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## Anisotropic effective medium theories

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**Résumé.** — Les propriétés optiques des milieux inhomogènes anisotropes sont étudiées dans le cadre des théories du milieu effectif, tant à trois dimensions (3D) (théories de Maxwell Garnett et de Bruggeman) qu'à deux dimensions (2D) (théorie de Yamaguchi *et al.*). L'anisotropie du milieu effectif peut provenir soit de l'alignement d'inclusions non sphériques dans un système à deux ou trois dimensions, soit de la distribution plane du système 2D, même pour des particules sphériques. Nous montrons ici que ce milieu effectif anisotrope induit une déformation fictive des inclusions qui va dans le sens d'une réduction de l'anisotropie et rapproche les fréquences de résonance de plasmon de surface vers celle de la sphère. Par ailleurs, dans le cas de la théorie de Bruggeman, cela modifie la valeur du seuil de percolation optique. Ces théories, bien qu'anciennes, sont toujours très utilisées, en particulier pour prédire l'absorption optique des composites. L'effet présenté ici doit donc impérativement être pris en compte.

**Abstract.** — The optical properties of anisotropic inhomogeneous media are studied within the framework of the classical 3D effective medium theories of Maxwell Garnett and Bruggeman, and the 2D theory of Yamaguchi *et al.* The origin of the anisotropy is either the nonspherical shape of the metallic inclusions in the 3D systems, or the distribution of the inclusions (even if spherical) on a substrate in the 2D configuration. In both cases, it leads to an anisotropic effective medium. In this paper, it is shown that this surrounding anisotropic medium induces a fictitious deformation of the inclusions which reduces the anisotropy and shifts the resonance wavelengths toward the sphere plasmon resonance. In the case of the mean field theory of Bruggeman, it also affects the percolation threshold value. Although some of these theories are now quite old, they are still extensively used, especially for the predictions of the absorption of the composite media. Therefore the effect presented here for the first time should be taken into account.

### 1. Introduction.

Heterogeneous matter constitutes since the seventies an important field of basic research and applications, in which granular films and nanocermetts, i.e. inclusions of metallic particles

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(dielectric function  $\epsilon_a$ ) of nanometric size in a dielectric host (dielectric function  $\epsilon_b$ ), take a growing importance, stimulated by their numerous applications in the field of spectrally selective coating.

Theoretical works on electromagnetic properties of inhomogeneous materials have their origin in the study of three dimensional (3D) inhomogeneous media at the beginning of the XXth century (Maxwell Garnett [1, 2], Bruggeman [3]. .). All these theories, extensively studied, first consider spherical isotropic inclusions and lead to an isotropic effective medium characterised by a scalar effective dielectric function (DF)  $\epsilon_e$ . The derivations of the Maxwell Garnett and Bruggeman theories for ellipsoidal inclusions aligned along the same axis  $j$  have not been developed for a long time [4-6] and came at the same time as most of the two dimensional (2D) theories (Yamaguchi *et al.* [7-9], Bedeaux and Vlioger [10-12]). All these approaches introduce depolarization factors along the main axes of the ellipsoid related to the ellipsoid shape in the 3D case [13], to the shape and interactions between neighbouring particles and with the substrate in the 2D case (one then speaks of effective de polarization factors). The effective DF deduced from these theories is now anisotropic and tensorial, for two fundamental distinct reasons : in 2 and 3 dimensions because the shape of the inclusions can be anisotropic (and the depolarization factor is a tensor) ; in two dimensions because the film itself is structurally anisotropic, even if made of spherical inclusions (Fig. 1).

