Theory of the optical properties of ionic crystal cubes

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A theory is developed for the optical properties of particles of arbitrary shape, composed of a homogeneous isotropic material with a dielectric constant $\epsilon(\omega)$. The particles are so small that retardation can be neglected. An expression is obtained for the average dielectric constant of a medium containing a small fractional volume of particles. Calculations for a cube show that six resonances contribute to the optical absorption. They span a frequency range such that $\epsilon'(\omega)$, the real part of the dielectric constant, lies between -3.68 and -0.42, as contrasted with the single resonance for a sphere at $\epsilon'(\omega) = -2$. A comparison of the theory with experiments on the optical absorption of NaCl and MgO cubes shows that the width of the absorption peak can be explained by the frequency range of the cube resonances. Previous theories which assumed spherical particles required an unphysically high damping in $\epsilon(\omega)$ to account for the width.

I. INTRODUCTION

The optical properties of spherical metallic or dielectric particles are well understood, and the agreement between theory and experiment is good.[1,2] There have also been many optical experiments on particles that are irregularly shaped, or that are sometimes in the form of cubes, but few theoretical studies exist for such particles. Several calculations of the normal modes of vibration and the infrared optical absorption of extremely small particles containing on the order of 100 atoms have been made using lattice-dynamical theories.[3,4] Since the number of atoms on the surface of such small particles is comparable to the number in the interior, the calculations show features characteristic of the surfaces, and may not be applicable to larger particles, for which the surfaces are relatively less important. van Gelder *et al.*[5] have calculated the polariton modes of a dielectric cube large enough that the material can be characterized by a macroscopic dielectric constant but small enough that retardation can be neglected. The electric potential outside the cube was expanded in a series of functions that are solutions to Laplace's equation in spherical polar coordinates. Since nine functions were used in the expansion, they found nine normal-mode frequencies, the eigenvalues of a 9×9 matrix. However, the contribution of each normal mode to the optical absorption was not estimated, so the calculation is of limited value for making a comparison with experiment.

In Sec. II a theory for the complex susceptibility of a small particle is developed; general properties of this susceptibility are considered in Sec. III. Section IV discusses the average dielectric constant of a medium containing a small fractional volume of particles, as well as the optical absorption and electron energy loss for such a mixture.

The theory is applied to a cube in Sec. V, and in Sec. VI a comparison is made with experiments.

II. THE SUSCEPTIBILITY OF A SMALL PARTICLE

We consider a particle composed of a homogeneous isotropic material with a dielectric constant $\epsilon(\omega) = 1 + 4\pi\chi(\omega)$, where $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$ is the complex dielectric susceptibility. To be specific, the material will be taken to be an ionic crystal such as NaCl, so the optical absorption is associated with the infrared-active transverse optical phonons. However, the theory is applicable to any material described by a frequency-dependent dielectric constant $\epsilon(\omega)$. The particle is of arbitrary shape, but is much smaller than the wavelength of light, so that retardation can be neglected. The electric field associated with the incident light can thus be approximated as a spatially uniform field oscillating with a frequency ω.

In the macroscopic approach being used here, the optical absorption of the particle is associated with the polariton normal modes. These modes are characterized by a polarization field $\vec{P}(\vec{r})$, a continuous function of the position, and slowly varying on the scale of the interatomic distance. When retardation can be neglected, the normal modes are of three types: (i) transverse modes, with $\nabla \cdot \vec{P} = 0$ everywhere, and occurring at ω_T, the long-wave transverse-optical phonon frequency; (ii) longitudinal modes, with $\nabla \times \vec{P} = 0$ everywhere, and occurring at ω_L, the long-wave longitudinal-optical frequency; (iii) surface modes, with $\nabla \cdot \vec{P} = \nabla \times \vec{P} = 0$ within the particle, but $\nabla \cdot \vec{P} \neq 0$ on the surface. The surface modes are those responsible for optical absorption.[6] They are not necessarily localized near the surface, as their name implies, but they are accompanied by polarization charge $\nabla \cdot \vec{P}$ on the surface. The longitudinal modes, in contrast, have polarization charge only within the

particle, and the transverse modes have no polarization charge anywhere. As we shall show, the optical absorption of the particle can be associated with the surface polarization charge.

It is possible to determine the surface mode frequencies by diagonalizing a matrix and to find the optical absorption by calculating the dipole moment for each mode. However, we shall use a more direct method which is also simpler mathematically. We apply a uniform external field $\vec{E}^0$ of frequency ω and calculate the induced dipole moment $\vec{M}$, which can be written in the form

$$M_\alpha = v \sum_{\beta=1}^{3} \langle \chi_{\alpha\beta}(\omega) \rangle E_\beta^0 , \tag{1}$$

where v is the volume of the particle, α and β are Cartesian indices. Equation (1) defines $\langle \chi_{\alpha\beta}(\omega) \rangle$, the complex dielectric susceptibility of the particle. $\langle \chi_{\alpha\beta}(\omega) \rangle$ exhibits resonant behavior at the frequencies of those polariton modes that have a dipole moment, the optical absorption being associated with the imaginary part, $\langle \chi_{\alpha\beta}''(\omega) \rangle$.

