Mie resonance for spherical metal particles in an anisotropic dielectric

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The absorption coefficient for small metal particles randomly distributed in a uniaxial dielectric host is calculated using the Maxwell-Garnett effective-medium theory. Explicit expressions for the absorption coefficient are given for the limit of low metallic volume fraction. Incorporation of dielectric anisotropy into the theory provides improved agreement with published data on colloidal Na in NaN_3.

I. INTRODUCTION

A comparison of the frequency for maximum absorption ω_0 and line shape of the sphere resonance as predicted by the classical Mie theory[1] with data on small metal particles supported in dielectric hosts reveals systematic discrepancies. For example, there is a red shift of the measured value of ω_0 with respect to Mie theory for alkali-metal particles in colored alkali halides.[2]

The dependence of ω_0 on the dielectric constant of the host might provide evidence to support or refute at least one proposed explanation[3] for the red shift. Unfortunately, it is very difficult to produce particles with the same properties (size, distribution, shape, etc.) reproducibly in a number of hosts, or even to determine the properties of the particles in a given sample.

An anisotropic dielectric in effect has more than one dielectric constant. A sample of spherical metal particles embedded in an anisotropic dielectric can be probed by electromagnetic waves of suitably chosen polarization and direction of propagation to accurately measure the dependence of ω_0 on the dielectric constant of the host.

The purpose of this paper is to discuss the absorption coefficient of a collection of small spherical metal particles randomly embedded in a uniaxial dielectric host using the Maxwell-Garnett[4] effective-medium theory. Explicit expressions for the absorption coefficient are given for the limit of small metal volume fraction f, for which the Mie theory applies. The specialization to the uniaxial case retains the important physics, simplifies the mathematics, and applies to the example, colloidal Na in sodium azide (NaN_3), chosen to illustrate the effect. For Na in NaN_3 the relative splitting predicted by the theory is less than 1% of ω_0.

This paper is organized as follows: Section II briefly reviews the physics of electromagnetic waves propagating in a transparent anisotropic dielectric. Section III derives the Maxwell-Garnett effective dielectric function for small metal spheres embedded in a uniaxial dielectric host. Section IV derives the absorption coefficient for both ordinary and extraordinary waves propagating in this uniaxial effective medium and presents explicit results for the low-f limit. Finally, Sec. V applies the theory to colloidal Na in NaN_3 and compares the results with the experimental data of Smithard.[5]

II. ELECTROMAGNETIC WAVES IN A UNIAXIAL DIELECTRIC

Landau and Lifshitz and Born and Wolf,[6,7] among others, discuss the propagation of electromagnetic waves in a uniaxial nonabsorbing dielectric crystal. The symmetric dielectric tensor can be diagonalized to yield the eigenvalues ϵ_x, ϵ_y, and ϵ_z along the principal axes. Let the z axis be the axis of symmetry for the uniaxial crystal. Then $\epsilon_x=\epsilon_y\equiv\epsilon_\perp$ and $\epsilon_z\equiv\epsilon_{||}$. If $\epsilon_{||}>\epsilon_\perp$ the crystal is called "positive." For plane waves Maxwell's equations require that the triplets **D**, **H**, and the wave vector **k** and **E**, **H**, and the Poynting vector **S** be mutually perpendicular. Therefore, **E**, **D**, **k**, and **S** are coplanar. **S** specifies the direction of energy propagation, which determines where the light actually goes. For a direction denoted by either **k** or **S**, two linearly polarized waves propagate in the crystal. The "ordinary" wave behaves just like a wave in an isotropic medium (**k**||**S**, etc.). For the "extraordinary" wave, **S** is not parallel to **k** except for special directions. For example, both waves are ordinary for propagation parallel to the axis of symmetry. This degeneracy permits elliptically polarized waves as solutions.

A beam of light incident on a uniaxial crystal undergoes double refraction—there are two refracted beams. The Poynting vector of the extraordinary refracted wave need not lie in the plane of incidence.

