlation potential and unless stated otherwise we have used in (2) the form given by Vashishta and Singwi (1972). The values of r_s used by us were as follows: Mg, 2.65 au; Al, 2.07 au; Si, 2.00 au; Ge, 2.088 au; Ag, 3.02 au.

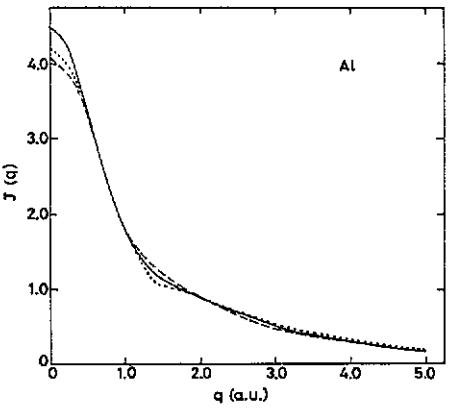

Figure 1. The CP $J(q)$ for metallic Al: – – –, experimental data (Pattison *et al* 1974); ·····, present theory using the BKCM–GP methods; ——, present theory using the phase-space method.

The density function (or the ECD) $\rho(r)$ obtained by the above procedure was used to calculate the x-ray form factor $f(k)$ for Mg, Al, Si and Ge using the well known relation

$$f(k) = \int \rho(r) \exp(ik \cdot r)\, dr \tag{5}$$

where

$$k = (2\pi \sin\theta)/\lambda.$$

Recently it has been shown that the ECD $\rho(r)$ can be transformed into the EMD $\gamma(p)$, using two methods (Singru and Mishra 1989). The first method is the scheme proposed by Burkhardt (1936), Konya (1949) and Coulson and March (1950) and modified by Gadre and Pathak (1981) (hereafter referred to as the BKCM–GP method), which has been applied to metals by Mishra and Singru (1986). The second method is based on the use of Wigner's phase-space function as applied to atoms and molecules by Parr *et al* (1986) and to metals by Mishra and Singru (1987). This method will be referred to as the phase-space method. Sohoni and Kanhere (1983a,b) have also carried out a transformation from $\rho(r)$ to $\gamma(p)$. The ECD $\rho(r)$ obtained by us for Mg, Al, Si, Ge and Ag using the AIJV model was transformed into the EMD $\gamma(p)$ using the BKCM–GP and phase-space methods as described by Mishra and Singru (1986, 1987). The results for the EMD $\gamma(p)$ were then used to calculate the isotropic CP

$$J(q) = \int_{|q|}^{\infty} \gamma(p) 2\pi p\, dp \tag{6}$$

and the momentum expectation values (or the moments of CP)

$$\begin{aligned} \langle p^n \rangle &= 2(n+1) \int_0^{q_{max}} q^n J(q)\, dq \qquad \text{for } n > 0 \\ \langle p^{-1} \rangle &= 2J(0) \qquad\qquad\qquad\qquad \text{when } n = -1 \end{aligned} \tag{7}$$

for these solids.

Table 1. X-ray form factors for metallic Al calculated using different exchange–correlation potentials.

	Theory	Present theory				Experiment
h k l	a	b	c	d	e	f
1 1 1	8.86	8.84	8.85	8.71	8.84	8.80(6)
2 0 0	8.42	8.34	8.34	8.56	8.34	8.38(6)
2 2 0	7.30	7.30	7.30	7.48	7.30	7.27(6)
3 1 1	6.64	6.64	6.65	6.58	6.65	6.66(6)
2 2 2	6.44	6.45	6.45	6.34	6.45	6.48(6)
4 0 0	5.73	5.74	5.74	5.60	5.74	5.78(6)
3 3 1	5.28	5.28	5.29	5.20	5.29	5.33(6)
4 2 0	5.14	5.15	5.15	5.08	5.15	5.20(5)
4 2 2	4.65	4.65	4.66	4.64	4.66	4.66(5)

[a] Rantala (1987).
[b] Hedin and Lundqvist (1971).
[c] Gunnarsson and Lundqvist (1976).
[d] Perdew and Zunger (1981).
[e] Vashishta and Singwi (1972).
[f] Raccah and Henrich (1969).

