Effect of Temperature on Atomic Scattering Curve

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Abstract

We have calculated the temperature dependence of the atomic scattering curve for the elements Si, C, Pt and Cu. At first we have drawn the general atomic scattering curve for the above elements. A quantity 'f', the atomic scattering factor, is said to describe the 'efficiency' of scattering of a given atom in a given direction. The actual calculation of 'f' involves sin θ, rather than θ, so that the net effect is that 'f' decreases as the quantity (sin θ)/λ increases. Secondly, we have considered Debye temperature factor using Debye model. And we observe that for Debye approximation, the curve decreases a little bit.

Introduction

The atomic scattering factor 'f' is defined as the ratio of amplitudes:

$$f = \frac{amplitude\ of\ the\ wave\ scattered\ by\ an\ atom}{amplitude\ of\ the\ wave\ scattered\ by\ one\ electron}$$

It is clear that $f=Z$ (atomic number) for any atom scattering in the forward direction [1]. As θ increases, the waves scattered by individual electrons become more and more out of phase and 'f' decreases [2]. The atomic scattering factor depends also on the wavelengths of the incident beam [3]. At a fixed value of θ, 'f' will be smaller, the shorter the wavelength, leading to greater interference between the scattered beams. Calculated values of 'f' for various atoms and various values of (sin θ)/λ are tabulated in the Tables 1-3. We see that the curve begins at the atomic number and decreases to very low values for scattering in the backward direction (θ near 90º) for very short wavelengths [4-8]. Again we observe that due to temperature factor, the general atomic scattering curve is affected for Debye temperature approximation. From this point of view, we have studied the temperature factor dependence of the atomic scattering curve for Debye temperature approximation [9-11].

Thermal (temperature factor) effects on the atomic scattering curve: (Debye approximation)

So far, a crystal has been considered as a collection of atoms located at fixed points in the lattice [12]. Actually, the atoms undergo thermal vibration about their mean positions even at the absolute zero of temperature, and the amplitude of this vibration increases as the temperature increases [13]. We need any quantitative information about the temperature factor e^{-M}, but it is convenient to describe the calculation here before considering other thermal effects. Formally, this effect is included by defining f as the atomic scattering factor of an atom undergoing thermal vibration, f_0 as the same quantity for an atom at rest, and the two is related by [14]

$$f=f_0 \times e^{-M} \tag{1}$$

The quantity f_0 is then the scattering factor as usually tabulated. Because the intensity of any line depends on f^2 calculated intensities must be multiplied by e^{-M} to allow for thermal vibration [15]. The quantity M depends on both the amplitude u of thermal vibration and the scattering angle 2θ:

$$M = 2\pi^2 \left(\frac{\overline{u}^2}{d^2} \right) = 8\pi^2 \overline{u}^2 \left(\frac{\sin\theta}{\lambda} \right)^2 = B \left(\frac{\sin\theta}{\lambda} \right)^2 \tag{2}$$

Where, u^{-2} is the mean square displacement of the atom in a direction normal to the diffracting planes. The exact calculation of u^{-2} as a function of temperature is extremely difficult [16], which means that M or B is tough to determine accurately. Peter Debye has given the following expression:

$$M = \frac{6h^2 T}{mk\Theta^2} \left[\varphi(x) + \frac{x}{4} \right] \left(\frac{\sin\theta}{\lambda} \right)^2, \text{ (Debye approximation)} \tag{3}$$

Where, h is the Planck's constant, T is the absolute temperature, m is the mass of the vibrating atom, k is the Boltzmann's constant, Θ is the Debye characteristic temperature of the substance in K, $x=/T$, and $\phi(x)$ is a function tabulated [17], along with values of Θ, $m=A/N$ where A=atomic weight and N=Avogadro's number, the coefficient of the bracketed terms becomes, by inserting the numerical values of the constants in eqn. (3):

$$\frac{6h^2 T}{mk\Theta^2} = \frac{6 \times (6.63 \times 10^{-34})^2 \times (6.023 \times 10^{23})T}{A\Theta^2 \times 10^{-20}} = \frac{1.15 \times 10^4 T}{A\Theta^2}$$

If λ is in angstroms. In eqn. (3) is approximate and applies only to elements with cubic crystal structure.

