On the X-ray Scattering Factor of Metallic Lithium in the Long-Wavelength Limit: The "Solid State Effect"

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By considering three successive approximations to the conduction-electron wavefunction of metallic lithium, it is shown that the X-ray scattering factor at small wavevectors is very sensitive to the model chosen for describing the electron density. It is demonstrated that, when screened pseudopotentials are used, the "solid state effect" is almost negligible in this region of wavevectors.

I. Introduction

Considerable interest attaches to the long-wavelength limit of the structure factor of liquid metals and alloys as it is directly related to thermodynamic properties, such as the activity of the components in a binary liquid alloy (see for example Thompson et al. [1]). Because of the presence of a central, non-diffracted beam this limit has to be obtained by extrapolation starting from, say, $q = 0.1\ \text{Å}^{-1}$; q represents the scattering vector.

Bhatia and Thornton [2] have shown that, for vanishing q, the X-ray intensity diffracted by a binary system contains an important term $(\delta - \{F_1(0) - F_2(0)\}/\langle F(0)\rangle)^2 S_{CC}(0)$ which represents the contribution from the composition fluctuations $S_{CC}(0)$. Here, $\delta = V^{-1}\,\mathrm{d}V/\mathrm{d}c$, where V is the volume, the $F_i(q)$ are the scattering factors of the constituent atoms $\langle F(0)\rangle = c\,F_1(0) + (1) - c)F_2(0)$ and c is the atomic fraction of component 1. It is not difficult to see that in many cases δ and $\{F_1(0) - F_2(0)\}/\langle F(0)\rangle$ are of the same order of magnitude so that the difference can be quite sensitive to small variations in δ as well as the $F_i(\boldsymbol{q})$.

For this reason, accurate knowledge of the scattering factors $F_i(\boldsymbol{q})$ near $q = 0$ is required. $F(\boldsymbol{q})$ is defined as the Fourier transform of the electronic density centered at an atomic nucleus in the investigated solid or liquid. In the case of a metal one usually assumes that the $F(\boldsymbol{q})$ of the free atom can be considered as a good approximation to the real scattering factor. However, as in a metal the conduction electrons are essentially delocalized ("solid state effect"), it is not a priori evident that the free atom scattering factor is appropriate in the limit $q \to 0$.

Greenfield e.a. [3] considered this problem more in general and concluded that there is no reason for concern. They state that the solid state effect on the $F(\boldsymbol{q})$ of copper is of order $\frac{1}{2}\%$ of $F(\boldsymbol{q})$, and that at $q = 0$, the solid state effect is identically zero. Measurements of $F(q)$ on a beryllium crystal by Brown [4] indicate a relatively larger, negative, solid state effect of about 10% at $q = 3.5\ \text{Å}^{-1}$. But we want to emphasize that the experimental $F(\boldsymbol{q})$ can only be obtained for $q > 0.5\ \text{Å}^{-1}$ by measuring the Bragg reflections of a crystal. Generally, this is outside the region of interest for determining the long-wavelength limit.

In order to get some semi-quantitative insight in the behaviour of $F(\boldsymbol{q})$ in this particular range of wavevectors, we have carried out some elementary calculations for lithium which, of all metals, should be most prone to the solid state effect.

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We have examined in a rigid core approximation the contribution of the conduction electrons to the scattering factor of metallic lithium, using various models for the wavefunctions of these electrons. It will be shown that Greenfield et al. [3] were correct in their general conclusion, but that specifically near $q=0$ the calculated $F(\boldsymbol{q})$ are extremely sensitive to the theoretical model used. Our aim is to illustrate this situation rather than to provide new, accurate numerical results. Therefore we will consider, in this order, plane waves, orthogonalized plane waves and wavefunctions derived from screened pseudopotentials. Finally, we will compare the resulting contribution of the conduction electrons to $F(\boldsymbol{q})$ with that of the 2 s-state of the free lithium atom.

