# Appendix A

# Width of (*hkl*) Diffraction Peak for a Hexagonal Structure Particle

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The reciprocal lattice was introduced by P. Ewald in 1921. Let *a*, *b*, *c* be the elementary translations of a space lattice. The reciprocal lattice is defined by translations $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$. For a hexagonal structure, the unit vector of the reciprocal lattice in Cartesian system can be obtained via transformation from trigonal to orthonormal axes:

$$\begin{cases} \dfrac{\vec{a}^*}{\left(\dfrac{4\pi}{\sqrt{3}a}\right)} = \hat{i} \\ \dfrac{\vec{b}^*}{\left(\dfrac{4\pi}{\sqrt{3}a}\right)} = \dfrac{1}{2}\hat{i} + \dfrac{\sqrt{3}}{2}\hat{j}, \\ \dfrac{\vec{c}^*}{\left(\dfrac{2\pi}{c}\right)} = \hat{k} \end{cases} \tag{A.1}$$

A reciprocal lattice vector is

$$\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*, \tag{A.2}$$

where *h*, *k*, *l* are integers.

An ellipsoid particle with the length of short axe $L_a$ and the length of long axe $L_c$ has the ellipsoid equation in reciprocal space:

$$\frac{x^2+y^2}{\left(\frac{\pi}{L_a}\right)^2}+\frac{z^2}{\left(\frac{\pi}{L_c}\right)^2}=1. \tag{A.3}$$

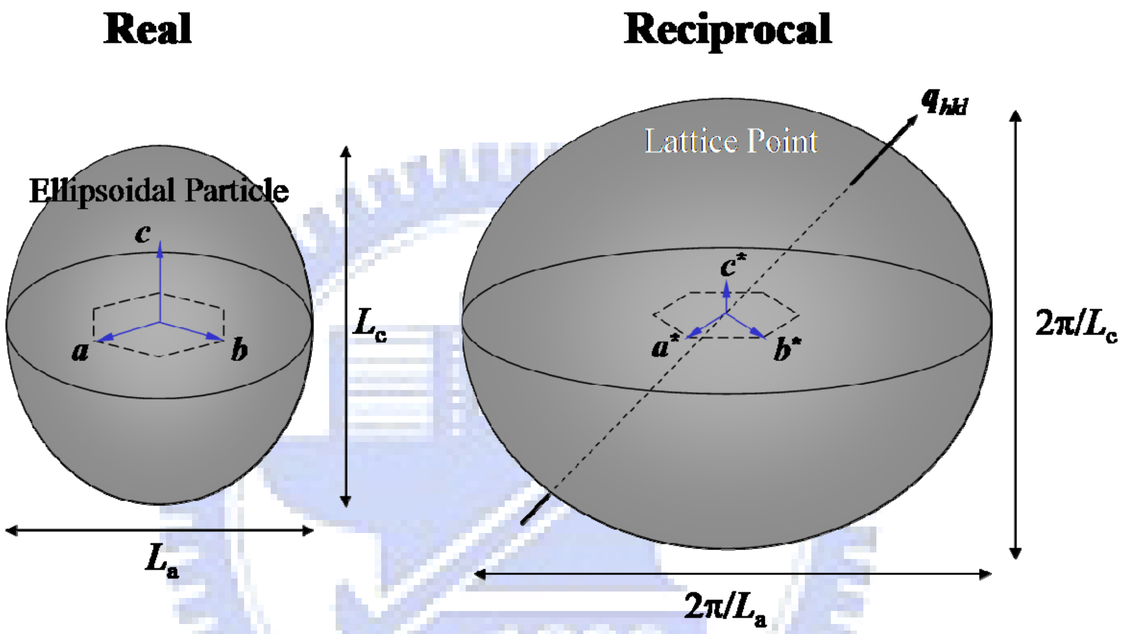


**FIG. A.1:** An ellipsoidal particle represents in real and reciprocal space.

For any (*hkl*), the reciprocal vector is $\vec{q}=(ha^*t, k\vec{b}^*t, l\vec{c}^*t)$, in which $t$ is a constant. In order to obtain the points of the reciprocal vector intersecting the ellipsoid surface, we should solve $t$. Substituting $\vec{q}$ into (A.3), we have

$$t=\pm\frac{1}{4\sqrt{\frac{(h^2+hk+k^2)}{3a^2}L_a^2+\frac{l^2}{4c^2}L_c^2}}. \tag{A.4}$$

