Energy band of photons and low-energy photon diffraction

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For a model system composed of identical dielectric spheres ordered in a three-dimensional lattice, the secular equation of the energy band of photons is derived and the diffraction of uv or visible light is formulated. The model simulates void lattices in irradiated metals or ordered lattices in polystyrene latexes, in which the large lattice constants and hence the low frequency of the diffracted electromagnetic waves give rise to a Bragg reflection orders of magnitude stronger than that involved in the x-ray diffraction. The present formulation is an extension of the theory of Mie and Debye. Also, it is an extension of the Korringa-Kohn-Rostoker formalism for energy-band calculations to Maxwell's equations or to the vector Helmholtz equation. Although the present paper is restricted to developing a formulation, some characteristic aspects anticipated in low-energy photon diffraction are discussed in relation to low-energy electron diffraction.

I. INTRODUCTION

In the diffraction of x rays in a solid, a self-consistent (SC) wave field is established as a result of multiple scattering of radiation. The dynamical theory of x-ray diffraction is built upon this SC wave field,[1] and it explains successfully many interesting phenomena such as the abnormal absorption and the pendulum solution that the geomentrical theory of diffraction fails to explain.

Since the energy of the x rays is many orders of magnitude larger than the characteristic excitation energies of a solid, the dielectric constant involved in the dynamical theory is almost unity. It is in fact quite remarkable that its deviation from unity, usually of the order of 10^{-6}, is the origin of the multiple scattering that causes photon Bragg reflection and gives rise to photon energy-band structure similar to that of Bragg-reflected electrons. Because of the smallness of this quantity, however, the ratio of the magnitudes of the band gaps to the x-ray energy, the quantity that provides a measure of the dynamical effect, is very small, being again of the order of 10^{-6}. In terms of band theory, therefore, the electromagnetic field associated with x-rays is "nearly free" in any ordinary solid-state system.

Recently a number of interesting systems that are characterized by large lattice constants have been found and investigated both theoretically and experimentally. Among these are void lattices in ion- or neutron-bombarded metals[2-4] and ordered lattices in aqueous polystyrene suspensions.[5-7] In these systems cavities (in void lattices) or spheres (in latex lattices) with a finite and almost constant radius, are ordered in three-dimensional regular lattices. Their experimental lattice constants are usually several hundreds in void lattices and a few thousands in latex lattices in angstrom units. The radius of the cavities or spheres is about $\frac{1}{3}$–$\frac{1}{5}$ the lattice constant.

These systems therefore provide a typical model system that enables visible light or uv light to be diffracted. In fact, the iridescence observed in latex lattices is attributed to the Bragg reflection of visible light. Also, for structural analyses, diffraction experiments using optical light beams have been already performed.[8-11]

The diffraction of visible or uv light is qualitatively different from that of x rays: the energy of the photons being much smaller than that of the x rays, the dielectric functions present very large spatial variations. For void lattices, for example, the optical properties of the metallic part may be described by the metallic dielectric constant, $\epsilon(\omega)=1-(\omega_p/\omega)^2$, whereas the dielectric constant of the interiors of the cavities is almost unity.[12] In consequence, we have $\epsilon(\omega)=0.91$ for uv light of 50 eV in a void lattice in an aluminum matrix. Therefore the dielectric function varies periodically between the two values 0.91 and 1.0, i.e., with an amplitude 10^5 times as large as that for x rays. Similarly, across the surface of a suspended sphere of a latex lattice the dielectric constant changes from 1.7 (water) to 2.6 (polystyrene) for visible light of 5000 Å wavelength.[13] Clearly, the electromagnetic fields involved in the diffraction are by no means nearly free.

The purpose of the present paper is to develop a dynamical theory of the diffraction of visible or uv light. As in ordinary diffraction theories, our task is to concentrate mainly on the SC electromagnetic field, the strong-scattering effect being taken into account. The theory is developed for a model dielectric system composed of identical spheres ordered in a three-dimensional lattice. This model simulates void and latex lattices, but extension to other geometries or systems, such

as an array of bundles of one-dimensional polymers of $(SN)_x$,[14,15] a regular array of macroscopic substances in some biological systems,[16] or arrayed spheres of silica in gem opals,[17] will be straightforward.

If we neglect all the spheres but one, the present problem reduces to the one solved rigorously by Mie[18] and Debye.[19] As is required by Maxwell's equations, the electromagnetic fields satisfy tangential-continuity conditions on the sphere surface, across which the optical properties change abruptly. In their original problem as well as in the present case, it is clear that any linear combination of a few plane waves by no means guarantees these boundary conditions.

In this connection let us note the inadequacy of the plane-wave expansion already familiar in low-energy electron diffraction (LEED).[20,21] As a matter of fact, atomic-scattering cross sections involved in LEED are so large that a simple plane-wave expansion is not at all adequate. Note furthermore that the geometry of the present problem is quite similar to that of the arrayed muffin-tin spheres used in band calculations.[22]

From these considerations we readily recognize that the Korringa-Kohn-Rostoker (KKR) method in band theory[22,23] and the formulation of LEED by Boudreaux and Heine[24] based on band structures serve as useful guides in the present problem. Because of the close relationship to LEED, we shall designate the diffraction treated here as low-energy photon diffraction (LEPD).

The difference between LEED and LEPD lies in the equations which govern the respective wave fields: the (scalar) Schrödinger equation in the former and the vector Helmholtz equation in the latter. Naturally, the vector fields involved in LEPD cause some complications, as is seen in the Mie and Debye formulations.[25] The general mathematical framework, however, is quite the same as the KKR formalism.

The present paper is divided roughly into two parts. The first and main part of the paper (Secs. II–IV) treats the SC electromagnetic field without considering an incident electromagnetic wave. The rest of the paper is concerned with how to obtain diffracted intensities in the present context of LEPD theory. The absorption of photons is taken into account in terms of complex dielectric functions, like the complex pseudopotentials usually employed in LEED theories.[20,21]

II. PRELIMINARIES

In this section, the derivation of the SC equation for the photon energy-band structures is presented and some useful properties of the vector Helmholtz equation are briefly reviewed. The usual time factor $e^{i\omega t}$ of the fields is dropped throughout the paper.

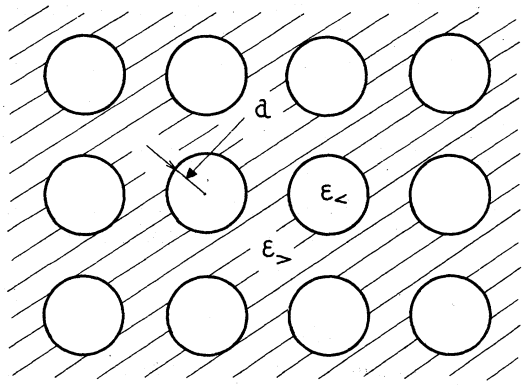

FIG. 1. Regular lattice of spheres. The radius of the sphere is a. The dielectric constant of the interior of the sphere is $\epsilon_<$ and that of the exterior is $\epsilon_>$.

We consider the system shown in Fig. 1: spheres with a constant radius a are arrayed in a three-dimensional lattice. The symmetry of the lattice is arbitrary except that the unit cell contains only one sphere (although this restriction is easily relaxed[26]). The exterior and interior regions are specified by the two dielectric constants $\epsilon_>$ and $\epsilon_<$. They are assumed to be r independent. Otherwise their forms are completely arbitrary: they may be real or complex and may depend on the frequency or on the size of the sphere.

The quantities that completely specify the present problem are the two wave numbers defined by

$$q_>^2=(\omega/c)^2\epsilon_>, \quad q_<^2=(\omega/c)^2\epsilon_< . \tag{2.1}$$

For simplicity we shall consider the spheres arrayed in free space ($\epsilon_>=1$), and in place of Eq. (2.1) we define

$$q_0^2=(\omega/c)^2, \quad q^2=(\omega/c)^2\epsilon_< . \tag{2.2}$$

We obtain result for the general case of Fig. 1 from this simplified case upon making the following substitution in the final results:

$$q_0 \to q_>, \quad q \to q_< . \tag{2.3}$$

In the Lorentz gauge the electric field is obtained from the vector potential,

$$\vec{E}(\vec{r})=iq_0[1+(1/q_0^2)\vec{\nabla}\vec{\nabla}\cdot]\vec{A}(\vec{r}), \tag{2.4}$$

where $\vec{\nabla}$ is the gradient operator. The vector potential is determined by the current:

$$(\Delta+q_0^2)\vec{A}(\vec{r})=4\pi iq_0\vec{P}(\vec{r}) . \tag{2.5}$$

The polarization $\vec{P}(\vec{r})$ is in turn connected to $\vec{E}(\vec{r})$ as follows:

$$\vec{P}(\vec{r})=(1/4\pi)(\epsilon_<-1)\vec{E}(\vec{r})\equiv\chi_<\vec{E}(\vec{r}) . \tag{2.6}$$

Note that $\vec{P}(\vec{r})$ is nonzero inside the arrayed

spheres. Equations (2.4)–(2.6) form our starting closed set.