II. Calculation of $F(q)$

The coherently scattered amplitude of an arbitrary collection of identical atoms can be written as

$$A(\boldsymbol{q}) = F(\boldsymbol{q}) \sum_j \exp(i\,\boldsymbol{q}\cdot\boldsymbol{R}_j)\,, \tag{1}$$

where the sum represents the structure factor. For obvious reasons, in the following we will denote by $A(\boldsymbol{q})$ the amplitude originating from the conduction electrons only. Denoting the wavefunctions by $|\,\psi_{\boldsymbol{k}}(\boldsymbol{r})\,\rangle$, we have

$$A(\boldsymbol{q}) = \sum_{\substack{\boldsymbol{k}\\ |\boldsymbol{k}|\leq k_{\mathrm{F}}}} \langle \psi_{\boldsymbol{k}}(\boldsymbol{r})\,|\exp(i\,\boldsymbol{q}\cdot\boldsymbol{R})\,|\,\psi_{\boldsymbol{k}}(\boldsymbol{r})\,\rangle\,. \tag{2}$$

Here the sum runs over the occupied conduction band states. The scattering factor $F(\boldsymbol{q})$, which is only dependent on the magnitude of the scattering vector $\boldsymbol{q}$, can be found from (1) and (2) once an expression for $|\,\psi_{\boldsymbol{k}}(\boldsymbol{r})\,\rangle$ is given. We will now present expressions for $F(\boldsymbol{q})$ derived from the three models for the conduction electron wavefunctions.

a) Plane Waves

This is a trivial case:

$$|\,\psi_{\boldsymbol{k}}(\boldsymbol{r})\,\rangle = V^{-\frac{1}{2}} \exp(-i\,\boldsymbol{k}\cdot\boldsymbol{r}) \equiv |\,\boldsymbol{k}\rangle\,. \tag{3}$$

The scattering factor of the conduction electrons, in this approximation denoted by $F^{\mathrm{PW}}(\boldsymbol{q})$, is then

$$F^{\mathrm{PW}}(\boldsymbol{q}) = Z\,\delta_{\boldsymbol{q},0} \tag{4}$$

where Z is the number of valence electrons per atom and $\delta_{q,0}$ is the Kronecker δ-symbol. This δ-peak behaviour reflects the complete delocalization of the conduction electrons in this primitive model.

b) Orthogonal Plane Waves

The OPW's are constructed from plane waves by orthogonalization to all the core states.

$$|\,\psi_{\boldsymbol{k}}(\boldsymbol{r})\,\rangle = (1-\sum_c |\,c\rangle\langle c\,|)\,|\,\boldsymbol{k}\rangle/(1-\langle\boldsymbol{k}\,|\,c\rangle\langle c\,|\,\boldsymbol{k}\rangle)^{\frac{1}{2}}\,. \tag{5}$$

c labels the core states as well as the ions to which the core states belong. For lithium only the 1 s-orbital wavefunction has to be considered; we have chosen the form

$$|\,c\rangle = (\alpha^3/\pi)^{\frac{1}{2}} \exp(-\alpha\,|\,\boldsymbol{r}-\boldsymbol{R}_j\,|)\,. \tag{6}$$

The $A(\boldsymbol{q})$ calculated from Eqs. (2), (5) and (6) contains the structure factor explicitly. We easily find for the scattering factor of the conduction electrons in the OPW approximation

$$F^{\mathrm{OPW}}(\boldsymbol{q}) = Z\,\{\delta_{\boldsymbol{q},0} + (1-\delta_{\boldsymbol{q},0})\,B \sum_{|\boldsymbol{k}|\leq k_{\mathrm{F}}} (h^2(\boldsymbol{k})\,h(\tfrac{1}{2}\,\boldsymbol{q}) - h(\boldsymbol{k})\,h(\boldsymbol{k}+\boldsymbol{q}) - h(\boldsymbol{k})\,h(\boldsymbol{k}-\boldsymbol{q}))\} \tag{7}$$

where $B = 64\,\pi\,N_{\mathrm{ion}}/\alpha^3\,V$ and $h(\boldsymbol{k}) = (1+k^2/\alpha^2)^{-2}\cdot N_{\mathrm{ion}}$ and N_{el} are the number of ions and electrons in the metal, respectively, and $Z = N_{\mathrm{el}}/N_{\mathrm{ion}}$; $\alpha = 2.55\,(\mathrm{a.u.})^{-1}$ is taken from Roothaan and Weiss [5]. As $B = 0.061$ for lithium and $h(\boldsymbol{k}) \approx 1$ when k is inside the Fermi sphere ($k_{\mathrm{F}} = 0.587\,(\mathrm{a.u.})^{-1}$), it is clear that the second term at the right hand side of (7) contributes only a small negative part to the scattering factor at $q \neq 0$. This fact has already been established by Brown [4] for beryllium. We see that, just like the plane wave model, the OPW model generates a discontinuity in the conduction electron scattering factor at $q=0$. Both models yield a homogeneous electron density outside the core, which is of great influence on the small-wavevector behaviour of the scattering factor, although: the OPW model is known to give a fairly correct conduction electron density within the core region.