The electric field at any point $\vec{r}$ can be written

$$\vec{E}(\vec{r}) = \int_S \frac{\vec{P}(\vec{r}') \cdot \hat{n}(\vec{r}')(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} dS' + \vec{E}^0 , \tag{2}$$

where the integral in Eq. (2) is the electric field produced by the surface polarization charge density $\vec{P}(\vec{r}') \cdot \hat{n}(\vec{r}')$, $\vec{P}(\vec{r}')$ being the polarization and $\hat{n}(\vec{r}')$ being a unit outward normal vector at the point $\vec{r}'$ on the surface. If one takes the point $\vec{r}$ just inside the surface, $\vec{E}(\vec{r})$ can be related to the polarization $\vec{P}(\vec{r})$ at the surface by the equation $\vec{P}(\vec{r}) = \chi(\omega)\vec{E}(\vec{r})$. Multiplying Eq. (2) by $\hat{n}(\vec{r})$ and letting $p(\vec{r}) = \vec{P}(\vec{r}) \cdot \hat{n}(\vec{r})$ denote the normal component of the polarization at the surface, we get

$$\frac{p(\vec{r})}{\chi(\omega)} = -2\pi p(\vec{r}) + \int_S' \frac{\hat{n}(\vec{r}) \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} p(\vec{r}') dS' + \vec{E}^0 \cdot \hat{n}(\vec{r}) . \tag{3}$$

The term $-2\pi p(\vec{r})$ is the electric field produced by the surface polarization charge at $\vec{r}'$ adjacent to $\vec{r}$, and the prime on the surface integral denotes that the integral extends over points $\vec{r}'$ distant from $\vec{r}$.[7] If the polarization is calculated at a discrete set of points $\vec{r}_i$, we write $p(\vec{r}_i) = p_i$, $\hat{n}(\vec{r}_i) = \hat{n}_i$, and replace the integral by a summation; Eq. (3) then becomes

$$[\chi^{-1}(\omega) + 2\pi]p_i = \sum_j R_{ij} p_j + \vec{E}^0 \cdot \hat{n}_i , \tag{4}$$

where

$$R_{ij} = \begin{cases} \dfrac{\hat{n}_i \cdot (\vec{r}_i - \vec{r}_j)\Delta S_j}{|\vec{r}_i - \vec{r}_j|^3} , & i \neq j \\ 0 , & i = j . \end{cases} \tag{5}$$

The αth component of the dipole moment of the particle is

$$M_\alpha = \int P_\alpha \, dV . \tag{6}$$

Since $\nabla \cdot \vec{P} = 0$ inside the particle, we have $P_\alpha = \sum_\beta \partial(P_\beta x_\alpha)/\partial x_\beta$, and the volume integral (6) can be converted to a surface integral involving $\vec{P} \cdot \hat{n}$ or $p(\vec{r})$, the surface polarization charge:

$$M_\alpha = \int \vec{P} \cdot \hat{n} \, x_\alpha \, dS \tag{7}$$

or

$$M_\alpha = \sum_i p_i(x_i)_\alpha \Delta S_i . \tag{8}$$

For a given frequency ω, the values of p_i determined by Eq. (4) are then used in Eq. (8) to calculate the dipole moment; a comparison with Eq. (1) then allows the particle susceptibility $\langle \chi_{\alpha\beta}(\omega) \rangle$ to be determined.

III. GENERAL PROPERTIES OF $\langle \chi_{\alpha\beta}(\omega) \rangle$

Before calculating $\langle \chi_{\alpha\beta}(\omega) \rangle$ for a cube, it is of interest to examine the general properties that hold for a particle of arbitrary shape.

Since $\langle \chi_{\alpha\beta}(\omega) \rangle$ is the Fourier transform of a causal response function, it is an analytic function in the upper half of the complex ω plane. This leads to Kramers-Kronig relations between the real and imaginary parts, $\langle \chi_{\alpha\beta}'(\omega) \rangle$ and $\langle \chi_{\alpha\beta}''(\omega) \rangle$, as well as the conductivity sum rule, to be discussed below. If one evaluates the integral of $\omega \langle \chi_{\alpha\beta}(\omega) \rangle$ for a contour extending along the real ω axis from $-\infty$ to $+\infty$, and closed by an infinite semicircle in the upper half ω plane, one gets

$$\int_{-\infty}^{\infty} \omega \langle \chi_{\alpha\beta}(\omega) \rangle \, d\omega + \pi i \lim_{\omega \to \infty} \omega^2 \langle \chi_{\alpha\beta}(\omega) \rangle = 0 . \tag{9}$$

An analogous expression holds for the material susceptibility $\chi(\omega)$. Since we have $\lim_{\omega \to \infty} \omega^2 \chi(\omega) = A$, where A is a real constant, in the $\omega \to \infty$ limit $\vec{P}(\vec{r})$ is negligible in comparison with $\vec{E}(\vec{r})$ and $\vec{E}^0$ in Eq. (2), so $\vec{P}(\vec{r}) = \chi(\omega)\vec{E}(\vec{r}) \approx \chi(\omega)\vec{E}^0$. From Eq. (6) one has, in the $\omega \to \infty$ limit,

$$M_\alpha = v\chi(\omega)E_\alpha^0 , \tag{10}$$

and it follows from a comparison of Eq. (10) with Eq. (1) that

$$\lim_{\omega \to \infty} \omega^2 \langle \chi_{\alpha\beta}(\omega) \rangle = \lim_{\omega \to \infty} \omega^2 \chi(\omega)\delta_{\alpha\beta} = A\delta_{\alpha\beta} . \tag{11}$$

Taking the imaginary part of Eq. (9) and the corresponding equation for $\chi(\omega)$ and using Eq. (11), we find[8]

$$\int_0^\infty \omega \langle \chi_{\alpha\beta}''(\omega) \rangle \, d\omega = \int_0^\infty \omega \chi''(\omega) \, d\omega \, \delta_{\alpha\beta} . \tag{12}$$

It will be shown later that the optical properties

of a dilute sample of particles is proportional to the diagonal terms in the imaginary part of the particle susceptibility $\langle \chi''_{\alpha\alpha}(\omega) \rangle$ multiplied by the frequency. Equation (12) thus contains the statement that the integral over frequency of the optical absorption of small particles is independent of the particle shape (for a fixed particle volume), and depends only on the dielectric properties of the material.

