

Calculation of the Contribution of Conduction Electrons to the Atomic Factors of Simple Metals

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Received October 6, 2006

Abstract—An expression for the Fourier transform of the screening electron density of simple metals has been derived using smooth nonlocal model potentials of simple metals. The expression describes the contribution of conduction electrons to the atomic factors of X-ray scattering in simple metals. Aluminum was used as an example for numerical checking. Comparison with the results of similar calculations for the form factor of the Krasko–Gurskii model potential shows the importance of taking the nonlocality of the model potential into account.

DOI: 10.3103/S0027134907040091

Calculation of atomic X-ray scattering factors has been the subject matter of many investigations [1–11]. The values of the atomic factors for atoms and ions are also given in [12]. The prevailing theoretical methods are based on the Thomas–Fermi statistical model of atoms and the Hartree–Fock model [13–18]. A specific feature of these approaches is that valence electrons are taken into account for isolated atoms. For the metal state, this can also be done by the method of model potential (pseudopotential) [19].

The purpose of this study is the development of a method for taking the contribution from conduction electrons of simple metals to the atomic X-ray scattering factors into account using the smooth nonlocal model potential (SNMP) proposed in [20].

In [21], the atomic factor $f(q)$ for a spherically symmetrical atom was taken in the form of an integral of the total electron density

$$f(q) = 4\pi \int_0^{\infty} \rho(r) \frac{\sin qr}{qr} r^2 dr, \quad (1)$$

where $\rho(r)$ is the total electron density in the free state of the atom, q is the absolute value of the X-ray scattering vector or the radius vector of a point in the reciprocal space in the method of model potential, and r is the radius vector of a point in direct space. The atomic factor can be represented as a sum

$$f(q) = f_c(q) + f_{ve}(q), \quad (2)$$

where $f_c(q)$ is the fraction of the atomic factor due to the “core” electrons and $f_{ve}(q)$ is that related to valence electrons. Figure 1 reproduces the data of [12] for the total atomic factor of aluminum and its term related to the core electrons. It is seen that the fraction of the atomic factor related to valence electrons is rather high

at small q and negligibly small at large q . The fraction of the atomic factor of a simple metal related to valence electrons, $f_{ve}(q)$, can be calculated from the expression

$$f_{ve}(q) = 4\pi \int_0^{\infty} \rho_{sc}(r) \frac{\sin qr}{qr} r^2 dr, \quad (3)$$

where the screening electron density of valence electrons $\rho_{sc}(r)$ can in turn be calculated by the method of model potential.

The model-potential method (MPM) has been successfully used in the last decades to calculate the physical properties of simple metals [22]. This method has proven applicable for analysis of the electron and

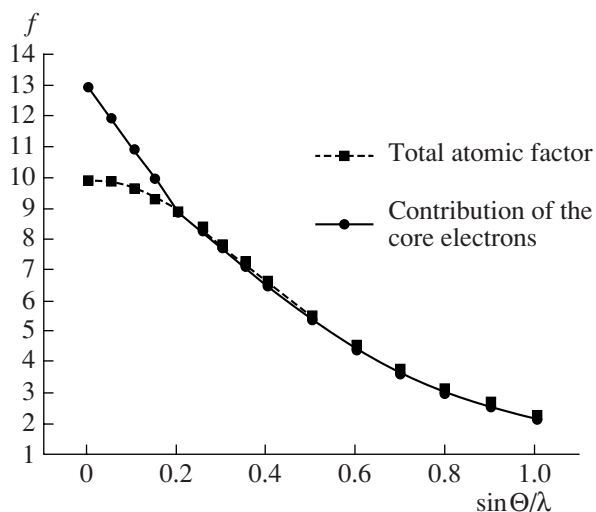


Fig. 1. Atomic factor f of aluminum (■) and the contribution of the core electrons (●) as a function of $\sin \Theta / \lambda$.