So, ultimately in eqn. (3) reduces to,

$$M = \frac{1.15 \times 10^4 T}{A\Theta^2} \left[\varphi(x) + \frac{x}{4} \right] \left(\frac{\sin\theta}{\lambda} \right)^2 \tag{4}$$

Again, $\phi(x)$ can be expressed as:

$$\varphi(x) + \frac{x}{4} = 1 + \frac{x^2}{36} - \frac{x^4}{3600}$$

Thus, M can be written as,

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$$M = \frac{1.15 \times 10^4 T}{A\Theta^2} \left[1 + \frac{x^2}{36} - \frac{x^4}{3600} \right] \left(\frac{\sin\theta}{\lambda} \right)^2 \qquad (5)$$

Finally, we get,

$$f = f_0 \exp\left[-\frac{1.15 \times 10^4 T}{A\Theta^2} \left(1 + \frac{x^2}{36} - \frac{x^4}{3600} \right) \left(\frac{\sin\theta}{\lambda} \right)^2 \right] \qquad (6)$$

Calculation of general scattering factor

As seen by incident X-ray photons, a sample consists of a spatially inhomogeneous sea of electrons. In fact, quantum mechanics indicates that each electron is itself spread into a diffuse cloud of negative charge. The important quantity is the charge density ρ which is normally expressed in electron units so that the quantity ρDv is the ratio of charge in volume dv to the charge of one electron. Thus, for each electron $\int \rho dV = 1$. The scattering from a single atom must take into account the phase differences for scattering from different "portions" of the atom, and f_0, the atomic scattering factor is made up of the contributions from individual electrons f_e given by

$$f_e = \int \exp\left[(2\pi i / \lambda)(\underline{S} - \underline{S}_0).\underline{r} \right] \rho dV$$

Calculation of the precise values of $f_0 = \sum (f_e)_n$ depends on the detailed knowledge of the charge distribution ρ_n.

While it may not be precisely true, assuming that the charge distribution of electrons in an atom is spherical and equals $\rho = \rho(r)$ is a very useful approximation and always a simple expression to be obtained for f_0. Using k=(4π/λ) sin θ and $(\underline{S} - \underline{S}_0).\underline{r} = 2r \sin\theta \cos\phi$ and

$$f_0 = \sum_n (f_e)_n = \sum_n \int_r^\infty \int_\phi^\pi \exp(ikr\cos\phi) \rho_n(r) 2\pi r^2 \sin\phi \, d\phi \, dr$$

$$= \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) \frac{\sin kr}{kr} dr \qquad (7)$$

We know that, at small angles, i.e., small k or (sin θ)/λ, approaches unity. If Z is the number of electrons in an atom,

Then,

$$\sum_n \int_0^\infty 4\pi r^2 \rho_n(r) dr = Z \qquad (8)$$

and f_0 approaches Z at all small values of sinθ/λ. Thus, the changes in electron density affect the amplitude of scattered x-radiation regardless of the ordering or lack of ordering of the scattering atoms.

A. Calculation of atomic scattering factors for SI

Using the proper charge distribution $\rho = \rho(r)$ of electrons in the atom of Si in eqn.(8), we readily obtain the atomic scattering factors for Si corresponding to(sin θ)/θ, below Table 1.

B. Calculation for scattered atomic scattering factor (Debye approximation)

Here, the equation:

$$f = f_0 \times \exp\left[-\frac{1.15 \times 10^4 T}{A\Theta^2} \left(1 + \frac{x^2}{36} - \frac{x^4}{3600} \right) \left(\frac{\sin\theta}{\lambda} \right)^2 \right] = f_0 \times e^{-M}$$

For Si, Atomic weight A=28.086, Debye characteristic Temperature Θ=645 K, Absolute Temperature T in Kelvin (100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650).

Using the information obtained in the Tables 1-3, we plot the atomic scattering curve, giving (sinθ)/λ in the x-direction and atomic scattering factors f_0 in the y-direction, we obtain the curve:

C. Calculation of atomic scattering factors for Cu

Similarly, using the proper charge distribution $\rho = \rho(r)$ of electrons in the atom of Cu in eqn. (8), we readily obtain the atomic scattering factors for Si corresponding to sinθ/λ, below:

D. Calculation for scattered atomic scattering factor (Debye approximation)

Here, the equation:

$$f = f_0 \times \exp\left[-\frac{1.15 \times 10^4 T}{A\Theta^2} \left(1 + \frac{x^2}{36} - \frac{x^4}{3600} \right) \left(\frac{\sin\theta}{\lambda} \right)^2 \right] = f_0 \times e^{-M}$$

For Cu, Atomic weight A=63.546, Debye characteristic Temperature Θ=343.5 K, Absolute Temperature T in K (100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700).