c) Screened Pseudopotentials

As the δ-peak behaviour is related to the electronic density at large distance from the core, it is obvious to consider the effect of conduction electron screening. In order to retain the connection with the OPW method we have made use of the pseudopotential formalism. The effect of screening can easily be incorporated in the pseudopotential by introducing the static dielectric function $\varepsilon(q)$ [6]. In this way, self-consistency is preserved.

It is supposed that the pseudopotential $W(\boldsymbol{r})$ can be written as a superposition of localized potentials:

$$W(\boldsymbol{r}) = \sum_j w(\boldsymbol{r} - \boldsymbol{R}_j) \tag{8}$$

where $w(\boldsymbol{r} - \boldsymbol{R}_j)$ is the pseudopotential of an ion at position $\boldsymbol{R}_j$. If the pseudowavefunction is calculated in first order, the corresponding true wavefunction reads:

$$|\psi_{\boldsymbol{k}}(\boldsymbol{r})\rangle = \left[(1 - \sum_c |c\rangle\langle c|) + \sum_{\substack{\boldsymbol{k}' \\ |\boldsymbol{k}'| > k_{\mathrm{F}}}} \frac{|\boldsymbol{k}'\rangle\langle\boldsymbol{k}'|W}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}'}}\right] |\boldsymbol{k}\rangle \tag{9}$$

where $E_k = \hbar^2 k^2/2m$ is the free electron energy of state $|\boldsymbol{k}\rangle$. Factorizing $W_k(\boldsymbol{q}) = \langle\boldsymbol{k}+\boldsymbol{q}|W|\boldsymbol{k}\rangle$ into a structure factor and a matrix element of the localized potential w, we find, in first order, a scattering factor $F^{\mathrm{pseudo}}(\boldsymbol{q})$ of the conduction electrons:

$$F^{\mathrm{pseudo}}(\boldsymbol{q}) = F^{\mathrm{OPW}}(\boldsymbol{q}) + 2 \sum_{\substack{\boldsymbol{k} \\ |\boldsymbol{k}| \le k_{\mathrm{F}}}} \sum_{\substack{\boldsymbol{k}-\boldsymbol{q} \\ |\boldsymbol{k}-\boldsymbol{q}| > k_{\mathrm{F}}}} \cdot \frac{\langle\boldsymbol{k}-\boldsymbol{q}|w|\boldsymbol{k}\rangle}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}}} . \tag{10}$$

Here $F^{\mathrm{OPW}}(\boldsymbol{q})$ is defined in (7) and the matrix element in (10) will be denoted by $w_{\boldsymbol{k}}(\boldsymbol{q})$. It is important to notice that $F^{\mathrm{OPW}}(\boldsymbol{q})$ contains a Kronecker $\delta_{q,0}$ while the last term in (10) is identically zero for $\boldsymbol{q} = 0$ because of the restrictions imposed on the summations.

In the following it is shown that the jump at $\boldsymbol{q} = 0$ in $F^{\mathrm{pseudo}}(\boldsymbol{q})$ disappears, provided a *selfconsistently-screened* pseudopotential is used.

Approximating w by a local pseudopotential (i. e. $w_{\boldsymbol{k}}(\boldsymbol{q})$ independent of $\boldsymbol{k}$), we write.

$$w_{\boldsymbol{k}}(\boldsymbol{q}) = w_{\mathrm{bare}}(\boldsymbol{q})/\varepsilon(\boldsymbol{q}) . \tag{11}$$

Remembering that, for large r, $w_{\mathrm{bare}}(\boldsymbol{r})$ is Coulombic, we find in the limit of vanishing q:

$$w_{\mathrm{bare}}(\boldsymbol{q}) \xrightarrow[(\boldsymbol{q}\to 0)]{} -e^2 Z_{\mathrm{eff}}/V q^2 \varepsilon_0 , \tag{12}$$

where $Z_{\mathrm{eff}} = Z(1+B)$ is the effective valency of the lithium ion including the so-called orthogonalization hole and ε_0 is the dielectric constant of vacuum.