atomic properties of simple metals and alloys. In the MPM for simple metals, it is assumed that the electrons can be divided into localized core electrons (electrons of closed shells with the electron configuration of rare gas atoms) and a sum of almost free electrons (valence electrons of atoms of a simple metal). In this approximation, the electron density distribution in a crystalline metal can be represented as a sum

$$\rho_{\text{cr}}(r) = \rho_i(r) + \rho_{\text{sc}}(r), \quad (4)$$

where $\rho_{\text{cr}}(r)$ is the density of electrons in the crystal, $\rho_i(r)$ is the density of the core (localized) electrons, and $\rho_{\text{sc}}(r)$ is the density of almost free (collectivized) conduction electrons that screen the positive ion potential. In the approximation of a small core, $\rho_i(r)$ only slightly differs from the density of ions in the free state. In the theory of pseudopotentials [23], $\rho_{\text{sc}}(r)$ is the sum

$$\rho_{\text{sc}}(r) = \rho_{\text{ps}}(r) + \rho_{\text{ort}}(r), \quad (5)$$

where $\rho_{\text{ps}}(r)$ is the pseudoelectron density constructed from the pseudowave function of the crystal and $\rho_{\text{ort}}(r)$ is the distribution density of the orthogonalization charge appearing in the MPM [19].

In the MPM, the Fourier transform of the electron density of the nearly free valence electrons can be separated out when deriving the expression for the self-consistent screening matrix element of an ion in the linear screening theory. The self-consistent screening potential of a metal is represented as a sum of the ion potentials and the screening potential produced by the electron density $\rho_{\text{sc}}(r)$ of the nearly free electrons [23]

$$V_{\text{cr}}(\mathbf{k}, \mathbf{k} + \mathbf{q}, E) = S(\mathbf{q})v_i(\mathbf{k}, \mathbf{k} + \mathbf{q}, E) + S(\mathbf{q})v_{\text{ee}}(q)\rho_{\text{sc}}(q), \quad (6)$$

where $v_{\text{ee}}(q)$ is the Fourier transform of the electron-electron interaction potential with allowance for exchange and correlation, $v_i(\mathbf{k}, \mathbf{k} + \mathbf{q}, E)$ is the Fourier transform of the pseudopotential of an unscreened ion in the crystal, $\rho_{\text{sc}}(q)$ is the Fourier transform of the screening potential of nearly free electrons, and $S(\mathbf{q})$ is the structure factor. If the consideration is restricted to the potential-linear terms, the Fourier transform of the pseudodensity can be represented as [24]

$$\rho_{\text{ps}}(q) = S(q)\Pi[\Omega V(\mathbf{k}, \mathbf{k} + \mathbf{q}, E)], \quad (7)$$

where Ω is the crystal volume per atom, $v(\mathbf{k}, \mathbf{k} + \mathbf{q}, E)$ is the Fourier transform of the screened nonlocal pseudopotential of the atom, and $\Pi[\Omega F(\dots)]$ is the screening functional [24]. For simple metals in the approximation of spherical Fermi surface, the screening potential is a sum in \mathbf{k} space in the domain $|\mathbf{k}| < k_f$,

where k_f is the radius of the Fermi sphere. This sum can be represented as the integral

$$\begin{aligned} \Pi[\Omega F(\mathbf{k}, \mathbf{k}', E)] &= 2 \sum_{k < k_f} \frac{2F(\mathbf{k}, \mathbf{k}', E)}{k^2 - k'^2} \\ &= \frac{2\Omega}{(2\pi)^3} \iiint_{k < k_f} \frac{2F(\mathbf{k}, \mathbf{k}', E)}{k^2 - k'^2} d\mathbf{k}. \end{aligned} \quad (8)$$

If the numerator in the integrand in (8) depends only on \mathbf{q} and does not depend on \mathbf{k} , we have

$$\Pi[\Omega F(q)] = F(q) \frac{1 - \varepsilon(q)}{v_{\text{ee}}(q)}, \quad (9)$$

where $\varepsilon(q)$ is the permittivity of the metal with allowance for exchange and correlation.

It follows from (5)–(7) that the screened form factor of the nonlocal ion pseudopotential can be written in the form

$$v_{\text{cr}}(\mathbf{k}, \mathbf{k} + \mathbf{q}, E_k) = v_i(\mathbf{k}, \mathbf{k} + \mathbf{q}, E_k) + v_{\text{opt}}(q) + v_{\text{ee}}(q)\Pi[\Omega v_{\text{cr}}(\mathbf{k}, \mathbf{k} + \mathbf{q}, E)], \quad (10)$$

where $v_{\text{opt}}(q)$ is the form factor of the potential produced by the electron density of an orthogonalization hole [24]. Let us divide the potential into the sum of the local and nonlocal parts. For simplicity of notation, we omit the arguments and rewrite (10) in the form