Using the information obtained in the Tables 4-6, we plot the atomic scattering curve, giving (sinθ/λ) in the x-direction and atomic scattering factors f_0 in the y-direction, we obtain the curve.

E. Calculation of atomic scattering factors for Pt

As above, from eqn. (8), we readily obtain the atomic scattering factors for Pt corresponding to (sinθ)/λ, below:

F. Calculation for scattered atomic scattering factor (Debye approximation)

Here, the equation:

$$f = f_0 \times \exp\left[-\frac{1.15 \times 10^4 T}{A\Theta^2} \left(1 + \frac{x^2}{36} - \frac{x^4}{3600} \right) \left(\frac{\sin\theta}{\lambda} \right)^2 \right] = f_0 \times e^{-M}$$

For Pt, Atomic weight A=195.08, Debye characteristic Temperature Θ=240 K, Absolute Temperature T in Kelvin (100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700).

(sinθ)/λ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
Si (f_0)	14	11.35	9.4	8.2	7.15	6.1	5.1	4.2	3.4	2.95	2.6	2.3

Table 1: General Atomic Scattering Factors for Si.

exp(-M)	1.0	0.9979	0.9901	0.9744	0.9484	0.9103	0.8592	0.7952	0.7195	0.6345	0.5438	0.4516
$f = f_0 \times e^{-M}$	14	11.33	9.31	7.99	6.78	5.55	4.38	3.34	2.45	1.87	1.41	1.03

Table 2: When the Debye Approximation temperature factor is considered as (e^{-M})

exp(-M)	1.00	0.9958	0.9804	0.9494	0.8994	0.8287	0.7383	0.6324	0.5176	0.4025	0.2957	0.2039
$f = f_0 \times e^{-2M}$	14	11.30	9.22	7.79	6.43	5.06	3.77	2.66	1.76	1.19	0.77	0.47

Table 3: Debye approximation temperature factor is considered as (e^{-2M}).

Using the information obtained in the Tables 7-9, we plot the atomic scattering curve for Pt, giving $(\sin\theta)/\lambda$ in the x-direction and atomic scattering factors f_0 in the y-direction, we obtain the curve:

G. Calculation of atomic scattering factors for C

Similarly, in eqn. (8), we readily obtain the atomic scattering factors for C corresponding to $(\sin\theta)/\lambda$, below:

H. Calculation for scattered atomic scattering factor (Debye approximation)

Here, the equation:

$$ f = f_0 \times \exp\left[-\frac{1.15 \times 10^4 T}{A\Theta^2}\left(1 + \frac{x^2}{36} - \frac{x^4}{3600}\right)\left(\frac{\sin\theta}{\lambda}\right)^2\right] = f_0 \times e^{-M} $$

For C, Atomic weight A=12.011, Debye characteristic Temperature Θ=2230 K, Absolute Temperature T in Kelvin (100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650).

Using the information obtained in the Tables 10-12 we plot the atomic scattering curve for C, giving $(\sin\theta)/\lambda$ in the x-direction and atomic scattering factors f_0 in the y-direction, we obtain the curve

Results and Discussions

Atomic scattering curve decreases with temperature factor. We have calculated the effect of temperature of the atomic scattering curve of the elements Si, Cu, Pt and C. for the calculation, firstly we have considered the general scattering and then considered the temperature factors (e^{-M}) and (e^{-2M}) and obtain the Figures 1-4, using Debye approximation where Debye temperature factor
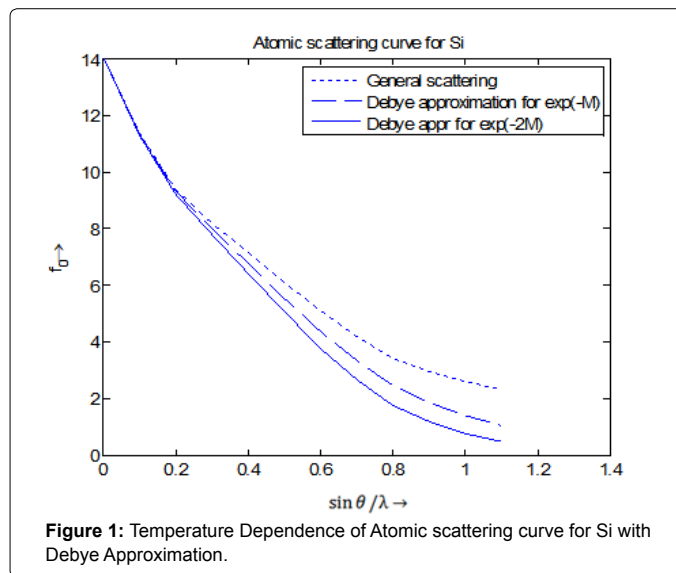