Since the spheres are arrayed periodically, Eq. (2.5) reduces to

$$\vec{A}_{\vec{k}}(\vec{r}) = 4\pi i q_0 \chi_< \int_{r'<a} G_{\vec{k}}(\vec{r},\vec{r}')E^<_{\vec{k}}(\vec{r}')d\vec{r}', \tag{2.7}$$

where, following KKR, the Green's function which satisfies the Bloch theorem is defined as[22,23]

$$G_{\vec{k}}(\vec{r},\vec{r}') = \frac{1}{v_0}\sum_{\vec{h}} \frac{e^{i(\vec{k}+\vec{h})\cdot(\vec{r}-\vec{r}')}}{q_0^2 - (\vec{k}+\vec{h})^2} \tag{2.8}$$

with v_0 the volume of the unit cell and $\vec{h}$ the reciprocal-lattice vector. The wave vector $\vec{k}$ within the first Brillouin zone specifies the eigenstates. The integral in Eq. (2.7) is within a *single* sphere centered at the origin [this sphere is called the r-sphere (reference sphere)]. To emphasize the inside field involved in Eq. (2.7), $\vec{E}^<_{\vec{k}}(\vec{r})$ is given the superscript <. Similarly let us use the superscript > to denote the field of the exterior region.

Since

$$(\Delta + q^2)\vec{E}^<_{\vec{k}}(\vec{r}) = 0, \quad r < a, \tag{2.9}$$

or [with $q^2 = q_0^2(1+4\pi\chi_<)$]

$$4\pi\chi_<\vec{E}^<_{\vec{k}}(\vec{r}) = -(1/q_0^2)(\Delta + q_0^2)\vec{E}^<_{\vec{k}}(\vec{r}), \tag{2.10}$$

the volume integral in Eq. (2.7) reduces to a surface integral. The result is

$$\begin{aligned} \vec{A}^>_{\vec{k}}(\vec{r}) &= (-i/q_0)\vec{I}^>_{\vec{k}}(\vec{r}), \quad r > a, \\ \vec{A}^<_{\vec{k}}(\vec{r}) &= (-i/q_0)[\vec{E}^<_{\vec{k}}(\vec{r}) + \vec{I}^<_{\vec{k}}(\vec{r})], \quad r < a. \end{aligned} \tag{2.11}$$

Here

$$\vec{I}^{>(<)}_{\vec{k}}(\vec{r}) = \int_{r'=a^-} d\vec{S}'\cdot\{G^{>(<)}_{\vec{k}}(\vec{r},\vec{r}')\vec{\nabla}'\vec{E}^<_{\vec{k}}(\vec{r}') - [\vec{\nabla}'G^{>(<)}_{\vec{k}}(\vec{r},\vec{r}')]\vec{E}^<_{\vec{k}}(\vec{r}')\} \tag{2.12}$$

defines the surface integral just inside the surface $r' = a$. The scalar product in Eq. (2.12) is taken between the surface normal $\vec{S}'$ and $\vec{\nabla}'$. The x component of the vector $\vec{I}^>_{\vec{k}}(\vec{r})$, for example, is thus related to the x component of $\vec{E}^<_{\vec{k}}(\vec{r})$. Note that it is $\vec{E}^<_{\vec{k}}(\vec{r})$ that determines *both* $\vec{I}^>_{\vec{k}}(\vec{r})$ and $\vec{I}^<_{\vec{k}}(\vec{r})$. The Green's functions $G^>_{\vec{k}}$ and $G^<_{\vec{k}}$ involved above are defined as

$$G^{>(<)}_{\vec{k}}(\vec{r},\vec{r}') = [G_{\vec{k}}(\vec{r},\vec{r}')]_{r>r'\ (r<r')}. \tag{2.13}$$

Combining Eq. (2.11) with Eq. (2.4), we obtain

$$\vec{E}^>_{\vec{k}}(\vec{r}) = [1 + (1/q_0^2)\vec{\nabla}\vec{\nabla}\cdot]\vec{I}^>_{\vec{k}}(\vec{r}), \quad r > a, \tag{2.14a}$$

$$[1 + (1/q_0^2)\vec{\nabla}\vec{\nabla}\cdot]\vec{I}^<_{\vec{k}}(\vec{r}) = 0, \quad r < a. \tag{2.14b}$$

These equations should be established irrespective of r. Eq. (2.14b) is the SC equation to be satisfied by the inside field $\vec{E}^<_{\vec{k}}(\vec{r})$, and determines the photon band structure. The outside field is derived from Eq. (2.14a) in terms of the SC inside field.

To calculate Eq. (2.14b) let us expand $G^<_{\vec{k}}(\vec{r},\vec{r}')$ in terms of spherical waves. This expansion is given by [combined with that for $G^>_{\vec{k}}(\vec{r},\vec{r}')$][22,23]

$$\left.\begin{matrix} G^>_{\vec{k}}(\vec{r},\vec{r}') \\ G^<_{\vec{k}}(\vec{r},\vec{r}') \end{matrix}\right\} = -iq_0\left(\sum_L Y_L(\vec{r})Y_L^*(\vec{r}')\begin{cases} h_l(q_0r)j_l(q_0r') \\ j_l(q_0r)h_l(q_0r') \end{cases} + \sum_{LL'} j_l(q_0r)Y_L(\vec{r})\Gamma_{LL'}(\vec{k})j_{l'}(q_0r')Y_{L'}^*(\vec{r}')\right), \tag{2.15}$$

where L is an abbreviation for (l,m), $Y_L(\vec{r})$ is the normalized spherical harmonics,[27] and $j_l(q_0r)$ [$h_l(q_0r)$] is the spherical Bessel function (Hankel function of the first kind).[28] Since only the Hankel function of the first kind is involved, the usual superscript 1 is dropped throughout the paper. The $\vec{k}$ dependence of the quantity $\Gamma_{LL'}(\vec{k})$ is the sole origin of the $\vec{k}$ dependence of the band structure.

As a trial electric field we take the linear combination of the solutions of Eq. (2.9) (for details on the vector Helmholtz equation, see Ref. 29):

$$\vec{E}^<_{\vec{k}}(\vec{r}) = \sum_{l=1}\sum_{m=-l}^{l}[{}^M\vec{E}^<_L(\vec{r})\alpha^M_L(\vec{k}) + {}^N\vec{E}^<_L(\vec{r})\alpha^N_L(\vec{k})], \tag{2.16}$$

wherein the spherical polar components (r,θ,ϕ) the M- and N-type fields are defined by

$${}^M\vec{E}^<_L(\vec{r}) = \left(0, -j_l(qr)\frac{1}{\sin\theta}\frac{\partial Y_L(\vec{r})}{\partial\phi}, j_l(qr)\frac{\partial Y_L(\vec{r})}{\partial\theta}\right), \tag{2.17a}$$

$${}^N\vec{E}^<_L(\vec{r}) = -\left(l(l+1)\frac{j_l(qr)}{qr}Y_L(\vec{r}), \frac{[qrj_l(qr)]'}{qr}\frac{\partial Y_L(\vec{r})}{\partial\theta}, \frac{[qrj_l(qr)]'}{qr\sin\theta}\frac{\partial Y_L(\vec{r})}{\partial\phi}\right), \tag{2.17b}$$

the prime indicating a derivative with respect to qr. The form (2.16) is dictated by two requirements: $\vec{E}^<_{\vec{k}}(\vec{r})$ should be regular at $\vec{r}=0$ and should be divergenceless (solenoidal), since $\mathrm{div}\vec{D}^<_{\vec{k}}(\vec{r}) = 0$ leads to $\mathrm{div}\vec{E}^<_{\vec{k}}(\vec{r}) = 0$ for the r-independent dielec-

tric constant. The unknown coefficients $\alpha_L^M(\vec{k})$ and $\alpha_L^N(\vec{k})$ in Eq. (2.16) are determined so that they may satisfy Eq. (2.14b). Thus they are $\vec{k}$ dependent. Note that Eq. (2.9) does not yield a divergenceless field for $l=0$. Of course, this does not imply that $Y_{0,0}(\vec{r})$ is not at all necessary for expression of the fields (see the Cartesian representations to follow).