The optical absorption of small particles arises from the excitation of the surface polariton normal modes, each mode making a certain contribution to the absorption. It is useful to derive an expression for $\langle \chi_{\alpha\beta}(\omega) \rangle$ which exhibits such a connection with the normal modes. Let U be a matrix which diagonalizes the matrix R of Eq. (4): $U^{-1}RU = \Lambda$, a diagonal matrix. Multiplying Eq. (4) by U^{-1} on the left, we get

$$[\chi^{-1}(\omega) + 2\pi - \lambda_m]\delta_{mk}U^{-1}_{ki}p_i = U^{-1}_{mi}\vec{E}^0 \cdot \hat{n}_i \ , \qquad (13)$$

where λ_m are the diagonal elements of Λ, and the indices k and i are summed. Solving Eq. (13) for p_i, calculating the dipole moment M_α from Eq. (8) and comparing the result with Eq. (1), we find that $\langle \chi_{\alpha\beta}(\omega) \rangle$ can be written as a sum over normal modes:

$$\langle \chi_{\alpha\beta}(\omega) \rangle = \sum_m \frac{C_{\alpha\beta}(m)}{\chi^{-1}(\omega) + 4\pi n_m} \ , \qquad (14)$$

where

$$n_m = \tfrac{1}{2} - \lambda_m/4\pi \qquad (15)$$

is the depolarization factor associated with the mth normal mode, and

$$C_{\alpha\beta}(m) = v^{-1}\sum_{ij}(x_i)_\alpha(n_j)_\beta U_{im}U^{-1}_{mj}\Delta S_i \ . \qquad (16)$$

Writing Eq. (14) in the limit as $\omega \to \infty$ and using Eq. (11), one immediately obtains a sum rule for the $C_{\alpha\beta}(m)$:

$$\sum_m C_{\alpha\beta}(m) = \delta_{\alpha\beta} \ , \qquad (17)$$

a result which can also be found directly from Eq. (16).

The particle susceptibility tensor for a symmetric particle such as a cube is diagonal, and the diagonal elements are equal:

$$\langle \chi_{\alpha\beta}(\omega) \rangle = \langle \chi(\omega) \rangle \delta_{\alpha\beta} \ . \qquad (18)$$

The scalar particle susceptibility can then be written

$$\langle \chi(\omega) \rangle = \sum_m \frac{C(m)}{\chi^{-1}(\omega) + 4\pi n_m} \ , \qquad (19)$$

with

$$\sum_m C(m) = 1 \ . \qquad (20)$$

The depolarization factors n_m in the denominator of Eq. (19) determine the normal-mode resonance frequencies. A peak in $\langle \chi''(\omega) \rangle$ occurs when $\mathrm{Re}\chi^{-1}(\omega) \approx -4\pi n_m$ or $\epsilon'(\omega) = 1 - n_m^{-1}$, whereas $C(m)$ gives the strength of the peak. n_m is defined in Eq. (15) to agree with the usual result for uniform polarization; in a sphere, for example, only the uniformly polarized mode contributes to optical absorption and the depolarization factor is $n = \tfrac{1}{3}$, so that

$$\langle \chi(\omega) \rangle = \frac{1}{\chi^{-1}(\omega) + 4\pi/3} \ \text{(sphere)} \ . \qquad (21)$$

Equation (21) leads to the well-known condition $\epsilon'(\omega) = -2$, which determines the frequency of the absorption peak for a sphere.

IV. PARTICLES IN A HOST MATERIAL

A. General theory

In this section we discuss a system in which many identically shaped particles are contained in a host material. Consider first a single particle with dielectric constant ϵ embedded in a host material with dielectric constant ϵ_h. A uniform electric field $\vec{E}^0$ at the frequency ω is again applied to the particle; $\vec{E}^0$ is now the macroscopic field in the host medium at a large distance from the particle. We calculate the induced dipole moment of the particle, just as in Sec. II. The electric field at any point $\vec{r}$ is given by an equation of the form (2), in which $\vec{P}(\vec{r}') \cdot \hat{n}(\vec{r}')$ is replaced by $[\vec{P}(\vec{r}') - \vec{P}^h(\vec{r}')] \cdot \hat{n}(\vec{r}')$, where $\vec{P}^h(\vec{r}')$ is the polarization in the host medium just outside the particle. One again takes $\vec{r}$ to lie just inside the particle, and eliminates $\vec{P}^h(\vec{r}')$, using the equation

$$\nabla \cdot \vec{D}(\vec{r}') = [(\chi_h^{-1} + 4\pi)\vec{P}^h(\vec{r}') - (\chi^{-1} + 4\pi)\vec{P}(\vec{r}')] \cdot \hat{n}(\vec{r}') = 0, \qquad (22)$$

where χ_h and χ are the electric susceptibilities of the host and the particle, respectively. In place of Eq. (3) one finds

$$(t\chi^{-1} + 2\pi)p(\vec{r}) = \int' \frac{\hat{n}(\vec{r}) \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} p(\vec{r}') \, dS'$$
$$+ t\vec{E}^0 \cdot \hat{n}(\vec{r}) \ , \qquad (23)$$

where

$$t = \frac{\epsilon_h(\epsilon - 1)}{\epsilon - \epsilon_h} \ .$$

Equation (23) differs from Eq. (3) through the replacement of $\vec{E}^0$ by $t\vec{E}^0$, and χ^{-1} by $t\chi^{-1}$. Using Eq. (7) or (8) to calculate the dipole moment, one finds, in place of Eq. (1), the result[9]