Figure 1: Temperature Dependence of Atomic scattering curve for Si with Debye Approximation.

Sinθ/λ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Cu (f_0)	29	25.9	21.6	17.9	15.2	13.3	11.7	10.2	9.1	8.1	7.3	6.6	6.0

Table 4: Atomic scattering for Cu.

exp(-M)	1.0000	0.9974	0.9868	0.9644	0.9266	0.8713	0.7982	0.7092	0.6082	0.5012	0.3951	0.2965	0.2109
$f=f_0 \times e^{-M}$	29	25.83	21.31	17.26	14.08	11.58	9.34	7.23	5.53	4.05	2.88	1.96	1.27

Table 5: Debye approximation temperature factor is e^{-M}.

exp(-2M)	1.000	0.9948	0.9739	0.9300	0.8585	0.7592	0.6372	0.5029	0.3699	0.2512	0.1561	0.0879	0.0445
$f=f_0 \times e^{-2M}$	29	25.77	21.04	16.65	13.05	10.10	7.46	5.13	3.37	2.03	1.14	0.58	0.27

Table 6: Debye approximation temperature factor is e^{-2M}.

Sinθ/λ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Pt (f_0)	78	72.6	64.0	56.2	48.9	43.1	39.2	35.6	32.5	29.5	27.0	24.7	22.7

Table 7: Atomic scattering for Pt.

exp(-M)	1.0000	0.9984	0.9915	0.9767	0.9512	0.9133	0.8617	0.7966	0.7192	0.6323	0.5397	0.4458	0.3552
$f=f_0 \times$ exp(-M)	78	72.48	63.46	54.89	46.51	39.36	33.79	28.36	23.37	18.65	14.57	11.01	8.06

Table 8: Debye approximation temperature factor is considered as (e^{-M}).

exp(-2M)	1.0000	0.9967	0.9831	0.9539	0.9049	0.8341	0.7425	0.6345	0.5173	0.3998	0.2912	0.1987	0.1262
$f=f_0 \times e^{-2M}$	78	72.36	62.92	53.61	44.25	35.95	29.11	22.59	16.81	11.79	7.86	4.91	2.86

Table 9: Debye approximation temperature factor is considered as (e^{-2M}).

Sinθ/λ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
C (f_0)	6	4.6	3.0	2.2	1.9	1.7	1.6	1.4	1.3	1.16	1.0	0.9	22.7

Table 10: Atomic scattering for C.

exp(-M)	1.0000	1.0019	0.9998	0.9937	0.9845	0.9723	0.9567	0.9377	0.9150	0.8882	0.8575	0.8227	0.3552
$f=f_0 \times$ exp(-M)	6	4.61	3.0	2.19	1.87	1.65	1.53	1.31	1.19	1.03	0.86	0.74	8.06

Table 11: Debye Approximation temperature factor is considered as (e^{-M}).

exp(-2M)	1.0000	1.0015	0.9995	0.9875	0.9693	0.9453	0.9154	0.8793	0.8371	0.7890	0.7353	0.6769	0.1262
$f=f_0 \times e^{-2M}$	6	4.60	2.99	2.17	1.84	1.61	1.46	1.23	1.09	0.92	0.74	0.61	2.86

Table 12: Debye approximation temperature factor is considered as (e^{-2M}).

Figure 2: Temperature Dependence of Atomic scattering curve for Cu with Debye Approximation.

Figure 3: Temperature dependence of atomic scattering curve for Pt with Debye approximation.