The M- and N-type fields defined above have orthogonal properties. Define the inner product between the two vector fields by

$$(\vec{A}(\vec{r}),\vec{B}(\vec{r}))=\int d\Omega\,\vec{A}^*(\vec{r})\cdot\vec{B}(\vec{r}), \tag{2.18}$$

where the integral is over the solid angle, with r held fixed. By definition, it is r dependent. It then holds that ($\beta,\beta'=M$ or N)

$$({}^{\beta}\vec{E}_L^{<}(\vec{r}),{}^{\beta'}\vec{E}_{L'}^{<}(\vec{r}))=\delta_{\beta\beta'}\delta_{LL'}\,{}^{\beta}n_L^{<}(r), \tag{2.19}$$

where $\delta_{\beta\beta'}$ and $\delta_{LL'}$ are the Kronecker symbols and

$$\begin{aligned}{}^{M}n_L^{<}(r)&=l(l+1)\left|j_l(qr)\right|^2,\\ {}^{N}n_L^{<}(r)&=[l(l+1)/(2l+1)]\left[(l+1)\left|j_{l-1}(qr)\right|^2\right.\\ &\qquad\left.+\,l\left|j_{l+1}(qr)\right|^2\right]\end{aligned} \tag{2.20}$$

are the normalizing constants.

To calculate the vector $\vec{I}_{\vec{k}}^{<}(\vec{r})$ defined by Eq. (2.12) we need the Cartesian components of ${}^{\beta}\vec{E}_L^{<}(\vec{r})$. After a lengthy calculation using the recurrence formulas for $P_l^m(\cos\theta)$,[30] Eq. (2.17a) yields

$$\left.\begin{matrix}{}^{M}E_L^{<}(\vec{r})_x\\ {}^{M}E_L^{<}(\vec{r})_y\\ {}^{M}E_L^{<}(\vec{r})_z\end{matrix}\right\}=\left.\begin{matrix}-iA_{0-}(l,m)Y_{l,m-1}-iA_{0+}(l,m)Y_{l,m+1}\\ A_{0-}(l,m)Y_{l,m-1}-A_{0+}(l,m)Y_{l,m+1}\\ imY_{l,m}\end{matrix}\right\}j_l(qr), \tag{2.21}$$

where we have dropped the $(\vec{r})$ in $Y_L(\vec{r})$. The coefficients A_{0-} and A_{0+} are given by

$$A_{0\mp}(l,m)=\tfrac{1}{2}[l\pm m)(l\mp m+1)]^{1/2}. \tag{2.22}$$

The coefficients of $Y_{l,-l-1}$ or $Y_{l,l+1}$ in Eq. (2.21) should be zero.

From Eq. (2.17b) we have

$$\begin{aligned}{}^{N}E_L^{<}(\vec{r})_x&=(l+1)(-B_{--}Y_{l-1,m-1}+B_{-+}Y_{l-1,m+1})j_{l-1}(qr)+l(B_{+-}Y_{l+1,m-1}-B_{++}Y_{l+1,m+1})j_{l+1}(qr),\\ {}^{N}E_L^{<}(\vec{r})_y&=-i(l+1)(B_{--}Y_{l-1,m-1}+B_{-+}Y_{l-1,m+1})j_{l-1}(qr)+il(B_{+-}Y_{l+1,m-1}+B_{++}Y_{l+1,m+1})j_{l+1}(qr),\\ {}^{N}E_L^{<}(\vec{r})_z&=-(l+1)C_{-0}Y_{l-1,m}j_{l-1}(qr)-lC_{+0}Y_{l+1,m}j_{l+1}(qr),\end{aligned} \tag{2.23}$$

where the B_{--}'s are abbreviations for $B_{--}(l,m)$'s. They are defined by

$$\begin{aligned}B_{-\mp}(l,m)&=\frac{1}{2}\left[\frac{(l\pm m-1)(l\pm m)}{(2l-1)(2l+1)}\right]^{1/2},\\ B_{+\mp}(l,m)&=\frac{1}{2}\left[\frac{(l\mp m+1)(l\mp m+2)}{(2l+1)(2l+3)}\right]^{1/2},\end{aligned} \tag{2.24}$$

and

$$\begin{aligned}C_{-0}(l,m)&=\left[\frac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2},\\ C_{+0}(l,m)&=\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2}.\end{aligned} \tag{2.25}$$

The meanings of the subscripts -0, $--$, etc., in Eqs. (2.21) and (2.23) are obvious.

Before embarking on the transformation of the SC equation, let us introduce matrix notation. Let $\underline{Y}(\vec{r})$ and $\underline{\alpha}^{\beta}(\vec{k})$ be *column* vectors defined by

$$\underline{Y}(\vec{r})=(Y_{0,0}(\vec{r}),Y_{1,-1}(\vec{r}),Y_{1,0}(\vec{r}),Y_{1,1}(\vec{r}),\ldots)^t, \tag{2.26a}$$

$$\underline{\alpha}^{\beta}(\vec{k})=(\alpha_{1,-1}^{\beta}(\vec{k}),\alpha_{1,0}^{\beta}(\vec{k}),\alpha_{1,1}^{\beta}(\vec{k}),\ldots)^t, \tag{2.26b}$$

with t denoting a transposed matrix and $\beta=M,N$ as before. Note that $\alpha_{0,0}^{\beta}(\vec{k})$ is missing in column (2.26b). Let us also use the matrices $\underline{j}$, $\underline{h}$, and $\underline{\Gamma}$. Their (L,L') matrix elements are ($l,l'\geq 0$)

$$\begin{aligned}[\underline{j}(q_0r)]_{LL'}&=\delta_{LL'}j_l(q_0r),\\ [\underline{h}(q_0r)]_{LL'}&=\delta_{LL'}h_l(q_0r),\\ [\underline{\Gamma}(\vec{k})]_{LL'}&=\Gamma_{LL'}(\vec{k}).\end{aligned} \tag{2.27}$$

In matrix notation, the Green's function $G_{\vec{k}}^{<}(\vec{r},\vec{r}')$ is expressed as

$$G^<_{\vec{k}}(\vec{r},\vec{r}') = -iq_0[\underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{h}(q_0 r')Y^*(\vec{r}') + \underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{\Gamma}(\vec{k})\underline{j}(q_0 r')\underline{Y}^*(\vec{r}')], \tag{2.28}$$

and the orthonormality relation of the spherical harmonics reduces to

$$\int d\Omega\, \underline{Y}^*(\vec{r})\underline{Y}^t(\vec{r}) = \underline{E}, \tag{2.29}$$

with an $\infty\times\infty$ unit matrix $\underline{E}$.

III. SECULAR EQUATION FOR PHOTON BAND STRUCTURES

Now let us concentrate on the SC condition (2.14b). The suffix $\vec{k}$ is dropped in this section.