$$M_\alpha = v\sum_{\beta=1}^{3}\langle \chi^R_{\alpha\beta}(\omega) \rangle t E^0_\beta \ , \qquad (24)$$

where $\langle \chi_{\alpha\beta}^R(\omega) \rangle$ is the particle susceptibility calculated using $t\chi^{-1}$ in Eq. (3) instead of χ^{-1}. If we note that $\chi^{-1} = 4\pi(\epsilon - 1)^{-1}$ and $t\chi^{-1} = 4\pi(\epsilon/\epsilon_h - 1)^{-1}$, it is clear that $\langle \chi_{\alpha\beta}^R(\omega) \rangle$ is to be calculated using the relative dielectric constant ϵ/ϵ_h in place of ϵ in Eq. (3). The normal-mode expansion of $\langle \chi_{\alpha\beta}^R(\omega) \rangle$, analogous to Eq. (14), is

$$\langle \chi_{\alpha\beta}^R(\omega) \rangle = \frac{1}{4\pi} \sum_m \frac{C_{\alpha\beta}(m)}{(\epsilon/\epsilon_h - 1)^{-1} + n_m} \; ; \quad (25)$$

for a symmetric particle such as a cube, Eq. (19) becomes

$$\langle \chi^R(\omega) \rangle = \frac{1}{4\pi} \sum_m \frac{C(m)}{(\epsilon/\epsilon_h - 1)^{-1} + n_m} \; . \quad (26)$$

An expression for the average dielectric constant ϵ_{av} of the host material containing many randomly oriented identical particles can now be obtained. It is assumed that the spacing between particles is much larger than the particle size, so that the same uniform field $\vec{E}^0$ acts on each particle. Furthermore, since the particles are much smaller than the wavelength of light, the scattering of light by the particles is negligible in comparison with the absorption, and it is valid to characterize the system by an average dielectric constant. The average dipole moment of a randomly oriented particle is, from Eq. (24),

$$\vec{M}_{av} = v \langle \chi^R(\omega) \rangle t \vec{E}^0 , \quad (27)$$

where

$$\langle \chi^R(\omega) \rangle = \tfrac{1}{3} \text{Tr} \langle \chi_{\alpha\alpha}^R(\omega) \rangle \quad (28)$$

is the rotationally averaged particle susceptibility or the scalar particle susceptibility for a symmetric particle. The average electric field in the mixture is

$$\vec{E}_{av}^c = f\vec{E}_{av} + (1 - f)\vec{E}_{av}^h , \quad (29)$$

and the average polarization is

$$\vec{P}_{av}^c = f\vec{P}_{av} + (1 - f)\vec{P}_{av}^h , \quad (30)$$

where f is the fraction of the total volume occupied by the particles, $\vec{E}_{av}$ and $\vec{E}_{av}^h$ are the average electric field inside and outside the particles, and $\vec{P}_{av}$ and $\vec{P}_{av}^h$ are the average polarization inside and outside the particles, respectively. Using the relations[10] $\vec{E}_{av}^h \approx \vec{E}^0$, $\vec{P}_{av}^h \approx \chi_h \vec{E}^0$, $\vec{P}_{av} = v^{-1}\vec{M}_{av}$, $\vec{E}_{av} = (v\chi)^{-1}\vec{M}_{av}$, and Eq. (27) we find that the average susceptibility of the mixture is

$$\chi_{av} = \frac{|\vec{P}_{av}^c|}{|\vec{E}_{av}^c|} = \frac{ft \langle \chi^R(\omega) \rangle + (1 - f)\chi_h}{ft \chi^{-1} \langle \chi^R(\omega) \rangle + (1 - f)} \; . \quad (31)$$

Finally, the average dielectric constant is

$$\epsilon_{av} = 1 + 4\pi\chi_{av}$$
$$= \frac{4\pi f \epsilon \langle \chi^R(\omega) \rangle + (\epsilon - \epsilon_h)(1 - f)}{4\pi f \epsilon_h \langle \chi^R(\omega) \rangle + (\epsilon - \epsilon_h)(1 - f)} \epsilon_h . \quad (32)$$

Although Eq. (32) approaches the correct limiting values for both $f \to 0$ and $f \to 1$, it is valid only in the low-particle-density limit $f \ll 1$. If terms of order f^2 and smaller are neglected, Eq. (32) can be written

$$\epsilon_{av} = \epsilon_h[1 + 4\pi f \langle \chi^R(\omega) \rangle] . \quad (33)$$

For spherical particles

$$4\pi \langle \chi^R(\omega) \rangle = \frac{1}{(\epsilon/\epsilon_h - 1)^{-1} + \frac{1}{3}} \; ; \quad (34)$$

Eq. (32) then reduces to the well-known result[11,12]

$$\epsilon_{av} = \frac{\epsilon(2f + 1) + 2\epsilon_h(1 - f)}{\epsilon(1 - f) + \epsilon_h(2 + f)} \epsilon_h . \quad (35)$$

B. Optical absorption

An often-used experimental arrangement for determining the optical properties of small particles is to measure the transmission of light through a thin slab of the host material containing the particles. The absorption coefficient of the slab is

$$\alpha = \frac{\omega}{c} \frac{\text{Im}\epsilon_{av}}{\text{Re}\sqrt{\epsilon_{av}}}$$
$$\approx 4\pi \frac{\omega}{c} \sqrt{\epsilon_h} f \text{Im} \langle \chi^R(\omega) \rangle \quad (36)$$

for $f \ll 1$, where, in the last expression, the absorption of the host material has been neglected by taking ϵ_h real.