Born and Wolf discuss propagation of light[8] in an absorbing uniaxial crystal in the limit of weak absorption, since the general problem is mathematically tedious. The dielectric tensor is now complex, but otherwise the derivation resembles that for the transparent dielectric. The solutions are elliptically polarized and **D** is not perpendicular to **k**.

III. THE EFFECTIVE DIELECTRIC FUNCTION

Consider the propagation of electromagnetic waves of wavelength λ in a medium of small spherical metal particles of radius a and complex dielectric function $\hat{\epsilon}=\epsilon'+i\epsilon''$ distributed randomly in a transparent uniaxial dielectric host characterized by the diagonal elements $\epsilon_x=\epsilon_y\equiv\epsilon_\perp$ and $\epsilon_z\equiv\epsilon_{||}$ in the principal coordinate system. In the quasistatic limit, $\lambda\gg a$, the response of the medium can be described by an effective dielectric tensor $\bar{\epsilon}_{ij}(\omega)$. Let E_i be the component of $\mathbf{E}$ parallel to the ith principal axis of the host. The Maxwell-Garnett[4] effective dielectric function follows from a volume average of the electric field and electric displacement vectors, given by

$$\begin{aligned}\bar{E}_i&=fE_i^{(i)}+(1-f)E_i^{(e)}\ ,\\ \bar{D}_i&=\bar{\epsilon}_i\bar{E}_i=f\hat{\epsilon}E_i^{(i)}+(1-f)\epsilon_iE_i^{(e)}\ ,\end{aligned}\tag{1}$$

where $E_i^{(i)}$ and $E_i^{(e)}$ are the ith components of the electric fields inside and external to the metal particle, respectively, and f is the volume fraction of metal in the medium. Also required is the electrostatic boundary condition[9]

$$E_i^{(i)}=\frac{\epsilon_i}{\epsilon_i-L_i(\epsilon_i-\hat{\epsilon})}E_i^{(e)}\ .\tag{2}$$

The depolarization factor is[9]

$$L_i=\frac{a^3}{2(\epsilon_{||}\epsilon_\perp^2)^{1/2}}\int_0^\infty\frac{ds}{(s^2+a^2/\epsilon_i)R_s}\ ,\tag{3}$$

where

$$R_s^2=(s+a^2/\epsilon_\perp)^2(s+a^2/\epsilon_{||})\ .\tag{4}$$

The integrals can be evaluated.[9] According to Landau and Lifshitz,

$$L_{||}=\begin{cases}\dfrac{1-e^2}{2e^3}\left[\ln\left|\dfrac{1+e}{1-e}\right|-2e\right], & \epsilon_{||}<\epsilon_\perp\\ \dfrac{1+e^2}{e^3}(e-\tan^{-1}e), & \epsilon_{||}>\epsilon_\perp,\end{cases}\tag{5}$$

$$L_\perp=(1-L_{||})/2\ ,$$

where

$$e=|(\epsilon_{||}/\epsilon_\perp)-1|^{1/2}\ .\tag{6}$$

The field-matching condition in Eq. (2) is identical to that for an ellipsoidal particle in an isotropic dielectric,[10] for which the depolarization factors are determined by the shape of the ellipsoid. The Maxwell-Garnett effective dielectric tensor in the principal coordinate system, obtained by combining Eqs. (1) and (2), is

$$\bar{\epsilon}_i=\frac{\epsilon_i\{[\epsilon_i-L_i(\epsilon_i-\hat{\epsilon})]-f(1-L_i)(\epsilon_i-\hat{\epsilon})\}}{[\epsilon_i-L_i(\epsilon_i-\hat{\epsilon})]+fL_i(\epsilon_i-\hat{\epsilon})}\ .\tag{7}$$

The complex effective dielectric function retains uniaxial symmetry, so that $\bar{\epsilon}_x=\bar{\epsilon}_y=\bar{\epsilon}_\perp$ and $\bar{\epsilon}_z=\bar{\epsilon}_{||}$.