Next we notice that, if the Hartree dielectric function is chosen for $\varepsilon(q)$, we have, by definition:

$$2 \sum_{\substack{\boldsymbol{k} \\ |\boldsymbol{k}| \le k_{\mathrm{F}}}} \sum_{\substack{\boldsymbol{k}-\boldsymbol{q} \\ |\boldsymbol{k}-\boldsymbol{q}| > k_{\mathrm{F}}}} \frac{1}{E_{\boldsymbol{k}} - E_{\boldsymbol{k}-\boldsymbol{q}}} = (1 - \varepsilon(q))\, \varepsilon_0 q^2 V/e^2 . \tag{13}$$

Since $\varepsilon(q)$ exhibits the well-known $1/q^2$ behaviour for small q, the long-wavelength limit of $F^{\mathrm{pseudo}}(\boldsymbol{q})$ can be evaluated after substituting (11), (12) and (13) in (10):

$$F^{\mathrm{pseudo}}(\boldsymbol{q}) \xrightarrow[(q\to 0)]{} F^{\mathrm{OPW}}(\boldsymbol{q}) + Z_{\mathrm{eff}}(1 - \delta_{\boldsymbol{q},0}) . \tag{14}$$

Since $F^{\mathrm{OPW}} - BZ$ for small q (Eq. (7))· and $Z_{\mathrm{eff}} = Z(1+B)$ it is obvious that in (14) the jump at $q = 0$ found earlier in the scattering factor is now reduced to almost zero.

We have also numerically evaluated Eq. (10) for $q > 0.005\, k_{\mathrm{F}}$. The first term at the right hand side of (10) is given in (7), the last term of (10) can be calculated by using a self-consistently screened pseudopotential. In the literature, the pseudopotentials are usually presented by giving a matrix element $w_{k_{\mathrm{F}}}(\boldsymbol{q})$ as a function of q, with $|\boldsymbol{k}_{\mathrm{F}} + \boldsymbol{q}| = k_{\mathrm{F}}$. The matrix elements $w_{\boldsymbol{k}}(\boldsymbol{q})$ for arbitrary $\boldsymbol{k}$ cannot directly be dericed from these listed matrix elements as a consequence of the nonlocality of the pseudopotential.

The pseudopotential of lithium is known to contain a large non-local part but, as Shaw [7] shows, this non-local part is a slowly varying function of q. Approximating the non-local part $w_{\boldsymbol{k}}^{\mathrm{NL}}(\boldsymbol{q})$ of $w_{\boldsymbol{k}}(\boldsymbol{q})$ by:

$$w_{\boldsymbol{k}}^{\mathrm{NL}}(\boldsymbol{q}) \propto \langle\boldsymbol{k}|E - H)P|\boldsymbol{k}+\boldsymbol{q}\rangle \tag{15}$$

with $P = |1\,\mathrm{s}\rangle\langle 1\,\mathrm{s}|$, we can evaluate $w_{\boldsymbol{k}}^{\mathrm{NL}}(\boldsymbol{q})$ for arbitrary $\boldsymbol{k}$ from the value $w_{k_{\mathrm{F}}}^{\mathrm{NL}}(\boldsymbol{q})$ provided by Shaw [7]:

$$w_{\boldsymbol{k}}^{\mathrm{NL}}(\boldsymbol{q}) \cong w_{k_{\mathrm{F}}}^{\mathrm{NL}}(\boldsymbol{q})\, h(\boldsymbol{k}+\boldsymbol{q})\, h(\boldsymbol{k}) / (h(\boldsymbol{k}_{\mathrm{F}}))^2 . \tag{16}$$