Table 2. Theoretical momentum expectation values $\langle p^n \rangle$ for metallic Al using different exchange correlation potentials.

	Momentum expectation values (au)				
	Present theory[a,b]	Present theory[a,c]	Present theory[a,d]	Present theory[a,e]	Experiment[f]
$\langle p^{-1} \rangle$	7.98	7.98	7.98	7.98	7.75
$\langle p \rangle$	21.68	21.68	21.68	21.68	21.75
$\langle p^2 \rangle$	66.60	66.59	66.61	66.59	64.71

[a] All values are calculated by the BKCM–GP method up to $q_{max} = 5.0$ au.
[b] Hedin and Lundqvist (1976).
[c] Gunnarsson and Lundqvist (1976).
[d] Perdew and Zunger (1981).
[e] Vashishta and Singwi (1972).
[f] Pattison *et al* (1974).

3. Results and discussion

We shall first discuss our results for $f(k)$, $J(q)$ and $\langle p^n \rangle$ for metallic Al. The x-ray form factors $f(k)$ for Al calculated using different exchange–correlation potentials, namely those of Hedin and Lundqvist (1971), Gunnarsson and Lundqvist (1976), Perdew and Zunger (1981) and Vashishta and Singwi (1972) are given in table 1 where they are compared with experiment (Raccah and Henrich 1969) and with the previous AIJV calculations (Rantala 1987). These results show that the values of $f(k)$ are not very sensitive to different exchange–correlation potentials although the values obtained for the potential of Perdew and Zunger (1981) appear to yield slightly lower values. The present theory shows good agreement with experiment as well as with the results of Rantala (1987). The present results for metallic Al in the momentum space are shown in the form of the CP $J(q)$ (figure 1) and the momentum expectation values $\langle p^n \rangle$ (table 2). It is observed that except for in the region $q = 1$–2 au

where our results show a less pronounced kink at $q = p_F$, the Fermi momentum, the BKCM–GP method predicts a CP which is in good agreement with experiment. In comparison the phase-space method shows poorer agreement with experiment. Sohoni and Kanhere (1983a, b) have calculated the total energy and CP of Al from the ECD using the locally averaged method within the neutral pseudo-atom model and their results for the CP show features similar to those observed in figure 1. The momentum expectation values $\langle p^{-1} \rangle$, $\langle p \rangle$ and $\langle p^2 \rangle$ for Al appear to be insensitive to different exchange–correlation potentials and all these theoretical results show good agreement with experiment (Pattison *et al* 1974). These results for Al are encouraging in that they indicate that the AIJV model provides a satisfactory description of $f(k)$, CP and $\langle p^n \rangle$.

Table 3. X-ray form factors for Si.

	X-ray form factor				
h k l	Present theory	Experiment[a]	Experiment[b]	Experiment[c]	Experiment[d]
1 1 1	10.58	10.80±0.08	11.12±0.04	10.766(8)	10.658(5)
2 2 0	8.57	8.70±0.06	8.78±0.09	8.603(7)	8.440(5)
3 1 1	8.11	8.07±0.08	8.05±0.07	7.941(8)	7.738(5)
4 0 0	7.50	7.69±0.08	7.40±0.14	7.382(8)	6.053(4)
3 3 1	7.15	7.41±0.10	7.32±0.12	7.069(8)	6.787(4)
4 2 2	6.69	6.83±0.10	6.72±0.06	6.489(9)	6.158(4)
3 3 3	6.43	6.50±0.08	6.43±0.08	6.192(9)	5.835(5)
5 1 1	6.43	6.56±0.09	6.40±0.08	6.200(7)	5.845(5)
4 4 0	6.03	6.05±0.08	6.04±0.15	5.760(9)	5.389(4)
4 4 4	4.97	5.10±0.08	5.00±0.10	4.620(8)	4.170(3)

[a] DeMarco and Weiss (1965).
[b] Raccah *et al* (1970).
[c] Aldred and Hart (1973).
[d] Teworte and Bonse (1984).