For a plane wave of wave vector $\mathbf{k}$ (direction $\hat{k}$) propagating in the effective medium, manipulation of Maxwell's equations and the constitutive relation yields

$$(\bar{n}^2-\bar{\epsilon}_\perp)[\bar{n}^2\bar{\epsilon}_\perp(1-\hat{k}_z^2)+\bar{n}^2\bar{\epsilon}_{||}\hat{k}_z^2-\bar{\epsilon}_{||}\bar{\epsilon}_\perp]=0\ ,\tag{8}$$

where $\bar{n}^2=\bar{\epsilon}=\bar{\epsilon}'+i\bar{\epsilon}''$. The roots of Eq. (8) are

$$\begin{aligned}\bar{\epsilon}_o&=\bar{\epsilon}_\perp\ ,\\ \bar{\epsilon}_e&=\frac{\bar{\epsilon}_{||}\bar{\epsilon}_\perp}{\bar{\epsilon}_\perp(1-\hat{k}_z^2)+\bar{\epsilon}_{||}\hat{k}_z^2}\ ,\end{aligned}\tag{9}$$

for the ordinary and extraordinary waves, respectively. Let θ be the angle between $\hat{k}$ and the z axis. For the extraordinary wave,

$$\begin{aligned}\bar{\epsilon}_e'&=\frac{\bar{\epsilon}_\perp'(\bar{\epsilon}_{||}'^2+\bar{\epsilon}_{||}''^2)\cos^2\theta+\bar{\epsilon}_{||}'(\bar{\epsilon}_\perp'^2+\bar{\epsilon}_\perp''^2)\sin^2\theta}{(\bar{\epsilon}_{||}'\cos^2\theta+\bar{\epsilon}_\perp'\sin^2\theta)^2+(\bar{\epsilon}_{||}''\cos^2\theta+\bar{\epsilon}_\perp''\sin^2\theta)^2}\ ,\\ \bar{\epsilon}_e''&=\frac{\bar{\epsilon}_\perp''(\bar{\epsilon}_{||}'^2+\bar{\epsilon}_{||}''^2)\cos^2\theta+\bar{\epsilon}_{||}''(\bar{\epsilon}_\perp'^2+\bar{\epsilon}_\perp''^2)\sin^2\theta}{(\bar{\epsilon}_{||}'\cos^2\theta+\bar{\epsilon}_\perp'\sin^2\theta)^2+(\bar{\epsilon}_{||}''\cos^2\theta+\bar{\epsilon}_\perp''\sin^2\theta)^2}\ .\end{aligned}\tag{10}$$

IV. THE ABSORPTION COEFFICIENT

The problem has been reduced to a calculation of the absorption coefficient of a homogeneous absorbing anisotropic medium. For the ordinary wave,

$$\alpha_o=\frac{\omega}{c}(2|\bar{\epsilon}_o|-2\bar{\epsilon}_o')^{1/2}\ .\tag{11}$$

If $f\ll1$,

$$\alpha_o=\frac{f\omega\epsilon_\perp^{3/2}}{c}\frac{\epsilon''}{[\epsilon_\perp-L_\perp(\epsilon_\perp-\epsilon')]^2+L_\perp^2\epsilon''^2}\ .\tag{12}$$

For Drude-metal particles with bulk plasma frequency ω_p and high-frequency dielectric constant ϵ_∞, the frequency of the sphere resonance is approximately

$$\omega_\perp=\omega_p/[\epsilon_\infty+(L_\perp^{-1}-1)\epsilon_\perp]^{1/2}\ .\tag{13}$$