Using Eqs. (2.21) and (2.23), we express the Cartesian components of the trial internal field (2.16) as $(i=x,y,z)$

$$E^<(\vec{r})_i = \sum_\beta \underline{Y}^t(\vec{r})\underline{j}(qr)\underline{P}_i^\beta\,\underline{\alpha}^\beta(\vec{k}). \tag{3.1}$$

Here the $\infty\times\infty$ matrices $\underline{P}_i^M$ and $\underline{P}_i^N$ are defined by

$$\begin{aligned}
\underline{P}_x^M &= [-iA_{0-}, -iA_{0+}],\\
\underline{P}_y^M &= [-A_{0-}, A_{0+}],\\
\underline{P}_z^M &= [im],
\end{aligned} \tag{3.2}$$

and

$$\begin{aligned}
\underline{P}_x^N &= [-(l-1)B_{--}, (l-1)B_{-+},\\
&\qquad (l+2)B_{+-}, -(l+2)B_{++}],\\
\underline{P}_y^N &= [i(l-1)B_{--}, i(l-1)B_{-+},\\
&\qquad -i(l+2)B_{+-}, -i(l+2)B_{++}],\\
\underline{P}_z^N &= [-(l-1)C_{-0}, -(l+2)C_{+0}],
\end{aligned} \tag{3.3}$$

where only the nonzero matrix elements within the (l,m)th row are shown. The quantities A_{0-}, B_{--}, etc., are defined in Sec. I [they are abbreviations of $A_{0-}(l,m), B_{--}(l,m)$, etc.]. The subscript $0-$ of A_{0-} indicates here the $(l,m-1)$th component of the row (l,m). Therefore in the (l,m)th row of the matrix $\underline{P}_x^M$ there are two nonzero matrix elements: the element $(l,m;l,m-1)$ given by $-iA_{0-}(l,m)$ and the element $(l,m;l,m+1)$ given by $-iA_{0+}(l,m)$. The other matrices of Eqs. (3.2) and (3.3) read in the same way [$\underline{P}_z^M$ defined by Eq. (3.2) is a diagonal matrix]. Note that, according to the definition [(2.26b)] of $\underline{\alpha}^\beta(\vec{k})$, $\underline{P}_i^\beta$ is not strictly a square matrix [$l\geq 0$ and $l'\geq 1$ in the definition of $(\underline{P}_i^\beta)_{LL'}$].

Substituting Eqs. (2.28) and (3.1) into Eq. (2.12) and noting the identity $\int d\vec{S}\cdot\vec{\nabla}' = a^2\int d\Omega'\partial/\partial r'$, we have

$$\begin{aligned}
I^<(\vec{r})_i &= -iq_0 a^2 \underline{Y}^t(\vec{r})\, j(q_0 r)\\
&\quad\times[\underline{D}^< + \underline{\Gamma}(\vec{k})\underline{D}^>]\sum_\beta \underline{P}_i^\beta\underline{\alpha}^\beta(\vec{k}).
\end{aligned} \tag{3.4}$$

The diagonal matrices $\underline{D}^<$ and $\underline{D}^>$ are given by $(l,l'\geq 0)$

$$(\underline{D}^{<(>)})_{LL'} = \delta_{LL'} d_l^{<(>)}, \tag{3.5}$$

with

$$\begin{aligned}
d_l^< &= [qh_l(q_0 a)j_l'(qa) - q_0 h_l'(q_0 a)j_l(qa)],\\
d_l^> &= [q j_l(q_0 a)j_l'(qa) - q_0 j_l'(q_0 a)j_l(qa)].
\end{aligned} \tag{3.6}$$

To obtain the expression for $\vec{\nabla}\vec{\nabla}\cdot\vec{\Gamma}^<(\vec{r})$, let us consider the quantity $\partial[\underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{\xi}]/\partial x_i$, $\underline{\xi}$ being an arbitrary r-independent column vector. This is calculated by first expressing the vector $\vec{\nabla}[\underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{\xi}]$ in the (r,θ,ϕ) components and afterwards obtaining from them the Cartesian components. After some calculations we have

$$\frac{\partial}{\partial x_i}[\underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{\xi}] = q_0\underline{Y}^t(\vec{r})\underline{j}(q_0 r)\underline{Q}_i\underline{\xi}. \tag{3.7}$$

Here, in the same notation as used in Eqs. (3.2) and (3.3),

$$\begin{aligned}
\underline{Q}_x &= [-B_{--}, B_{-+}, -B_{+-}, B_{++}],\\
\underline{Q}_y &= [iB_{--}, iB_{-+}, iB_{+-}, iB_{++}],\\
\underline{Q}_z &= [-C_{-0}, C_{+0}]
\end{aligned} \tag{3.8}$$

define the (l,m)th row of the (square) transformation matrices.

From Eqs. (3.4) and (3.7), our SC condition (2.14b) reduces to

$$\begin{aligned}
K^<(r)_i &\equiv [\vec{\Gamma}^<(\vec{r}) + (1/q_0^2)\vec{\nabla}\vec{\nabla}\cdot\vec{\Gamma}^<(\vec{r})]_i\\
&= -iq_0 a^2 \underline{Y}^t(\vec{r})\,\underline{j}(q_0 r)\\
&\quad\times\sum_\beta\sum_j(\delta_{ij}\underline{E} + \underline{Q}_i\underline{Q}_j)[\underline{D}^< + \underline{\Gamma}(\vec{k})\underline{D}^>]\underline{P}_j^\beta\underline{\alpha}^\beta(\vec{k})\\
&= 0.
\end{aligned} \tag{3.9}$$

This is the SC condition written in matrix notation. Corresponding to $i=x,y,z$, Eq. (3.9) yields three conditions for the two unknown sets. These three conditions, therefore, should not all be independent. To obtain the two (genuine) independent conditions let us resolve the vector $\vec{k}^<(\vec{r})$ into a superposition of M- and N-type fields.

The presence of the matrix $\underline{Y}^t(\vec{r})\underline{j}(q_0 r)$ in Eq. (3.9) leads us to introduce the field ${}^\beta\vec{E}_L^0(\vec{r})$ defined by

$${}^\beta\vec{E}_L^0(\vec{r}) = {}^\beta\vec{E}_L^<(q\to q_0), \tag{3.10}$$

where the right-hand side represents the substitution according to the definition (2.17). Next, define the two column vectors ${}^M\underline{\Theta}(r)$ and ${}^N\underline{\Theta}(r)$ as

follows:

$$\underline{{}^{\beta}\Theta}(r)=\left(({}^{\beta}\vec{E}^{0}_{1,-1}(\vec{r}),\vec{K}^{<}(\vec{r})),\ ({}^{\beta}\vec{E}^{0}_{1,0}(\vec{r}),\vec{K}^{<}(\vec{r})),\ \ldots\right)^{t}, \tag{3.11}$$

(,) being the inner product defined by Eq. (2.18). From the orthogonality condition (2.19), each element of ${}^{\beta}\Theta(r)$ gives the expansion coefficient of the vector $\vec{K}^{<}(\vec{r})$ in terms of the field ${}^{\beta}\vec{E}^{0}_{L}(\vec{r})$ (multiplied by the normalizing constant, of course). Noting that $[{}^{\beta}E^{0}_{L}(\vec{r})_{i}]^{*}$ is expressed as the (l,m)th component of the column vector $(\underline{P}^{\beta}_{i})^{\dagger}\underline{j}(q_0 r)\underline{Y}^{*}(\vec{r})$ and using the several auxiliary relations summarized in the Appendix, we finally obtain

$$\begin{aligned}
\underline{{}^{M}\Theta}(r)/iq_0a^2 &= -\underline{{}^{M}N^{0}}(r)\{[\underline{D}^{<}+\underline{\Gamma}^{MM}(\vec{k})]\underline{\alpha}^{M}(\vec{k})\\
&\quad+\underline{\Gamma}^{MN}(\vec{k})\underline{\alpha}^{N}(\vec{k})\},\\
\underline{{}^{N}\Theta}(r)/iq_0a^2 &= -\underline{{}^{N}N^{0}}(r)\{\underline{\Gamma}^{NM}(\vec{k})\underline{\alpha}^{M}(\vec{k})\\
&\quad+[\underline{W}^{<}+\underline{\Gamma}^{NN}(\vec{k})]\underline{\alpha}^{N}(\vec{k})\}.
\end{aligned} \tag{3.12}$$

Here

$$[\underline{{}^{\beta}N^{0}}(r)]_{LL'}=\delta_{LL'}\,{}^{\beta}n^{0}_{l}(r) \tag{3.13}$$

defines the diagonal matrix in terms of the normalizing factor ${}^{\beta}n^{0}_{l}(r)$ given by Eq. (2.20) (with $q\to q_0$). The matrix $\underline{W}^{<}$ is

$$\begin{aligned}
(\underline{W}^{(>)})_{LL'} &= \delta_{LL'}\omega_{l}^{<(>)}\\
&= \delta_{LL'}[l\alpha_{l+1}^{<(>)}+(l+1)\alpha_{l-1}^{<(>)}]/(2l+1)
\end{aligned} \tag{3.14}$$

(the matrix $\underline{W}^{>}$ will be used in Sec. III). The coupling terms $\underline{\Gamma}^{\beta\beta'}(\vec{k})$ between spheres are defined as

$$\underline{\Gamma}^{\beta\beta'}(\vec{k})=\underline{L}\sum_{i}(\underline{P}^{\beta}_{i})^{\dagger}\underline{\Gamma}(\vec{k})\underline{D}^{>}\underline{P}^{\beta'}_{i}, \tag{3.15}$$

with

$$(\underline{L})_{LL'}=\delta_{LL'}\,1/l(l+1). \tag{3.16}$$

Note that the matrices in Eq. (3.12), including $\underline{D}^{<}$ and $\underline{W}^{<}$ are needed in the space $l,l'\geq 1$.