C. Electron energy loss

If fast electrons pass through a thin sample, they can lose energy by generating excitations in the sample volume.[13] The probability that an electron loses energy $\hbar\omega = E_i - E_f$ while undergoing a wave vector change $\vec{k} = \vec{k}_i - \vec{k}_f$ is proportional to the energy-loss function $-\text{Im}\epsilon_{av}^{-1}(\vec{k}, \omega)$. If the experimental conditions are chosen such that $kl \ll 1$, where l is the particle size,[14] one can approximate $\epsilon_{av}(\vec{k}, \omega) \approx \epsilon_{av}(0, \omega)$, the dielectric response function for a uniform field. From Eq. (33) we then have

$$-\text{Im}\epsilon_{av}^{-1}(\omega) = 4\pi(f/\epsilon_h) \text{Im} \langle \chi^R(\omega) \rangle , \quad (37)$$

where it has again been assumed that ϵ_h is real. From a comparison of Eqs. (36) and (37) it is evident that apart from the factor ω in Eq. (36) and the possible ω dependence of ϵ_h, the ω dependence of both the optical absorption and the electron energy loss is determined by $\text{Im} \langle \chi^R(\omega) \rangle$, the imaginary part of the particle susceptibility.

V. PARTICLE SUSCEPTIBILITY OF A CUBE

The particle susceptibility $\langle \chi \rangle$ for a cube has been determined by applying an external field $\vec{E}^0$ along a cube axis, solving Eq. (4) for the values of the surface polarization charge p_i, and using
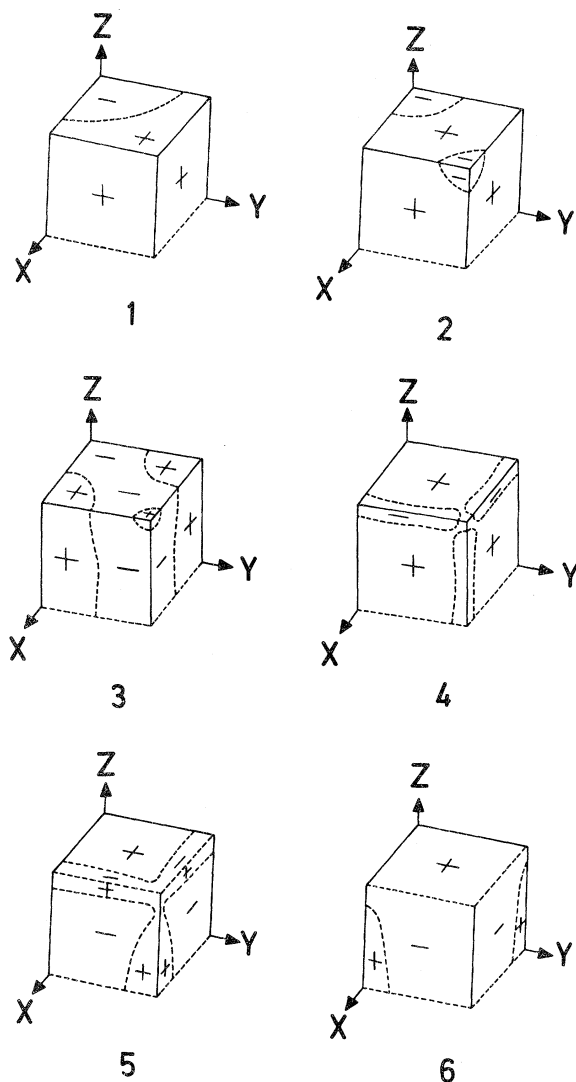
FIG. 1. Normal modes corresponding to the six major absorption peaks of a cube. The numbering corresponds to that of Table I.

Eq. (8) to calculate the dipole moment $\vec{M}$. Since $\vec{M}$ and $\vec{E}^0$ are parallel, we have, from Eqs. (1) and (18), $\langle \chi \rangle = v^{-1} |\vec{M}| / |\vec{E}^0|$. Each face of the cube was divided into $(2N)^2 = 144$ small squares (with $N = 6$), and the values of p_i were determined at the centers of the small squares. Only $N^2 + N(N+1)/2 = 57$ values of p_i, lying within or on the boundary of a region with $\frac{1}{16}$ the total surface area of the cube, are independent, the values at the remaining points being determined by symmetry. If χ' is varied in Eq. (4) while holding χ'' at a small constant positive value, the resonances of the cube appear as sharp peaks in $\langle \chi'' \rangle$ at certain values of χ', which we shall denote χ'_m. If the results are brought into the form of Eq. (19), the depolarization factors are determined by $n_m = -(4\pi\chi'_m)^{-1}$ and

the constants $C(m) = \langle \chi'' \rangle_{\max} \chi'' (\chi'_m)^{-2}$, where $\langle \chi'' \rangle_{\max}$ is the maximum value of $\langle \chi'' \rangle$ occurring when $\chi' = \chi'_m$.[15]

Nine or ten resonances appear, but only six of them have a significant strength.[16] The values of the depolarization factors n_m and the constants $C(m)$ for these six major resonances are given in Table I. Since $\sum_{m=1}^{6} C(m) = 0.96$, these six resonances account for all but 4% of the absorption.

The normal modes corresponding to the six major absorption peaks are shown in Fig. 1. In these figures the sign of the real part of p (the surface polarization charge or the normal component of $\vec{P}$) over one-eighth of the cube is shown. The applied field $\vec{E}^0$ is in the z direction, and the origin of the coordinate system lies at the center of the cube. The zeros of Re(p) on the surface are shown by dashed lines. The dipole moment is in the $+z$ direction for all normal modes. These normal modes belong to the representation Γ_{15} of the cubic point group O_h; there is fourfold symmetry about the z axis, and the Re(p) changes sign under reflection in the xy plane.