Table 4. X-ray form factors for Ge.

	X-ray form factor			
h k l	Present theory	Experiment[a]	Experiment[b]	Experiment[c]
1 1 1	27.51	27.55±0.2	27.23±0.09	27.88
2 2 0	23.55	23.90±0.2	23.63±0.10	23.73
3 1 1	22.21	—	22.00±0.06	22.18
4 0 0	20.34	20.90±0.6	20.31±0.06	20.25
3 3 1	19.38	—	19.52±0.11	19.60
4 4 2	17.98	—	17.98±0.09	18.05
3 3 3	17.24	17.52±0.2	—	17.33
4 4 0	16.08	16.62±0.15	—	—
4 4 4	13.43	13.50±0.15	—	—
5 5 5	10.62	10.23±0.15	—	—

[a] DeMarco and Weiss (1965).
[b] Takama and Sato (1981).
[c] Matsushita and Kohra (1974).

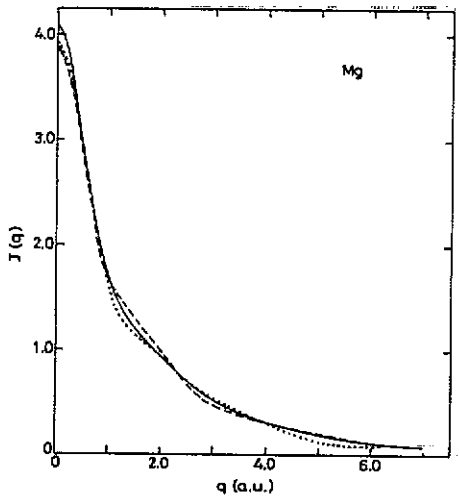

Figure 2. The CP $J(q)$ for Mg. The symbols for the three curves are the same as in figure 1 but the experimental data are from Manninen and Paakkari (1981).

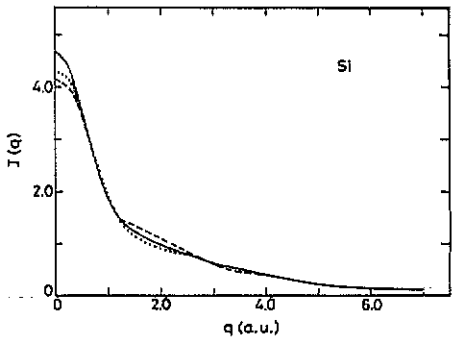

Figure 3. The CP $J(q)$ for Si. The symbols for the three curves are the same as in figure 1 but the experimental data are from Reed and Eisenberger (1972).

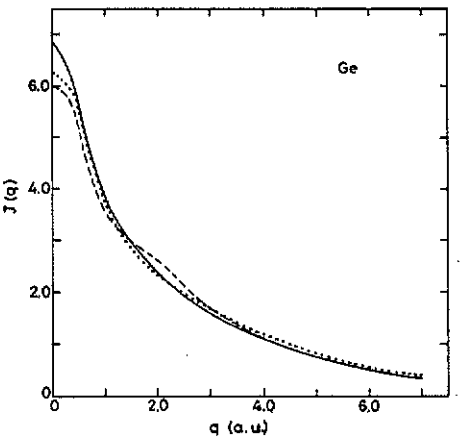

Figure 4. The CP $J(q)$ for Ge. The symbols for the three curves are the same as in figure 1 but the experimental data are from Reed and Eisenberger (1972).