From the SC condition (3.9) we have ${}^{\beta}\underline{\Theta}(r)=0$. Therefore

$$\begin{aligned}
&[\underline{D}^{<}+\underline{\Gamma}^{MM}(\vec{k})]\underline{\alpha}^{M}(\vec{k})+\underline{\Gamma}^{MN}(\vec{k})\underline{\alpha}^{N}(\vec{k})=0,\\
&\underline{\Gamma}^{NM}(\vec{k})\underline{\alpha}^{M}(\vec{k})+[\underline{W}^{<}+\underline{\Gamma}^{NN}(\vec{k})]\underline{\alpha}^{N}(\vec{k})=0,
\end{aligned} \tag{3.17}$$

or equivalently

$$\det\begin{vmatrix}\underline{D}^{<}+\underline{\Gamma}^{MM}(\vec{k}) & \underline{\Gamma}^{MN}(\vec{k})\\ \underline{\Gamma}^{NM}(\vec{k}) & \underline{W}^{<}+\underline{\Gamma}^{NN}(\vec{k})\end{vmatrix}=0. \tag{3.18}$$

Our remaining task is to confirm that the condition (3.17) or (3.18) is actually a sufficient one for the original condition (3.9) to be established. (If the sets of the vector fields form a complete set, this procedure is not necessary. However, the proof of the completeness is not found in the literature.[29]) To show this it suffices to see that the superposition of the fields $\{{}^{M}\vec{E}^{0}_{L}(\vec{r})\}$ and $\{{}^{N}\vec{E}^{0}_{L}(\vec{r})\}$, with the left-hand side of Eq. (3.17) used for the expansion coefficients, actually leads to the vector $\vec{K}^{<}(\vec{r})$ defined by Eq. (3.9). This is a straightforward task once we note the identity (shown, for example, by explicit calculation of the matrix elements)

$$\sum_{\beta}\underline{P}^{\beta}_{i}\underline{L}(\underline{P}^{\beta}_{j})^{\dagger}=\delta_{ij}\underline{E}+\underline{Q}_{i}\underline{Q}_{j} \tag{3.19}$$

in the superposition of the two vector fields.

In summary, the secular equation that provides the photon energy bands is given by Eq. (3.18). Its dimension is twice that of the KKR's, reflecting the transversality of the photon fields. Note the replacement (2.3) to obtain the general case. It is also to be noted that Eq. (3.17) or (3.18) is an equation for the wave vector $\vec{k}$.

It is interesting to consider some limiting cases of Eq. (3.18): (a) $\underline{\Gamma}^{\beta\beta'}(\vec{k})\to 0$, (b) $a\to 0$, and (c) q_0, $q\to 0$. The limit (a) corresponds to a single sphere. Equation (3.18) or $\det\underline{D}^{<}=\det\underline{W}^{<}=0$ yields the eigenvalues of the collective oscillations of a dielectric sphere or around a cavity[31] [to transform $\underline{W}^{<}$, use Eq. (4.6)]. In the limit (b), our system reduces to a regular lattice of point dipoles.[32] The present secular equation yields the polariton dispersion relation [photon–phonon (-exciton) coupled modes].[33] The limit (c) describes the nonretardation regime. From Eq. (3.18) follow the eigenvalues of the collective modes that exist on each sphere and interact with each other by way of a nonretarded interaction.[34] By a lengthy but straightforward calculation, we see that the present SC equation (3.18) reproduces correctly the known results of the above three limiting cases.

IV. SC FIELD EXPRESSION

The purposes of this section are (1) to confirm that the eigenvalues and the eigenvectors derived from Eqs. (3.17) and (3.18) actually guarantee the boundary conditions of the electromagnetic fields and (2) to resolve the fields into plane waves in order to apply the present formalism to the low-energy photon diffraction. In this section we consider the general case shown in Fig. 1, so that q_0 and q should be replaced according to Eq. (2.3).

Since the SC electromagnetic wave is a Bloch wave, we may restrict ourselves to one unit cell. If the radial component of the displacement field, for example, is shown to be continuous across the

surface of the r-sphere, it is automatically continuous across all the spheres. We concentrate here on the calculation of the electric field.

The electric field inside the r-sphere is given by Eq. (2.16) or (3.1) with Eq. (3.17), whereas the outside field is obtained from Eq. (2.14a). From the definition (2.12), the quantity $\vec{I}_{\vec{k}}^{>}(\vec{r})$ involved in Eq. (2.14a) is different from $\vec{I}_{\vec{k}}^{<}(\vec{r})$ only in the definition of the Green's function. Thus, following once again the procedure that leads to Eq. (3.11), we get

$$\begin{aligned} E_{\vec{k}}^{>}(\vec{r})_i = -iq_> a^2 \{ & \underline{Y}^t(\vec{r})\underline{h}(q_> r)[\underline{P}_i^M \underline{D}^> \underline{\alpha}^M(\vec{k}) \\ & + \underline{P}_i^N \underline{W}^> \underline{\alpha}^N(\vec{k})] + \underline{Y}^t(\vec{r})\underline{j}(q_> r) \\ & \times \sum_j (\delta_{ij}\underline{E} + \underline{Q}_i \underline{Q}_j)\underline{\Gamma}(\vec{k})\underline{D}^> \sum_\beta \underline{P}_j^\beta \underline{\alpha}^\beta(\vec{k})\}, \end{aligned} \tag{4.1}$$

where the terms without $\underline{\Gamma}(\vec{k})$, collected into the first term, are derived by means of relations (A1) and (A4). The definitions of the diagonal matrices $\underline{h}$ and $\underline{W}^>$ are given by Eqs. (2.27) and (3.14), respectively. The second term of Eq. (4.1), which describes the contributions from spheres other than the r-sphere, is simplified by the help of the SC condition (3.9). Then, noting the equivalence of the two alternative expressions (2.16) and (3.1), we have

$$\begin{aligned} \vec{E}_{\vec{k}}^{>}(\vec{r}) = iq_> a^2 \sum_{l=1}^{} \sum_{m=-l}^{l} \{ & [d_l^{<M} \vec{E}_L^{<}(q_>\vec{r}) \\ & - d_l^{>M} \vec{E}_L^{>}(q_>\vec{r})]\alpha_L^M(\vec{k}) \\ & + [\omega_l^{<N} \vec{E}_l^{<}(q_<\vec{r}) - \omega_l^{>N} \vec{E}_L^{>}(q_>\vec{r})]\alpha_L^N(\vec{k})\}. \end{aligned} \tag{4.2}$$

The definitions of the new fields ${}^\beta\vec{E}_L^{<}(q_>\vec{r})$ and ${}^\beta\vec{E}_L^{>}(q_>\vec{r})$ are

$${}^\beta\vec{E}_L^{<}(q_>\vec{r}) = {}^\beta\vec{E}_L^{<}(q \to q_>)$$

and

$${}^\beta\vec{E}_L^{>}(q_>\vec{r}) = {}^\beta\vec{E}_L^{<}(j_l \to h_l; q \to q_>), \tag{4.3}$$

where the right-hand side represents, as before, the substitution in the definition (2.17).

Let us check here only the continuity of the radial component of the displacement field at $r=a$:

$$\epsilon_> E_k^{>}(a)_r = \epsilon_< E_k^{<}(a)_r. \tag{4.4}$$

The continuity of the θ and ϕ components of the electric field may be shown in an analogous manner.