The calculation of p for each normal mode was made by taking χ for the material real and slightly smaller (more negative) than the value χ_m at which resonance occurs. Since Re(p) and the total dipole moment Re(M_z) become infinite when χ is exactly at the resonance values χ_m, the contribution of the other normal modes can be neglected when χ is sufficiently near a given χ_m. Under the conditions of the calculation, with $\chi < \chi_m$, Re(M_z) > 0. If $\chi > \chi_m$, Re(p) and Re(M_z) reverse sign.

Figure 1 gives no indication of the relative amplitude of the polarization charge on different parts of the surface. For normal modes 1 and 2 the amplitude is particularly high at the corners, and for modes 5 and 6 it is high at the center of the faces parallel to the xy plane. A comparison of the normal modes with those of an infinite wedge is made in the Appendix.

VI. RESULTS AND DISCUSSION

Using Eqs. (26) and (36) calculations of the infrared absorption coefficient α as a function of the

TABLE I. Values of $C(m)$, n_m, and $\epsilon'(\omega)$ for the six major absorption peaks of a cube. $\epsilon'(\omega)$, the value of the real part of the material dielectric function at each absorption peak, is given by $\epsilon'(\omega) = 1 - n_m^{-1}$.

m	$C(m)$	n_m	$\epsilon'(\omega)$
1	0.44	0.214	−3.68
2	0.24	0.297	−2.37
3	0.04	0.345	−1.90
4	0.05	0.440	−1.27
5	0.10	0.563	−0.78
6	0.09	0.706	−0.42
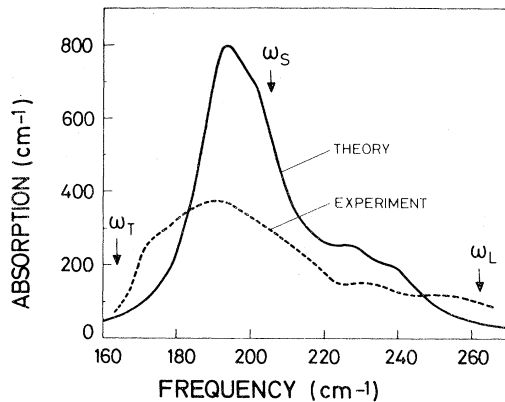
FIG. 2. Absorption coefficient for NaCl cubes in paraffin as a function of frequency. The arrows labeled ω_T, ω_L, and ω_S show, respectively, the transverse optical frequency, the longitudinal optical frequency, and the resonance frequency for a sphere.

frequency have been made for the following systems of small cubic particles: NaCl in paraffin, and MgO in air. In Fig. 2 the theoretical absorption for NaCl cubes is compared with the measurements of Bryksin et $al.$[17] for cubes about 2 μm in diameter embedded in paraffin. Figure 3 compares the theory with experiments of Genzel and Martin[12] on MgO cubes, with an average size of 0.1 μm, contained in air. Since the filling factor f was not known experimentally, a crudely estimated value of f was used in the calculation of α. The transmittance T of a thin layer of the sample was measured; this can be related to α by the approximate expression $T = e^{-\alpha x}$, where x is the sample thickness. Since x is not known, the experimental absorption in Figs. 2 and 3 was obtained by adjusting x so that the experimental and theoretical curves were in approximate agreement.

The single-oscillator expression

$$\epsilon = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)\omega_T^2}{\omega_T^2 - \omega(\omega + i\gamma)} \qquad (38)$$

was used for the dielectric constant, with the following parameters: For NaCl, $\epsilon_\infty = 2.33$, $\epsilon_0 = 5.93$, $\omega_T = \lambda_T^{-1} = 164$ cm^{-1}, $\gamma = 0.1\omega_T$, $\epsilon_h = 1.96$, and $f = 0.058$; for MgO, $\epsilon_\infty = 2.95$, $\epsilon_0 = 9.42$, $\omega_T = 394$ cm^{-1}, $f = 0.03$, and γ is a frequency-dependent damping function determined for bulk MgO, multiplied by a factor 2.5.

The damping factor γ in the dielectric constant broadens the six cube absorption peaks, giving a single asymmetric peak with a maximum at a frequency lower than the resonance frequency of a sphere. If one uses a damping factor appropriate for the bulk material, the six absorption peaks are partially resolved, and the low-frequency peak is much too high. The damping factors used in the calculation, $\gamma = 0.1\omega_T$ for NaCl and $\gamma = 2.5$ times the

bulk value for MgO, are large enough that little structure appears in the absorption, in agreement with the measurements. It can therefore be concluded that the damping in small particles is larger than the damping in the bulk.[18] The over-all width of the peak, however, is caused by the frequency spread of the cube resonances. Genzel and Martin[12] analyzed their experiment on MgO by considering the particles to be small spheres, and found that the bulk damping factor had to be multiplied by a factor of 8 in order to explain the width of the measured absorption peak. The present calculations show that such an extremely high damping factor in the small particles need not be assumed if the shape is treated properly.

The present theory for a cube predicts that no absorption peak should occur at the transverse optical frequency ω_T. In NaCl one indeed observes no peak at ω_T, but in MgO there is clearly a peak at $\omega_T = 394$ cm^{-1}. A peak at ω_T also has been observed by Martin[19] in KCl cubes, but no such peak is seen in AgBr cubes.[5]

The MgO samples were prepared by burning Mg ribbon in air and collecting the smoke on a transparent substrate. The density of the powder was estimated to be between 3 and 4% of the density of massive MgO. Such a small filling fraction was obtained by the formation of the MgO cubes into open chainlike networks.[20] Since the depolarization factor of a cylinder is zero for a field parallel to its axis, it is possible that the chainlike structure would have an absorption peak at ω_T if a chain of cubes behaves like a cylinder.