$$v_{\text{cr}} = v_{\text{L}} + v_{\text{NL}} + v_{\text{opt}} + v_{\text{ee}}\Pi[\Omega v_{\text{cr}}], \quad (11)$$

where $v_{\text{L}} = v_{\text{L}}(q)$ is the local \mathbf{k} -independent part of the form factor of the unscreened ion pseudopotential and $v_{\text{NL}} = v_{\text{NL}}(\mathbf{k}, \mathbf{k}', E_k)$ is the nonlocal \mathbf{k} - and E_k -dependent part of the form factor of the pseudopotential. Using relation (9), we have

$$\begin{aligned} \Pi[\Omega v_{\text{cr}}] &= \Pi[\Omega(v_{\text{L}} + v_{\text{NL}} + v_{\text{opt}})] \\ &+ (1 - \varepsilon)\Pi[\Omega v_{\text{cr}}]. \end{aligned} \quad (12)$$

From (11) and (12), we express the screening functional of the potential of a screened ion in terms of the screening functional of the potential of an unscreened ion and substitute it into (11). As a result, we obtain the potential of the screened ion of a simple metal in terms of the complete nonlocal theory. Finally,

$$v_{\text{cr}} = v_{\text{L}} + v_{\text{NL}} + \frac{v_{\text{L}}(1 - \varepsilon) + v_{\text{opt}} + v_{\text{ee}}\Pi[\Omega v_{\text{NL}}]}{\varepsilon}. \quad (13)$$

Comparing (13) with (6) and bearing in mind that $v_i = v_{\text{L}} + v_{\text{NL}}$, we come to the following expression for the form factor of the electron density of the almost free valence electrons in a simple metal:

$$\rho_{\text{sc}}(q) = \frac{v_{\text{L}}(q)(1 - \varepsilon(q)) + v_{\text{opt}}(q) + v_{\text{ee}}(q)\Pi[\Omega v_{\text{NL}}(\mathbf{k}, \mathbf{k} + \mathbf{q}, E)]}{v_{\text{ee}}(q)\varepsilon(q)}. \quad (14)$$

Parameters $A_0, A_1, A_2, K_f, E_f, \Omega$, and Z of aluminum

$A_0(E_f)$	$\left. \frac{dA_0(E)}{dE} \right _{E=E_f}$	$A_1(E_f)$	$\left. \frac{dA_1(E)}{dE} \right _{E=E_f}$	$A_2(E_f)$	$\left. \frac{dA_2(E)}{dE} \right _{E=E_f}$	R_m	Ω	Z
-2.300	-1.227	-1.123	-0.614	3.268	0.751	3.00	111.3	3

In this study, $\rho_c(q)$ was calculated by the method [20], where

$$v_L(q) = \frac{4\pi}{\Omega} \int_0^{\infty} v_{L,K}(r) \frac{\sin qr}{qr} r^2 dr. \quad (15)$$

Here $v_{L,K}$ is the sum of two terms, one of them has an analytical form and the other appears as an integral that can be taken only numerically, i.e.,

$$v_L(q) = \frac{4\pi Z}{\Omega q^2} [-B_1(q) + B_2(q)], \quad (16)$$

where

$$B_1(q) = 1 + C \frac{\pi R_m}{2^{12} 11! Z} e^{-X} X^2 f^{-1}(X), \quad (17)$$

$$B_2 = X \int_0^{\infty} \frac{\sin(t)}{(1+t^2)^{12}} dt, \quad X = qR_m,$$

and $f^{-1}(X)$ is the tenth-order polynomial to be defined below.

The nonlocal part of the form factor is a sum of two functions,

$$v_{NL}(\mathbf{k}, \mathbf{k} + \mathbf{q}; E_{\mathbf{k}}) = F_0(\mathbf{k}, \mathbf{k} + \mathbf{q}) + F_1(\mathbf{k}, \mathbf{k} + \mathbf{q}; E_{\mathbf{k}}), \quad (18)$$

where

$$F_0(\mathbf{k}, \mathbf{k} + \mathbf{q}) = -\frac{4\pi R_m^3}{\Omega} \sum_{l=0}^2 (2l+1) \times [A_l(E_F) - C] D_{K,l}(a, b) P_l(\cos \Theta), \quad (19)$$

$$F_1(\mathbf{k}, \mathbf{k} + \mathbf{q}; E_{\mathbf{k}}) = -\frac{4\pi R_m^3}{\Omega} \sum_{l=0}^2 (2l+1) \times \left[\left. \frac{dA_l(E)}{dE} \right|_{E=E_F} \right] (E_{\mathbf{k}} - E_F) D_{K,l}(a, b) P_l(\cos \Theta). \quad (20)$$