Substitution of Eq. (2.17) into Eq. (4.2) gives ($z_{<(>)} = aq_{<(>)}$)

$$\begin{aligned} E_{\vec{k}}^{>}(a)_r = -iq_> a^2 & \sum_L l(l+1) \\ & \times [\omega_l^{<} j_l(z_>)/z_> - \omega_l^{>} h_l(z_>)/z_>] Y_L(\vec{r})\alpha_L^N(\vec{k}). \end{aligned} \tag{4.5}$$

Since $\omega_l^{<(>)}$ is defined in terms of $d_{l\pm1}^{<(>)}$ [Eq. (3.14)], let us transform $d_{l\pm1}^{<(>)}$ defined by Eq. (3.6). Employing the recurrence formulas for cylindrical functions,[28] we find

$$\begin{aligned} d_{l+1}^{<} = & l(q_</z_> - q_>/z_<)h_l(z_>)j_l(z_<) \\ & - [q_< h_l'(z_>)j_l(z_<) - q_> h_l(z_>)j_l'(z_<)], \\ d_{l-1}^{<} = & -(l+1)(q_</z_> - q_>/z_<)h_l(z_>)j_l(z_<) \\ & - [q_< h_l'(z_>)j_l(z_<) - q_> h_l(z_>)j_l'(z_<)]. \end{aligned} \tag{4.6}$$

The quantity $d_{l+1}^{>}$ ($d_{l-1}^{>}$) is obtained from $d_{l+1}^{<}$ ($d_{l-1}^{<}$) if the Hankel function in the above is replaced by $j_l(z_>)$.

From Eqs. (3.14) and (4.6), Eq. (4.5) reduces to

$$\begin{aligned} E_{\vec{k}}^{>}(a)_r = iq_> a^2 & \sum_L l(l+1)[j_l(z_<)/z_>]q_< \\ & \times [j_l(z_>)h_l'(z_>) - h_l(z_>)j_l'(z_>)]Y_L(\vec{r})\alpha_L^N(\vec{k}). \end{aligned} \tag{4.7}$$

The quantity within the second pair of square brackets is the Wronskian. Hence[28]

$$\begin{aligned} E_{\vec{k}}^{>}(a)_r = -(q_</q_>)^2 & \sum_L l(l+1)[j_l(z_<)/z_<] \\ & \times Y_L(\vec{r})\alpha_L^N(\vec{k}). \end{aligned} \tag{4.8}$$

Thus from the definitions (2.1), (2.16), and (2.17) follows the relation (4.4).

Now we proceed to resolve the wave field into plane waves. Corresponding to

$$\vec{E}_{\vec{k}}(\vec{r}) = \sum_{\vec{h}} \vec{E}_{\vec{k}}(\vec{h}) e^{i(\vec{k}+\vec{h})\cdot\vec{r}}, \tag{4.9}$$

we have

$$\vec{E}_{\vec{k}}(\vec{h}) = \frac{1}{v_0} \int_{\text{cell}} d\vec{r}\, e^{-i(\vec{k}+\vec{h})\cdot\vec{r}} \vec{E}_{\vec{k}}(\vec{r}). \tag{4.10}$$

Since $\vec{E}_{\vec{k}}(\vec{r})$ has two different expressions depending on whether $r \lessgtr a$, $\vec{E}_{\vec{k}}(\vec{h})$ is composed of the two contributions

$$\vec{E}_{\vec{k}}(\vec{h}) = \vec{E}_{\vec{k}}^{<}(\vec{h}) + \vec{E}_{\vec{k}}^{>}(\vec{h}), \tag{4.11}$$

where $\vec{E}_{\vec{k}}^{<}(\vec{h})$ [$\vec{E}_{\vec{k}}^{>}(\vec{h})$] comes from the region $r<a$ ($r>a$) in the r integral of Eq. (4.10). For $\vec{E}_{\vec{k}}^{<}(\vec{h})$, we must use Eq. (2.16) or (3.1), and for $\vec{E}_{\vec{k}}^{>}(\vec{h})$ Eq. (4.2) should be employed. As before, the volume integral of Eq. (4.10) may be reduced to a surface integral by means of the identity

$$e^{-i(\vec{k}+\vec{h})\cdot\vec{r}} = \frac{q_{<(>)}^2 + \Delta}{q_{<(>)}^2 - (\vec{k}+\vec{h})^2} e^{-i(\vec{k}+\vec{h})\cdot\vec{r}}. \tag{4.12}$$

Expanding $e^{-i(\vec{k}+\vec{h})\cdot\vec{r}}$ into the superposition of spherical waves, we finally obtain [$(\underline{i})_{LL'} = \delta_{LL'} i^l$]

$$[E_{\vec{k}}(\vec{h})]_i = \frac{4\pi a^2}{v_0} \underline{Y}^t(\vec{k}+\vec{h})\, \underline{i}^* \{[\underline{e}^<_{\vec{k}}(\vec{h})]_i + [\underline{e}^>_{\vec{k}}(\vec{h})]_i\}, \tag{4.13}$$

where

$$[\underline{e}^<_{\vec{k}}(\vec{h})]_i = \frac{-1}{(\vec{k}+\vec{h})^2 - q_<^2} \underline{V}_1 [\underline{P}^M_i \underline{\alpha}^M(\vec{k}) + \underline{P}^N_i \underline{\alpha}^N(\vec{k})],$$

$$[\underline{e}^>_{\vec{k}}(\vec{h})]_i = \frac{iq_> a^2}{(\vec{k}+\vec{h})^2 - q_>^2} \{\underline{V}_2 [\underline{P}^M_i \underline{D}^< \underline{\alpha}^M(\vec{k}) + \underline{P}^N_i \underline{W}^< \underline{\alpha}^N(\vec{k})]$$

$$- \underline{V}_3 [\underline{P}^M_i \underline{D}^> \underline{\alpha}^M(\vec{k}) + \underline{P}^N_i \underline{W}^> \underline{\alpha}^N(\vec{k})]\}. \tag{4.14}$$

Here the three matrices $\underline{V}_1 - \underline{V}_3$ are related to $D^<$ and $D^>$ as follows [$l, l' \geq 0$ in $(\underline{V}_i)_{LL'}$]:

$$\underline{V}_1 = \underline{D}^>(q_0 \to q_<, q \to |\vec{k}+\vec{h}|),$$
$$\underline{V}_2 = \underline{D}^>(q_0 \to q_>, q \to |\vec{k}+\vec{h}|), \tag{4.15}$$
$$\underline{V}_3 = \underline{D}^<(q_0 \to q_>, q \to |\vec{k}+\vec{h}|).$$

The expressions for the displacement field and the magnetic field are obtained from Eq. (4.13) and the Maxwell equations. Corresponding to the same decomposition as Eq. (4.9), the result is

$$[D_{\vec{k}}(\vec{h})]_i = (4\pi a^2/v_0) \underline{Y}^t(\vec{k}+\vec{h})\, \underline{i}^* \{\epsilon_< [\underline{e}^<_{\vec{k}}(\vec{h})]_i + \epsilon_> [\underline{e}^>_{\vec{k}}(\vec{h})]_i\},$$
$$[H_{\vec{k}}(\vec{h})]_i = (1/q_0)[(\vec{k}+\vec{h}) \times \vec{E}_{\vec{k}}(\vec{h})]. \tag{4.16}$$

From Eqs. (4.13) and (4.14), we observe that the field associated with the vector $\vec{k}+\vec{h}$ is excited strongly when in $\vec{k}$ space the vector $\vec{k}+\vec{h}$ lies near either of the two Ewald spheres with radius $q_<$ and $q_>$. This is a situation in clear contrast to that of x-ray diffraction, in which only one Ewald sphere is involved.[1] On one hand, this feature is due to the assumption that the dielectric function undergoes an abrupt change across the sphere walls, and on the other hand it stems from the formulation employed here in which the plane-wave expansion is performed at the *final* stage using the *exact* expression for the electromagnetic fields.

We have considered up to now the SC electromagnetic fields established in an infinite lattice. The results are summarized in Eqs. (3.17), (3.18), (4.13), (4.14), and (4.16).

V. LOW-ENERGY PHOTON DIFFRACTION

The SC field considered so far is excited by an external electromagnetic field. An important case where the field lies partly outside a bounded system must now be considered. To apply the theory developed above to LEPD, we shall match the inside fields with the outside ones at external surfaces of the system. The discussion that follows of the matching problem is therefore an extension of that of Boudreaux and Heine,[24] Pendry,[35] and Capart[36] developed in LEED.