Several other mechanisms can be proposed as possible explanations of an absorption peak at ω_T, but none is convincing. Calculations for a sphere show that if retardation is included, an absorption peak should appear at ω_T as the sphere size is in-
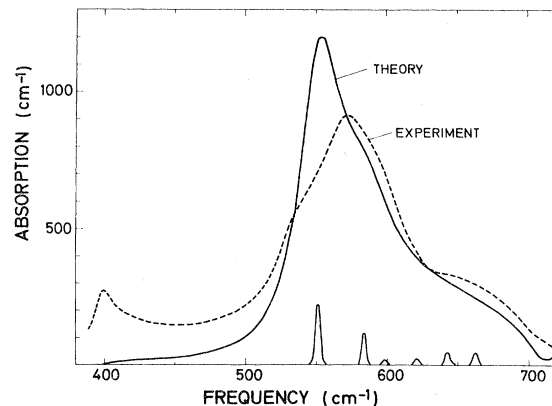

FIG. 3. Absorption coefficient for MgO cubes, as a function of frequency. The small unlabeled peaks show schematically the positions and relative amplitudes of the cube resonances.

creased, and then shift to lower frequencies for
still larger spheres. A similar effect should occur
for particles of different shapes. However, re-
tardation should be unimportant for particles small-
er than 1 μm, since such particles are much
smaller than the wavelength of light, 25 μm.

In this continuum theory without retardation
there are normal modes in a particle at ω_T, but
they produce no optical absorption since they are
not associated with surface polarization charge.
In a microscopic lattice dynamics theory, the
modification of the forces on the surface atoms
has two effects: an optical coupling to the modes
at ω_T is introduced, and strongly localized surface
modes, which can produce optical absorption, may
appear near ω_T.[21]

Martin[4] has shown, in a lattice-dynamical cal-
culation of the normal modes and optical absorp-
tion of very small rectangular alkali halide parti-
cles, containing on the order of 100 atoms, that
absorption indeed appears in the neighborhood of
ω_T. For crystals as large as those used in the
experiments, containing 10^7 or more atoms, such
effects should be negligible. An explanation of
this type also does not show why the absorption at
ω_T should be entirely absent in some experiments.

The energy-loss spectrum of electrons passing
through a sample containing small MgO cubes has
been determined,[22] and was found to be the same
as the optical absorption spectrum of a similar
sample, in agreement with the theory discussed in
Secs. IVB and IVC. A peak at ω_T was also found,
although it is not as distinct as the optical absorp-
tion peak because of the limited resolution of the
energy-loss experiment.

For both NaCl and MgO it has been found that the
experiments can best be fit if the damping parame-
ter γ for the bulk material is increased by a factor
of about 2.5. However, it is not certain whether
this increased damping is an intrinsic property of
a small cube, or only represents the effects of ir-
regular particle shapes, interaction between par-
ticles, or other sample irregularities, which would
also broaden the absorption peaks. To show that
the damping is an intrinsic property, a dependence
of γ on the cube size would have to be demonstrated.

ACKNOWLEDGMENTS

APPENDIX

The normal modes of a cube which we have found
will be discussed in more detail and compared with
the results of other calculations. The edges of the
cube are singular points in the integral equation (3),
since $\vec{r} - \vec{r}' \to 0$ if $\vec{r}$ and $\vec{r}'$ are on adjacent faces of

the cube and are allowed to approach the same
point on the edge common to the two faces. The
singularity has not been removed in the calculation,
so it is possible that the true behavior of the polar-
ization charge near the edges cannot be accurately
represented at a reasonable number of discrete
points. Therefore we shall attempt to assess the
accuracy of the results.

van Gelder et al.[5] have found the normal modes
by expanding the potential outside the cube in a
series of the form

$$\phi(r, \theta, \varphi) = \sum_{LM} C_{LM} \, r^{-(L+1)} Y_{LM}(\theta, \varphi) \; .$$

Nine functions, each belonging to the representa-
tion Γ_{15} of the cubic group O_h, were used. Their
procedure lead to the diagonalization of a 9×9 ma-
trix. The nine eigenvalues, expressed as the value
of the real part of the material dielectric function
at which the resonances occur, are $\epsilon' = -2.44$,
-1.32, -1.10, -1.08, -1.03, -1.02, -1.00,
-0.96, -0.79. The dipole moment associated
with each normal mode was not determined. These
eigenvalues span a much smaller range than the
six physically most important eigenvalues we have
found, as given in the last column of Table I. The
most likely explanation for the discrepancy is that
the fields cannot be represented with enough accu-
racy by only nine functions. We have found the
surface charge density at the center of $6 \times (2N)^2$
$= 864$ small squares (with $N = 6$) on the surface of
the cube.[23] The most rapid variation of surface
charge that can be represented is such that there
is a large change in amplitude at adjacent points,
which differ in angle by about $\pi/4N$ rad as seen
from the center of the cube. To allow such a rap-
id variation in a spherical harmonic expansion
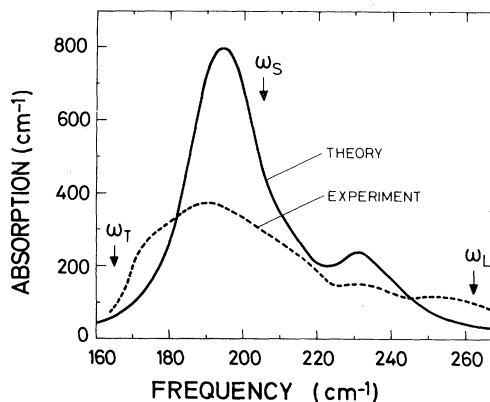would require L values up to about 25, which in-

FIG. 4. Absorption coefficient for NaCl cubes in paraf-
fin as a function of frequency. Extrapolated values of
n_m and $C(m)$ were used, as described in the text.

volves a total of about 50 spherical harmonics and yields 50 normal modes.[24] An examination of the normal modes (Fig. 1) shows that such a rapid variation must be allowed, especially near the cube edges.