The ordinary wave lives up to its name. For the extraordinary wave,

$$\alpha_e=\frac{\omega}{c}(2|\bar{\epsilon}_e|-2\bar{\epsilon}_e')^{1/2}\ ,\tag{14}$$

which is a complicated expression when written explicitly. In the Mie limit ($f\ll1$),

$$\begin{aligned}\alpha_e=\frac{f\omega}{c}&\frac{(\epsilon_\perp\epsilon_{||})^{3/2}\epsilon''}{[\epsilon_{||}\cos^2\theta+\epsilon_\perp\sin^2\theta]^{3/2}}\\ &\times\left[\frac{\cos^2\theta}{[\epsilon_\perp-L_\perp(\epsilon_\perp-\epsilon')]^2+L_\perp^2\epsilon''^2}\right.\\ &\left.+\frac{\sin^2\theta}{[\epsilon_{||}-L_{||}(\epsilon_{||}-\epsilon')]^2+L_{||}^2\epsilon''^2}\right].\end{aligned}\tag{15}$$

This result can also be obtained by following Born and Wolf's[8] procedure for the limit of weak absorption. For Drude-metal particles, unless $\theta=0$ or $\pi/2$, there are two resonance frequencies, $\omega_\perp$ [Equation (13)] and

$$\omega_{||}=\omega_p/[\epsilon_\infty+(L_{||}^{-1}-1)\epsilon_{||}]^{1/2}\ .\tag{16}$$

The relative strength of the resonances depends on θ. If

$\epsilon_\perp = \epsilon_{||}$, Eq. (15) reduces correctly to the familiar Mie expression for particles in an isotropic medium.

V. DISCUSSION

To measure the dependence of ω_0 on the dielectric constant of the host using small metal particles in a uniaxial dielectric, the ideal orientation of the sample is with the axis of symmetry in the plane of the surface. Then a linearly polarized wave at normal incidence could be coupled completely into the ordinary ($\omega_0 = \omega_\perp$) or extraordinary ($\omega_0 = \omega_{||}$) wave in turn by rotating the plane of polarization. Since the composite medium absorbs radiation, the solutions are elliptically polarized, but the polarization is nearly linear in the limit of weak absorption.

An example of the system under consideration for which the sphere plasma resonance has been studied experimentally[5] is colloidal Na in colored NaN_3. NaN_3 is a rhombohedral crystal with $n_o = \sqrt{\epsilon_\perp} = 1.38$ and $n_e = \sqrt{\epsilon_{||}} = 1.52$.[11] Smithard and Tran[12] performed a fit of the Drude model to the data of Smith[13] for ϵ' of Na to obtain $\hbar\omega_p = 5.54$ eV, and $\epsilon_\infty = 1.25$. For these values, Eqs. (5), (6), (13), and (16) give $e = 0.462$, $L_\perp = 0.320$, $L_{||} = 0.359$, $\hbar\omega_\perp = 2.41$ eV (5148 Å), and $\hbar\omega_{||} = 2.39$ eV (5185 Å). The splitting is less than 1% of the resonance frequency, but such an effect should be measurable in the visible.

Smithard[5] studied samples of Na in NaN_3 with the axis of symmetry perpendicular to the surface, since NaN_3 grows in thin plates and cleaves with the largest face in this orientation. The wavelength for maximum absorption depends on the annealing time, which is thought to be related to the mean particle size. The minimum measured wavelength for the peak was about 5200 Å. Smithard ignored the anisotropy of NaN_3 in his model. For Drude Na with the parameters given above and a relaxation time corrected for boundary scattering[14] by the conduction electrons $\tau = (\tau_B^{-1} + v_F/a)^{-1}$ with bulk relaxation $\tau_B = 3.36 \times 10^{-14}$ s, Fermi velocity $v_F = 1.03 \times 10^8$ cm/s, and particle radius $a = 15$ Å in an isotropic dielectric with constant $\epsilon_0 = 1.904$, Eq. (12) predicts a resonance at 5034 Å. Smithard's somewhat more complicated model yields 5020 Å for the peak. Taking the anisotropy of NaN_3 into account, the predicted resonance for Drude Na particles is at 5147 Å in substantially better agreement with experiment. The remaining red shift of the measured peak is about the same size as found by Smithard and Tran[12] for Na particles in isotropic NaCl. Several mechanisms[3,15–19] have been proposed to explain the increasing red shift with decreasing particle size for very small particles.