Consider a "slab" of ordered spheres cut from an infinite lattice by two parallel planes (Fig. 2). We must impose tangential continuity of the electromagnetic fields on the two surfaces S_1 and S_2. A monochromatic electromagnetic wave is incident on the surface S_1, with a given wave vector, amplitude, and polarization. We assume that there are N_1 reflected waves in the upper space and N_2 transmitted waves in the lower space, that is, we consider N_1 reciprocal-lattice rods on S_1 and N_2 on S_2. Because of transversality, two unknown constants are necessary to specify each reflected or transmitted wave. Outside the slab there are thus $2(N_1+N_2)$ unknown constants in all.

The tangential continuity of the wave vectors leads to N_1 sets of independent equations on S_1 and N_2 on S_2. For each rod we have four boundary conditions: two for the tangential continuity of $\vec{E}(\vec{r})$ and two more for $\vec{H}(\vec{r})$. Thus we have $4(N_1+N_2)$ independent conditions. So if we choose $2(N_1+N_2)$ Bloch waves inside the system and form a superposition of them by employing new $2(N_1+N_2)$ unknown constants, the total number of unknown constants becomes $4(N_1+N_2)$. Therefore the matching problem becomes exactly soluble.

In the case of a thick slab or a semi-infinite system, we have only to put N_2 equal to zero in

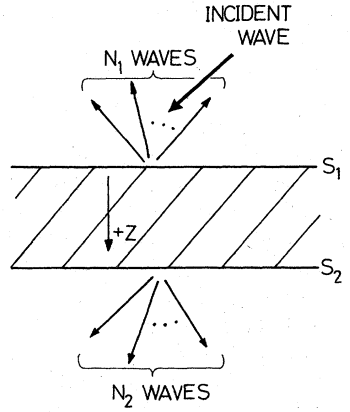

FIG. 2. System considered in the matching formulation, with S_1 and S_2 the two external plane surfaces. There are N_1 reflected waves and N_2 transmitted waves.

the above discussion. Here the $2N_1$ inside Bloch waves must be those whose energy flows decay in the thickness direction ($+Z$ direction in Fig. 2). As is seen above, the number of unknown constants involved in LEPD is larger than in LEED. They are properly determined by the vector nature of the continuity equations and the presence of the magnetic field in addition to the electric field.

In conclusion, the calculation of the band structure and the eigenvectors from Eqs. (3.17) and (3.18) may be performed in the same way as in LEED, and then the matching procedure using Eqs. (4.13) and (4.16) as outlined above will predict the reflected and the transmitted intensities of LEPD experiments.

Before closing this section, let us consider what will be expected in LEPD experiments. In LEED, several prominent features have been observed in the intensity versus voltage curves.[20,24,37] Among these are secondary Bragg peaks, surface-wave resonance peaks, and widths and positions of reflectivity maxima that a simple theory fails to explain. The last phenomenon is due to the large scattering cross section of low-energy electrons. The former two kinds of peaks are also of the same origin. However, the important point is that they are attributed to an abrupt appearance or disappearance of an energy-transporting channel. Namely, they are examples of general facts applying to such scatterings which involve a number of scattering channels. For the occurrence of this type of peaks and dips in electron scattering, see the textbook by Landau and Lifshitz,[38] for example. About the electromagnetic fields, it suffices to recall the discussion by Hopfield and Thomas concerning the reflectivity curve of some ionic compounds.[39]

Thus, it can be said that the phenomena observed in LEED are not restricted to LEED, but in principle are expected to occur in the diffraction of low-energy photons.

One interesting situation peculiar to LEPD may be the case in which the frequence dependences of the dielectric constants are such as to induce a collective mode in the system. When the frequency of the incident field is matched with that of the collective mode, a resonant coupling between them will occur, which results in an energy splitting in the electromagnetic-field dispersion relation. Consider the case (b) at the end of Sec. III, where dipolar modes become polaritons.[33] If the wave vector of the strongest mixing lies far away from a Brillouin-zone boundary, the reflection and the transmission of electromagnetic waves will be governed by the mechanism discussed by Hopfield and Thomas.[39] When, on the other hand, it lies near the zone boundary, the band splitting will be enhanced due to the combined effect of Bragg reflection and resonant mixing. In the latter case, it is no longer photons but polaritons that experience Bragg reflection. In the actual situation, the finite radius of the spheres may complicate the resonance and in void lattices, for example, the above situation is not expected.[40] However, the present theory will be capable of describing possible resonant Bragg reflections without any modification.

VI. SUMMARY AND DISCUSSION

In this paper I have presented a formal treatment of photons subject to strong scattering in a translationally symmetric system. The systems considered here are regular lattices of spheres whose lattice constants range from a few hundred to a few thousand angstroms. Photons with comparable wavelengths undergo very strong Bragg reflections since the spatial inhomogeneity felt by them is very large owing to a general behavior of the frequency dependence of the dielectric constants. Therefore, in decribing these photons, a new dynamical theory of diffraction is required, just as was LEED theory in electron diffraction. The theory of low-energy photon diffraction developed in this paper is along this direction.

The present work is an extension of the theory of Mie[18] and Debye[19] in that light scattering of an infinite number of spheres in a regular lattice is considered. Besides, the present theory is an extension of the KKR formalism of band-structure calculations.[22,23] The secular equation obtained in this paper yields the photon energy band. Also, the matching of the inside Bloch field with the outside field to obtain the diffracted intensities is an extension of the LEED procedure originally developed in high-energy-electron and x-ray diffraction.[1]

As in LEED, it is expected that all the essential features that an actual LEPD experiment will bring about will be covered by the present theory. Besides some peculiar phenomena discussed in Sec. V, another possible example of the characteristic features of LEPD is the abnormal absorption[1] in the optical region. Also, the shift from the Mie and Debye theories to the present one may be directly checked when the random scatterers become ordered, as is in fact the case in the latex lattice.

One essential difference between the formulations of LEPD and LEED is the difference of the dimensions involved in the two. In this sense, the calculation of the band structure and the matching calculation at external surfaces in LEPD are more laborious than in LEED. In actual applications of LEED theories, however, one of the most

time-consuming tasks is the determination of the pseudopotential felt by the incident electrons.[35,36,41] As long as the known dielectric constants in the uv or optical range are employed in LEPD, an extra effort due to the doubled dimensionality would thus be well compensated.

Let us next consider the inelastic-scattering effect. In LEED, the mean free path of an incident electron is of the order of a few angstroms.[20,21] If inelastic damping of electrons is neglected, the agreement between experiment and theory is only limited.

Generally, the inelastic scattering of photons, the Raman scattering, for example, has a cross section much smaller than that of the electrons.[42] Apart from the large elastic scattering, therefore, the dominant mechanism that causes the decaying of a light beam is absorption. As in LEED, the absorption of photons is incorporated into dielectric constants. If we use two appropriate complex dielectric constants, the present theory is capable of taking into account the damping effects.

To estimate the photon penetration depth, let us consider a void lattice in a metal matrix. The photons which have energies smaller than $\hbar\omega_p$ do not penetrate into the metal. In a good aluminum sample, the penetration of photons is of the order of 5000 Å, for $15 < \hbar\omega < 70$ eV ($15\text{ eV} = \hbar\omega_p$, 70 eV is the L absorption edge).[43] Therefore, in contrast to LEED, a transmission experiment may be possible in LEPD, if we prepare a sample whose thickness is, say, 1–2 μm. This is why we have considered a slab in the matching problem. However, we must remember that the lattice constants involved in LEPD are orders of magnitude larger than those of ordinary solids. For a void lattice whose lattice constant is ~200 Å, the mean free path of photons is about 20–30 layers even in good aluminum. In actual samples containing voids, the situation is probably worse.

Therefore in LEPD as well as in LEED there are situations in which the penetration of incident photons is limited to the surface region of the lattice. Although the present theory may cover these cases as do the matching theories in LEED, it will be of practical importance to elaborate the LEPD theories that concentrate on multiple scattering of the surface layer or the surface region. Evidently, the extension to LEPD of the MacRae[37,44] Beeby,[45] and Kambe[46] LEED theories is in accord with this purpose. Furthermore, it will also be important to develop a practical method of calculation such as the layer-by-layer iterative method, devised recently in LEED.[21]

It is clear that the theory developed in this paper will serve as a basis for development in these directions. In future works, numerical applications of the present theory will be presented and attempts will be made to modify the LEPD theory along these lines.