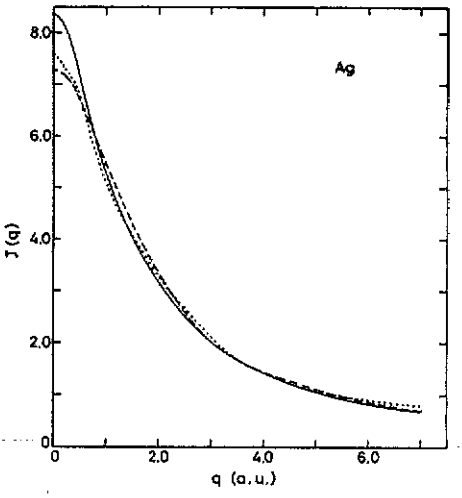

Figure 5. The CP $J(q)$ for Ag. The symbols for the three curves are the same as in figure 1 but the experimental data are from Sharma *et al* (1987).

We shall now discuss our results for the x-ray form factors $f(k)$ for Si and Ge (tables 3 and 4) and their comparison with experiment. In the case of Si, different experimental results do not show good agreement among themselves. However, the present theoretical values show closer agreement with the $f(k)$-values reported by DeMarco and Weiss (1965). In comparison the measured values of $f(k)$ for Ge agree among themselves and they all show satisfactory agreement with the present

Table 5. Comparison of theoretical and experimental momentum expectation values $\langle p^n \rangle$.

	$\langle p \rangle^{-1}$			$\langle p \rangle$		
	Present theory			Present theory		
Solid	BKCM–GP	Phase space	Experiment	BKCM–GP	Phase space	Experiment
Mg	7.63	8.02	7.57[a]	27.33	26.27	25.72[a]
Si	8.52	9.19	8.04[b]	33.13	30.48	30.97[b]
Ge	11.75	12.96	11.16[b]	75.65	69.65	73.57[b]
Ag	13.72	15.34	13.09[c]	80.08	82.00	80.09[c]

	$\langle p^2 \rangle$		
	Present theory		
Solid	BKCM–GP	Phase space	Experiment
Mg	99.93	96.13	92.64[a]
Si	134.35	116.29	119.13[b]
Ge	334.04	297.64	324.45[b]
Ag	323.55	336.73	325.95[c]

[a] Manninen and Paakkari (1981).
[b] Reed and Eisenberger (1972).
[c] Sharma *et al* (1987).

theoretical results.

In figures 2, 3, 4 and 5 we show the CPs for Mg, Si, Ge and Ag, respectively, calculated in the present theory. In each case the theoretical CP is calculated using the BKCM–GP and the phase-space method and compared with experiment. These results show a trend similar to figure 1 for Al. In each case the BKCM–GP method seems to give closer agreement with experiment than the phase-space method does. A similar observation was made earlier (Singru and Mishra 1989) for V and Cu. The BKCM model shows differences with experiment in the region $p = 1.5$–2.5 au and we ascribe these to the limitations of the spherical approximation used by us.

The momentum expectation values calculated by us for Mg, Si, Ge and Ag are compared with experiment in table 5. Once again the BKCM–GP method yields values which are closer to experiment except for the $\langle p \rangle$- and $\langle p^2 \rangle$-values for Si. The overall agreement between the BKCM–GP theory and experiment (table 5) is satisfactory.

4. Conclusions

The x-ray form factors $f(k)$, the CPs $J(q)$ and the momentum expectation values $\langle p^n \rangle$ have been calculated in the spherical approximation using the AIJV model. The results show satisfactory agreement with experiment and they show that the spherically averaged charge density of the AIJV model is good enough for calculating these quantities in some solids. The non-spherical contribution of the valence charge density perhaps plays a minor role but it is important for explaining the observed differences between experiment and theory. These conclusions not only support the results of Rantala (1987) but also show that their extension to momentum space is valid.

Acknowledgments

The authors thank Dr R R Mishra for his help in some stages of this work.

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