In (19) and (20), Θ is the angle between vectors \mathbf{k} and $\mathbf{k} + \mathbf{q}$, $E_{\mathbf{k}}$ is the energy of the electron with momentum \mathbf{k} , and E_F is the electron energy at the Fermi level,

$$b = |\mathbf{k} + \mathbf{q}| R_m, \quad a = |\mathbf{k}| R_m, \quad R = b - a, \quad S = b + a, \quad (21)$$

$$D_l(a, b) = \frac{1}{ab} \int_0^{\infty} \left[\frac{j_l(at) j_l(bt)}{(1+t^2)^{12}} \right] t^2 dt,$$

where $j_l(x)$ are the spherical Bessel functions of the l th order. Analytical expressions for particular values of l have the form

$$D_0(a, b) = \frac{1}{2ab} (f^0(R) - f^0(S)) \frac{\pi}{2^{12} 11!},$$

$$D_1(a, b) = \frac{-1}{2(ab)^2} [(f^{-1}(R) - ab f^0(R)) - (f^1(S) + ab f^0(S))] \frac{\pi}{2^{12} 11!}, \quad (22)$$

$$D_2(a, b) = \frac{3}{2(ab)^3} [(f^2(R) - ab f^1(R)) - (f^2(S) + ab f^1(S))] \frac{\pi}{2^{12} 11!} + D_0(a, b).$$

In expressions (22),

$$f^{-1}(X) = \sum_{j=0}^{10} \frac{X^{10-j}}{2^j} C_{10}^j \frac{(10+j)!}{10!},$$

$$f^0(X) = \sum_{j=0}^{11} \frac{X^{11-j}}{2^j} C_{11}^j \frac{(11+j)!}{11!},$$

$$f^1(X) = \sum_{j=0}^{12} \frac{X^{12-j}}{2^j} C_{12}^j \frac{(12+j)!}{12!},$$

$$f^2(X) = \sum_{j=0}^{13} \frac{X^{13-j}}{2^j} C_{13}^j \frac{(13+j)!}{13!}.$$

Parameters R_m , $A_l(E_F)$, and $\left. \frac{dA_l(E)}{dE} \right|_{E=E_F}$ were calculated by the method [25] and are listed in the table.

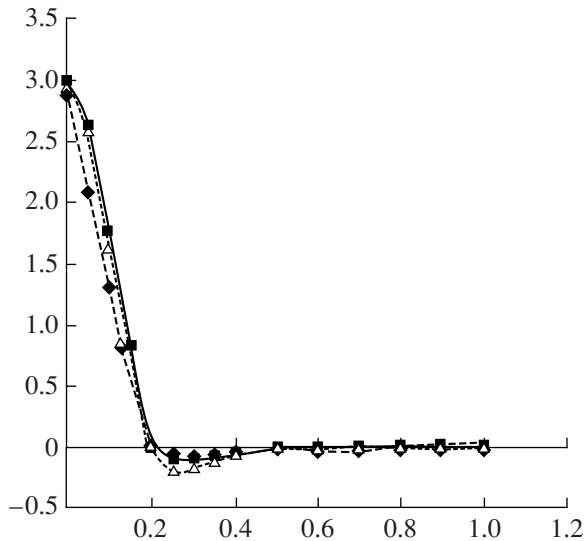


Fig. 2. Dependence of ρ_{sc} on $\sin\Theta/\lambda$ calculated in terms of (■) the SNMP, (Δ) the Krasko–Gurskii local potential, and (◆) the Hartree–Fock model [24].

CONCLUSION

In this study, the form factor $\rho_{sc}(q)$ was calculated for aluminum with the smooth nonlocal model potential (SNMP) described in [20]. The results of the calculations are shown in Fig. 2. The results of the calculation in terms of the SNMP are seen to agree satisfactorily with the data [12]. Figure 2 also shows the results of the calculation using the Krasko–Gurskii model potential which was constructed disregarding nonlocality effects. Comparison between these curves testifies to the higher reliability of the SNMP in the case of aluminum.

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