The dependence of the depolarization factors n_m and the absorption strength factors $C(m)$ on the quantity N has been investigated. Repeating the calculation for $N = 5$, 6, and 7, a systematic dependence on N was found, such that when n_m and $C(m)$ were plotted as functions of N^{-1} a linear extrapolation could be made to $N^{-1} = 0$ or $N = \infty$. Such an extrapolation cannot be justified mathematically; however, it gives the values $n_1 = 0.193$, $n_2 = 0.251$, $n_3 = 0.294$, $n_4 = 0.396$, $n_5 = 0.605$, $n_6 = 0.719$, $C(1) = 0.31$, $C(2) = 0.31$, $C(3) = 0.07$, $C(4) = 0.07$, $C(5) = 0.13$, $C(6) = 0.04$. Although these extrapolated values of n_m and $C(m)$ differ considerably from those given in Table I for $N = 6$, there is little difference in the final calculated absorption, if the damping in the dielectric constant is large enough that the individual modes cannot be resolved. This is illustrated by Fig. 4, which shows the absorption for NaCl cubes in paraffin calculated with $N = \infty$; clearly this is similar to the absorption shown in Fig. 2, which was calculated with $N = 6$.

The normal modes of a cube show certain similarities to the electrostatic edge modes in a dielectric wedge formed by the intersection of two semi-infinite planes, which were investigated analytically by Dobrzynski and Maradudin.[25] In a cylindrical coordinate system (r, θ, z) with the z axis along the edge, the normal mode frequency of the wedge is found to be a function of a continuous variable μ which determines the r and θ variation of the fields; for increasing values of μ the fields are more strongly localized at the vacuum-dielectric interfaces and at the edge ($r = 0$). The solutions can be divided into two classes, such that the fields have either even or odd parity about the plane bisecting the wedge. For a 90° wedge, the even-parity modes appear if the dielectric function is in the range $-3 < \epsilon' < -1$, and the odd-parity modes appear for $-1 < \epsilon' < -\frac{1}{3}$. Thus the over-all range of ϵ' for which solutions exist for the wedge is $-3 < \epsilon' < -\frac{1}{3}$, corresponding qualitatively to the range $-3.68 \leq \epsilon' \leq -0.42$ for the normal modes of a cube. This correspondence indicates that the 90° edges of a cube play an important role in determining the spread of ϵ' values for the normal modes. The shift for the cube normal modes toward somewhat more negative values, as compared with the normal modes of a 90° wedge, can be attributed to the finite extent of the cube edges.

Figure 1 shows that the surface polarization charge for the cube modes 1-4, which occur for $\epsilon' < -1$, has the same sign on either side of the edges perpendicular to the z axis, a behavior analogous to that of the even-parity wedge modes in the same ϵ' range. Similarly in the range $\epsilon' > -1$, the polarization charge for the cube modes 5 and 6 reverses sign at these edges, a behavior analogous to that of the odd-parity wedge modes. The edges of the cube therefore exert an important influence on both the form of the normal modes and the range of ϵ' over which normal modes exist.

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[2] U. Kreibig, J. Phys. F: Metal Phys. **4**, 999 (1974).

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[5] A. P. van Gelder, J. Holvast, J. H. M. Stoelinga, and P. Wyder, J. Phys. C **5**, 2757 (1972).

[6] If the particles are large enough that retardation is important, the transverse modes will also be associated with optical absorption.

[7] Separating the term $-2\pi p(\vec{r})$ does not remove the singular behavior of the integral as $|\vec{r} - \vec{r}'| \to 0$ when $\vec{r}$ and $\vec{r}'$ are on adjacent faces of a cube.

[8] This conductivity sum rule can also be derived from the Kramers-Kronig relations.

[9] Even when the particles are embedded in a host medium, the dipole moment is given by Eq. (6), the volume integral of the polarization within the particle, or the equivalent surface integral (7). If the contribution of the surface polarization charge of the host material were included, Eq. (7) would become $M_\alpha = \int (\vec{P} - \vec{P}^h) \cdot \hat{n} \, x x_\alpha \, dS$, and the factor t would be missing from Eq. (24).

The final result (32) is independent of how the dipole moment is defined.

[10] $\vec{E}_{av}^h \approx \vec{E}^0$ if the particles are well separated ($f \ll 1$).

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[13] Surface excitations and Čerenkov radiation are ignored in the following discussion. It is also assumed that only single scattering occurs.

[14] The electron scattering angle θ must be small and the electron energy E_i must be high in order to make the change in both the direction and magnitude of the wave vector small. That is, $\theta \ll (k_i l)^{-1}$ and $E_i \gg m l^2 \omega^2$, where m is the electron mass.

[15] n_m and $C(m)$ could also be determined from Eqs. (15) and (16). However, this would require that the eigenvalues and eigenvectors of the real, unsymmetric matrix R_{ij} be determined. The eigenvalues of R_{ij} are not necessarily real, although physically they must be real. The surface polarization eigenvectors of R_{ij} are orthogonal only if they are of different symmetry. If one were to consider the volume polarization, all normal modes would be orthogonal.

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[23]Of these 864 points, only 57 are independent; our calculation thus yields 57 normal modes belonging to Γ_{15}.

[24]The spherical harmonics $Y_L^M (\theta, \varphi)$ belonging to Γ_{15} have $L = 2l + 1$ and $M = 4m$, where l and m are integers. For $L \leq 25$ there are about 50 such spherical harmonics, a number comparable to the 57 normal modes obtained in the present calculation.

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