A disadvantage with the Na in NaN_3 system is that the particles have not yet been examined under an electron microscope to determine sizes and shapes. If the particles are oriented ellipsoids of revolution, rather than spheres, there are two resonance frequencies,

$$\omega_i = \omega_p / [\epsilon_\infty + (L_i^{-1} - 1)\epsilon_0]^{1/2} , \tag{17}$$

where the subscript $i = ||, \perp$ identifies the principal axes. The depolarization factors L_i are given by Eqs. (5) and (6) with $\epsilon_{||}/\epsilon_\perp$ replaced by $(d_\perp/d_{||})^2$, where $d_{||}$ and $d_\perp$ are the axes of the ellipsoid parallel and perpendicular to the direction of uniaxial symmetry. The absorption spectrum for oriented ellipsoidal particles with only a 1% difference between the lengths of the two axes would show a splitting comparable in magnitude to the prediction for Na in NaN_3, for which $\sqrt{\epsilon_{||}/\epsilon_\perp} = 1.10$. The difference is due to the replacement of $\epsilon_\perp$ and $\epsilon_{||}$ in Eqs. (13) and (16) by ϵ_0 in Eq. (17). Such a small ellipticity would be difficult to measure by electron microscopy.

In conclusion, this paper generalized the Maxwell-Garnett effective-medium theory to include the case of small spherical metal particles embedded in a uniaxial dielectric. Explicit expressions for the absorption coefficient obtained for low volume fractions of metal provide improved agreement with published experimental results on Na in NaN_3. This type of system could be used to study the effect of the dielectric constant of the host on the optical properties of the particles, but the samples must be well characterized and controlled with respect to morphology to avoid competing effects due to ellipticity of the particles.

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[1] G. Mie, Ann. Phys. (Leipzig) **25**, 377 (1908).
[2] A. E. Hughes and S. C. Jain, Adv. Phys. **28**, 717 (1979).
[3] R. P. Devaty and A. J. Sievers, Phys. Rev. B **24**, 1079 (1981).
[4] J. C. Maxwell-Garnett, Philos. Trans. R. Soc. London **203**, 385 (1904); **205**, 237 (1905).
[5] M. A. Smithard, Solid State Commun. **14**, 407 (1974).
[6] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960), pp. 315–324.
[7] M. Born and E. Wolf, *Principles of Optics,* Fifth ed. (Pergamon, Oxford, 1975), pp. 665–681.
[8] M. Born and E. Wolf, in *Principles of Optics,* Ref. 7, pp. 708–713.
[9] L. D. Landau and E. M. Lifshitz, in Ref. 6, problem 6, p. 62 and pp. 20–27.
[10] W. L. Bragg and A. B. Pippard, Acta. Crystallogr. **6**, 865 (1953).
[11] R. W. Dreyfus and P. W. Long, Proc. R. Soc London Ser. A **246**, 233 (1958).
[12] M. A. Smithard and M. Q. Tran, Helv. Phys. Acta **46**, 869 (1974).
[13] N. V. Smith, Phys. Rev. Lett. **21**, 96 (1968); Phys. Rev. **183**, 634 (1969).
[14] U. Kreibig and C.v Fragstein, Z. Phys. **224**, 307 (1969).
[15] G. Mukhopadhyay and S. Lundqvist, Solid State Commun. **44**, 1379 (1982).
[16] P. Apell and A. Ljungbert, Solid State Commun. **44**, 1367 (1982).
[17] R. Ruppin, J. Phys. Chem. Solids **39**, 233 (1978); J. Opt. Soc. Am. **66**, 449 (1976).
[18] A. D. Boardman and B. V. Paranjape, J. Phys. F **7**, 1935 (1977).
[19] P. Ascarelli and M. Cini, Solid State Commun. **18**, 385 (1976).