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APPENDIX: SOME RELATIONS USEFUL IN THE DERIVATION OF EQ. (3.12)

Only the results are summarized, for the proof is straightforward [except Eq. (A2)] if we calculate the matrix elements explicitly. All the matrices to follow are defined in the text.

To simplify the vector $\vec{K}^{<}(\vec{r})$ defined by Eq. (3.9), use

$$\underline{D}^{<(>)}\underline{P}_i^M = \underline{P}_i^M \underline{D}^{<(>)}, \tag{A1}$$

$$\underline{Q}_i \underline{\Gamma}(\vec{k}) = \underline{\Gamma}(\vec{k})\underline{Q}_i, \tag{A2}$$

$$\sum_j \underline{Q}_j \underline{P}_j^M = 0, \tag{A3}$$

$$\sum_j (\delta_{ij}\underline{E} + \underline{Q}_i\underline{Q}_j)\underline{D}^{<(>)}\underline{P}_j^N = \underline{P}_i^N \underline{W}^{<(>)}. \tag{A4}$$

Since the matrix element $(\underline{P}_i^\beta)_{LL'}$ is defined in the space $l \geq 0$, $l' \geq 1$, it must be understood that the diagonal matrices $\underline{D}^{<(>)}$ and $\underline{W}^{<(>)}$ on the right-hand side of Eqs. (A1) and (A4) are defined in the space $l, l' \geq 1$.

In reducing $\underline{\Theta}^\beta(r)$ defined by Eq. (3.11), employ the orthogonality relation in the matrix notation

$$\sum_i (\underline{P}_i^\beta)^\dagger \underline{j}^2(q_0 r)\underline{P}_i^{\beta'} = \delta_{\beta\beta'}\,{}^\beta\underline{N}^0(r), \tag{A5}$$

and use the following identities:

$$(\underline{P}_i^M)^\dagger \underline{j}^2(q_0 r) = {}^M\underline{N}^0(r)\underline{L}(\underline{P}_i^M)^\dagger, \tag{A6}$$

$$\underline{Q}_i\underline{Q}_j = \underline{Q}_j\underline{Q}_i, \tag{A7}$$

$$\sum_j (\underline{P}_j^N)^\dagger \underline{j}^2(q_0 r)(\delta_{ij}\underline{E} + \underline{Q}_i\underline{Q}_j) = {}^N\underline{N}^0(r)\underline{L}(\underline{P}_i^N)^\dagger, \tag{A8}$$

where ${}^\beta\underline{N}^0(r)$ and $\underline{L}$ are defined in the space $l, l' \geq 1$.

In order to prove Eq. (A2), state the following evident identity in matrix notation, using Eq. (3.7) and its Hermitian conjugate:

$$\frac{\partial}{\partial x_i} G_{\vec{k}}(\vec{r}, \vec{r}') = -\frac{\partial}{\partial x_i'} G_{\vec{k}}(\vec{r}, \vec{r}'). \tag{A9}$$

From the property $\underline{Q}_i = -(\underline{Q}_i)^\dagger$ follows Eq. (A2).

[1]See, e.g., R. W. James, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1968), Vol. 15, p. 53; B. W. Batterman and H. Cole, Rev. Mod. Phys. 36, 681 (1964).
[2]J. H. Evans, Nature 229, 403 (1971).
[3]B. L. Eyre and J. H. Evans, *Void Formed by Irradiation of Reactor Materials*, edited by S. F. Pugh, M. H. Loretto, and D. I. R. Norris, (British Nuclear Energy Society, London, 1971), p. 323.
[4]D. J. Mazey, F. Susan, and J. A. Hudson, AERE Report No. R7301, 1972 (unpublished).
[5]P. S. Hiltner and I. M. Krieger, J. Phys. Chem. 73, 2386 (1969).
[6]S. Hachisu, Y. Kobayashi, and A. Kose, J. Colloid Interface Sci. 42, 342 (1972).
[7]R. Williams, R. S. Crandall, and P. J. Wojtwitz, Phys. Rev. Lett. 37, 348 (1976).
[8]V. W. Luck, N. Klier, and H. Wesslau, Die Naturw. 14, 485 (1963).
[9]P. A. Hiltner, Y. S. Papir, and I. M. Krieger, J. Phys. Chem. 75, 1881 (1971).
[10]R. Williams and R. S. Crandall, Phys. Lett. A 48, 225 (1971).
[11]H. Fujita and K. Ametani, Jpn. J. Appl. Phys. 16, 1907 (1977).
[12]A. A. Lucas, Phys. Rev. B 12, 5372 (1975).
[13]The value of the bulk dielectric constant of polystyrene at room temperature.
[14]H. P. Geserich and L. Pintschovius, Adv. Solid State Phys. 16, 65 (1976).
[15]G. B. Street and R. L. Greene, IBM J. Res. Dev. 21, 99 (1977).
[16]M. H. F. Wilkins, A. R. Stokes, W. E. Seeds, and G. Oster, Nature 166, 127 (1950); B. K. Vainstein, *Diffraction of X-Rays by Chain Molecules* (Elesevier, Amsterdam, 1966).
[17]J. V. Sanders and M. J. Murray, Nature 275, 201 (1978).
[18]G. Mie, Ann. Phys. 25, 377 (1908).
[19]P. Debye, Ann. Phys. 30, 57 (1909).
[20]J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1964).
[21]S. Y. Tong, Prog. Surf. Sci. 7, 1 (1975).
[22]See, e.g., J. Callaway, *Energy Band Theory* (Academic, New York, 1964), p. 86.
[23]J. Korringa, Physica (Utrecht) 35, 392 (1947); W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).
[24]D. S. Boudreaux and V. Heine, Surf. Sci. 8, 426 (1967).
[25]For a review of the Mie and Debye theory, see, e.g., M. Born and E. Wolf, *Principles of Optics*, 5th ed. (Pergamon, New York, 1975), p. 633.
[26]B. Segall, Phys. Rev. 105, 108 (1957); and Ref. 46.
[27]We employ the definition

$$Y_{l,m}(\vec{r}) = \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\phi}$$

with Ferrer's definition of $P_l^m(\cos\theta)$ $(-l \le m \le l)$ (see Ref. 30). That is,

$$Y_{l,-m}(r) = (-1)^m Y_{l,m}^*(r) \quad (m \ge 0).$$

[28]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1964), p. 437.
[29]See, e.g., J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), p. 397; D. S. Jones, *The Theory of Electromagnetism* (Pergamon, New York, 1964), p. 483.
[30]See Ref. 28, p. 331.
[31]See, e.g., R. Engleman and R. Ruppin, Rep. Prog. Phys. 33, 149 (1970).
[32]G. D. Mahan, J. Chem. Phys. 43, 1569 (1965).
[33]J. J. Hopfield, Phys. Rev. 112, 1555 (1958).
[34]K. Ohtaka, Phys. Lett. A 63, 298 (1977).
[35]J. B. Pendry, J. Phys. C 2, 2273 (1969); 4, 2501 (1971); 4, 2514 (1971).
[36]G. Capart, Surf. Sci. 13, 361 (1969); 26, 429 (1971).
[37]E. G. McRae, J. Chem. Phys. 45, 3258 (1966).
[38]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, 2nd ed. (Pergamon, London, 1965), p. 542.
[39]J. J Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).
[40]In the frequency region $\omega < \omega_p$ where the cavity plasmon modes exist, the metallic dielectric constant $\epsilon(\omega) = 1 - (\omega_p/\omega)^2$ is negative, so that the propagating electromagnetic waves, and hence the polaritons, do not exist.
[41]J. B. Pendry, J. Phys. C 2, 1215 (1969).
[42]R. Loudon, Adv. Phys. 13, 423 (1964).
[43]H. J. Hagemann, W. Gudat, and C. Kunz, J. Opt. Soc. Am. 65, 742 (1975).
[44]E. G. McRae, Surf. Sci. 11, 479 (1968).
[45]J. L. Beeby, J. Phys. C 1, 82 (1968).
[46]K. Kambe, Z. Naturforsch. A 22, 322 (1967); 22, 422 (1967); 23, 1280 (1968).