The distance between these two intersection points, which is the width of the diffraction peak referring to the domain size, is

$$W_{hkl} = 2\sqrt{(h\vec{a}^{*}t)^2 + (k\vec{b}^{*}t)^2 + (l\vec{c}^{*}t)^2}$$

$$= 2\pi\sqrt{\frac{\dfrac{h^2+hk+k^2}{3a^2}+\dfrac{l^2}{4c^2}}{\dfrac{h^2+hk+k^2}{3a^2}L_a^2+\dfrac{l^2}{4c^2}L_c^2}}\ . \qquad \text{(A.5)}$$

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# Appendix B

# Electrostatic Calculation for the Ionization Energy of a Dielectric Particle

In spherical coordinates ($r$, $\theta$, $\phi$), the Laplace equation can be written in the form:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\Phi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=0, \quad \text{(B.1)}$$

in which $\Phi$ is the potential. For the form of the Laplace equation in spherical coordinates with an azimuthal symmetry, the general solution is:

$$\Phi(r,\theta)=\sum_{l=0}^{\infty}\left[A_k r^k+B_k r^{-(k+1)}\right]P_k(\cos\theta), \quad \text{(B.2)}$$

where $A_k$ and $B_k$ can be determined from the boundary conditions and $P_k$ is a Legendre polynomial. Consider a charge $q$ at $\vec{r}_q$ inside a dielectric sphere, the potential at $\vec{r}$ due to a point charge can be expressed as:

$$\frac{1}{\left|\vec{r}-\vec{r}_q\right|}=\sum_{l=0}^{\infty}\frac{r_<^k}{r_>^{k+1}}P_k(\cos\gamma), \quad \text{(B.3)}$$

where $r_<$ ($r_>$) is the smaller (larger) of $|\vec{r}\,|$ and $|\vec{r}_q|$, and $\gamma$ is the angle between $\vec{r}$ and $\vec{r}_q$.

Suppose $\vec{r}_q$ on the z axis, as shown in Fig. B.1, the potential inside and outside the dielectric sphere can be written as:

$$\Phi_{in}(r,\theta)=\sum_{l=0}^{\infty}\left(A_k r^k+\frac{q}{\varepsilon}\frac{r_<^k}{r_>^{k+1}}\right)P_k(\cos\theta)\,, \tag{B.4}$$

$$\Phi_{out}(r,\theta)=\sum_{l=0}^{\infty}\left(C_k\frac{1}{r^{k+1}}\right)P_k(\cos\theta)\,. \tag{B.5}$$

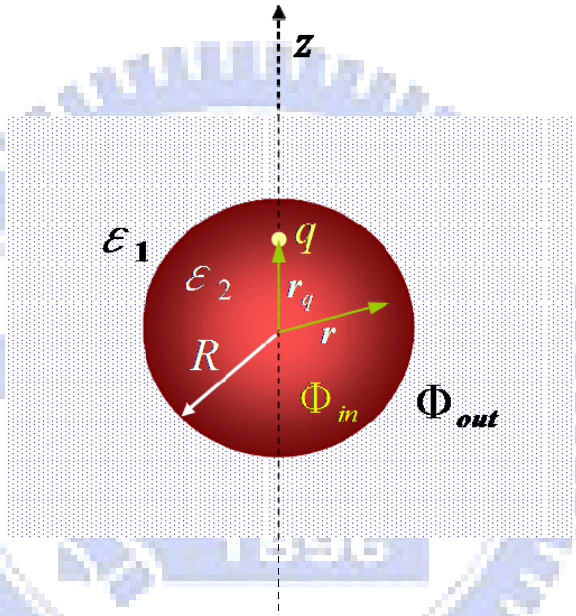


**FIG. B.1:** The representation of a charge $q$ inside a dielectric sphere embedded in a medium.

By solving the electrostatic boundary-value problem according to Maxwell's equation, we can obtain that