Figure 4: Temperature dependence of atomic scattering curve for C with Debye approximation.
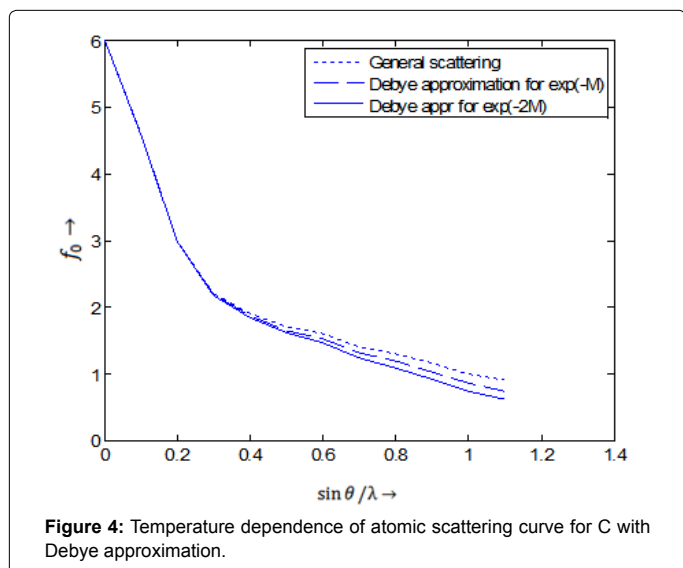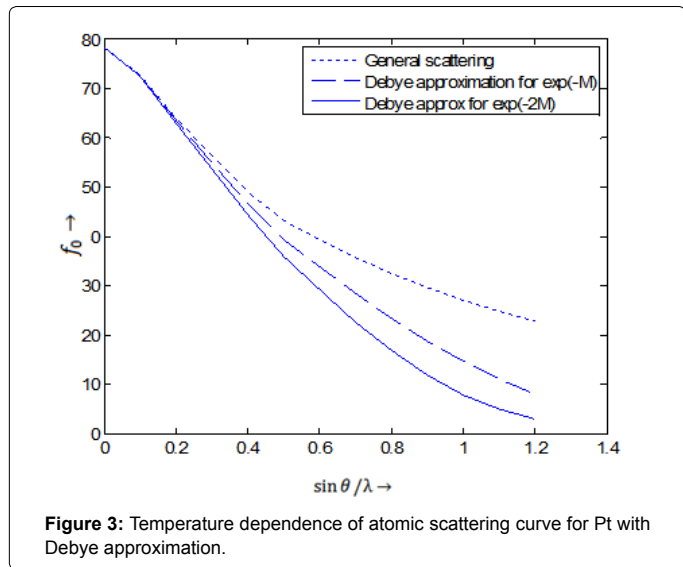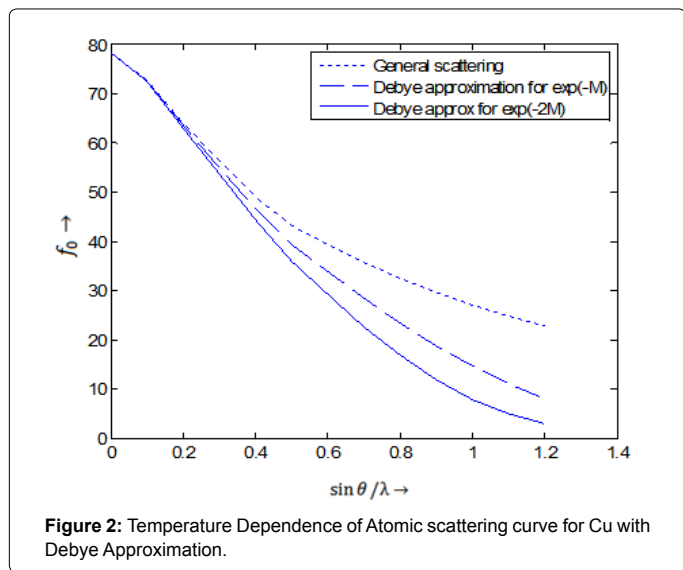
$$\exp\left[-\frac{1.15\times10^4 T}{A\Theta^2}\left(1+\frac{x^2}{36}-\frac{x^4}{3600}\right)\left(\frac{\sin\theta}{\lambda}\right)^2\right]$$ and observe that the atomic scattering curve decreases a little bit compared with general scattering curve. So, atomic scattering curve is affected by the temperature factor.

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