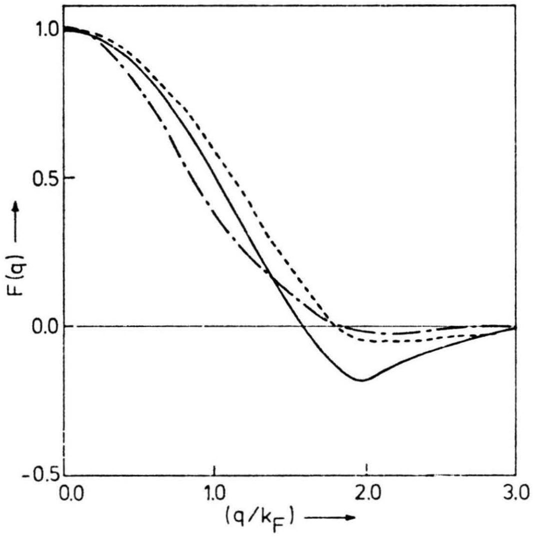

Fig. 1. The X-ray scattering factor $F(q)$ of Li versus q/k_{F}. ——— Present calculation, Equation (10). – – – – Perrin, Taylor and March [9]. – · – · – Atomic $F(q)$.

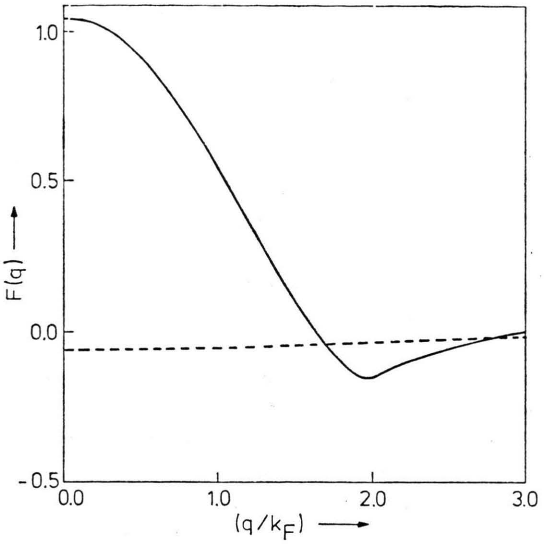

Fig. 2. The two contributions of the X-ray scattering factor $F(q)$ versus q/k_F of Eq. (10) for Li.
——— $F(q) - F^{\mathrm{OPW}}_{(q)}$. - - - - $F^{\mathrm{OPW}}_{(q)}$.

$h(k)$ is already specified in (7). The value of the matrix element $w_{k_F}(\boldsymbol{q})$ is obtained from Appapillai et al. [8].

The results obtained by evaluating (10) are shown in Fig. 1 and compared with those by Perrin, Taylor and March [9]. The contributions from the two terms at the right hand side of (10) are presented separately in Figure 2.

III. Conclusion

Evidently, in the screened pseudopotential approximation, the scattering factor approximates the atomic scattering factor very closely for vanishing q. In this limit, screening removes the unphysical discontinuity in the scattering factor found in the two simpler models.

As a consequence of the employment of first order perturbation theory and of the approximations made in the calculation of the non-local part of the pseudopotential, one can't expect accurate values of $F^{\mathrm{pseudo}}(\boldsymbol{q})$ for larger q. More particularly, the depth of the minimum near $q = 2\,k_F$ in our calculations proves to be quite sensitive to the choice of the model potential. Taking this into account, the agreement with KKR calculations by Perrin et al. [9] is satisfactory.

Obviously, whereas the dynamics of the conduction electrons in the alkali metals can be described well by a nearly free electron model, the density of the conduction electrons in the metallic phase has more or less retained the shape of the valence-electron density of a collection of free atoms. This result is in accordance with the concept of the pseudoatom introduced by Ziman [10]. It follows from our considerations that an accurate calculation of $F(\boldsymbol{q})$ near $q = 0$ is quite tricky and that great care should be exercised in the description of the long-distance behaviour of the conduction electrons. To check this point further, we have also calculated $F(\boldsymbol{q})$ using more sophisticated screening procedures, taking into account the effects of electron correlation and exchange (see e. g. Hubbard [11], Singwi et al. [12], Shaw [13, 14], Vashishta and Singwi [15]). These calculations were based on the Ashcroft-empty-core-potential [16]. The results indicate that mutual discrepancies of the order of 0.15 may arise in the $F(\boldsymbol{q})$ at larger values of q, whereas at smaller q the results agree significantly better. It appears that not only the choice of the screening affects the scattering factor but that also the change from the bare ion potential used by Appapillai (a Shaw optimized potential) to the empty-core-potential has a significant influence. For these reasons it seems not appropriate to give a more detailed, quantitative account of these results.

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