$$A_k=\frac{qr_q^k}{R^{2k+1}}\frac{(k+1)(1-\frac{\varepsilon_1}{\varepsilon_2})}{\varepsilon_1(k+1)+\varepsilon_2 k}\,, \tag{B.6}$$

$$C_k=qr_q^k\frac{2k+1}{\varepsilon_1(k+1)+\varepsilon_2 k}\,, \tag{B.7}$$

in which $R$ is the radius of the dielectric sphere and $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of the surrounding medium and the sphere, respectively. Thus,

$$\Phi_{in}(r,\theta)=\sum_{l=0}^{\infty}\frac{qr_q^k}{R^{2k+1}}(1-\frac{\varepsilon_1}{\varepsilon_2})\frac{(k+1)}{\varepsilon_1(k+1)+\varepsilon_2 k}r^k P_k(\cos\theta)+\frac{q}{\varepsilon_2}\frac{1}{\left|\vec{r}-\vec{r}_q\right|}, \tag{B.8}$$

$$\Phi_{out}(r,\theta)=\sum_{l=0}^{\infty}qr_q^k\frac{2k+1}{\varepsilon_1(k+1)+\varepsilon_2 k}\frac{1}{r^{k+1}}P_k(\cos\theta). \tag{B.9}$$

If the dielectric sphere is embedded in vacuum ($\varepsilon_1=1$), Eqs. (B.8) and (B.9) will correspond to Eqs. (4.1) and (4.2), respectively.

Consider now the photoionization process: the photoelectron and the photohole are created by the absorption of the incident-photon energy, then the photoelectron is emitted from the matter with a photohole. If the photoelectron travels to infinity, there is no interaction between the photoelectron and the remaining system. The energy of the final state is the interaction energy between the photohole ($q$=+$e$) and its image.

$$\begin{aligned}E_f(r_h)&=\frac{1}{2}e\Phi_{in}\\&=\frac{e^2}{2R}\left(\frac{\varepsilon-1}{\varepsilon}\right)\sum_{k=0}^{\infty}\frac{k+1}{k(\varepsilon+1)+1}\left(\frac{r_h}{R}\right)^{2k}+\frac{e^2}{2\varepsilon}\frac{1}{\delta},\end{aligned} \tag{B.10}$$

where $\varepsilon$ is the dielectric constant of the sphere, $r_h$ is the position of the photohole residing in the dielectric sphere, and $\delta$ is an atomic dimension in order to prevent the problem of infinite self-energies. After rearrangement to facilitate numerical computation, the final-state energy can be rewritten as

$$E_f(r_h)=\frac{e^2}{2R}\left(\frac{\varepsilon-1}{\varepsilon}\right)+\frac{e^2}{2R\varepsilon}\left(\frac{\varepsilon-1}{\varepsilon+1}\right)\frac{r_h^{\,2}}{R^2-r_h^{\,2}}+\frac{e^2}{2R}\left(\frac{\varepsilon-1}{\varepsilon+1}\right)\sum_{k=1}^{\infty}\frac{1}{k(\varepsilon+1)+1}\left(\frac{r_h}{R}\right)^{2k}+\frac{e^2}{2\varepsilon}\frac{1}{\delta}, \tag{B.11}$$

in which the factor one half denotes the self energy or the integration of $q$ from 0 to $e$. The last term was considered in the literature by Brus [Ref. 18 in Chap IV] but is dropped in our discussion in Chapter IV because it is independent of the spherical radius and is cancelled with respect to bulk [see Eq. (4.4)]. In metal case, the dielectric constant $\varepsilon$ goes to infinity, the last term vanishes. This reflects perfect screening.

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