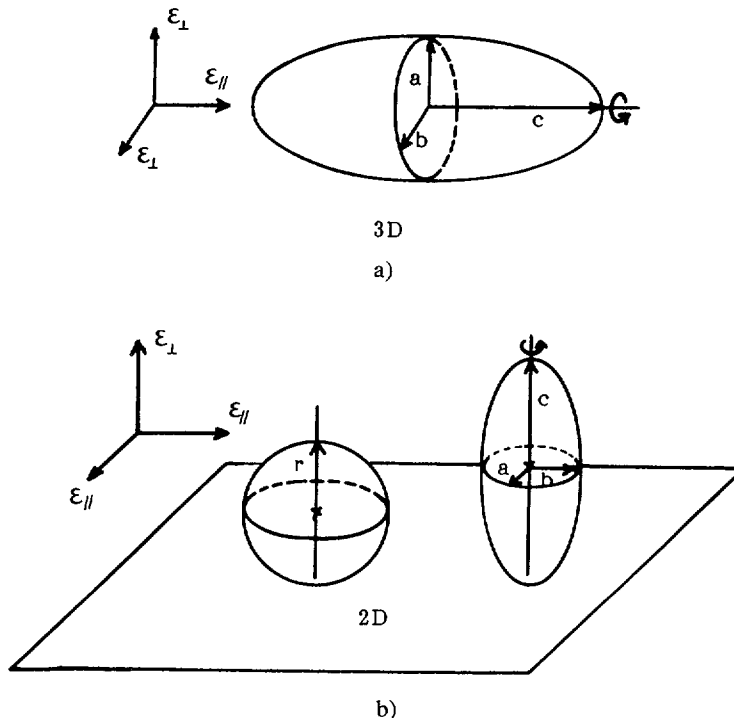


Fig. 1. — The origins of the anisotropy of the effective medium in 3D and 2D configurations.

In both cases, each theory allows the determination of the three mean values of the tensorial effective DF  $\epsilon_e$ , each one independently from the others. In other words, these approaches neglect the fact that the unit cells modelling the inclusion and its environment are now immersed in an anisotropic medium. It is the aim of this paper to present improved effective

medium theories in order to account for the anisotropic effect on the depolarization tensor. The exact formulation of the effective depolarization tensor is outlined in section 2. In section 3, we revisit, in this context, the historical and still extensively used 3D theories of Maxwell Garnett and Bruggeman, and the original 2D theory of Yamaguchi. The main results are summarised in section 4.

**2. The effective depolarization tensor.**

In most classical effective medium theories (EMT) it is assumed that the particles do not interact so that the inhomogeneous media can be modelled as single coated inclusions immersed in the effective medium [14, 15] (Fig. 2).

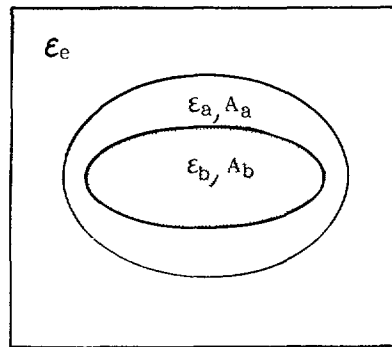


Fig. 2. — A unit cell modelling the effective medium in the quasi static theories. Material a is immersed in material b, the coated inclusion is immersed in the effective medium. If materials a and b have the same shape, we find the classical expression of Maxwell Garnett, if both are directly immersed in the effective medium, it gives the Bruggeman theory.

The relation between  $\epsilon_e$  and the dielectric functions of the constituents  $\epsilon_a$  and  $\epsilon_b$  is then obtained by determining the polarizability of the coated inclusion when submitted to a local (and generally static) electric field. One then obtains equations of the following form for 3D theories :

$$\frac{\epsilon_e - \epsilon_b}{\epsilon_b + A_b(\epsilon_e - \epsilon_b)} = p \frac{\epsilon_a - \epsilon_b}{\epsilon_b + A_a(\epsilon_a - \epsilon_b)} \quad \text{MG ,} \quad (1)$$

$$p \frac{\epsilon_a - \epsilon_e}{\epsilon_e + A_a(\epsilon_a - \epsilon_e)} + (1 - p) \frac{\epsilon_b - \epsilon_e}{\epsilon_e + A_b(\epsilon_b - \epsilon_e)} = 0 \quad \text{BR ,} \quad (2)$$

where  $p$  is the metal volume filling factor,  $A_a$  and  $A_b$  are the depolarization factors of the inner and outer ellipsoids, respectively, generally assumed to be identical, so that equations (1) and (2) reduce to the classical expressions of Maxwell Garnett and Bruggeman.

For the 2D theory of Yamaguchi, we have :

$$\left\{ \begin{aligned} \epsilon_{e\parallel} &= \epsilon_b \frac{\epsilon_a(F_{\parallel} + p) + \epsilon_b(1 - F_{\parallel} - p)}{\epsilon_a F_{\parallel} + \epsilon_b(1 - F_{\parallel})} \\ \epsilon_{e\perp} &= \epsilon_b \frac{\epsilon_a F_{\perp} + \epsilon_b(1 - F_{\perp})}{\epsilon_a(F_{\perp} + p) + \epsilon_b(1 - F_{\perp} - p)} \end{aligned} \right. \quad (3)$$

$$\left\{ \begin{aligned} \epsilon_{e\parallel} &= \epsilon_b \frac{\epsilon_a(F_{\parallel} + p) + \epsilon_b(1 - F_{\parallel} - p)}{\epsilon_a F_{\parallel} + \epsilon_b(1 - F_{\parallel})} \\ \epsilon_{e\perp} &= \epsilon_b \frac{\epsilon_a F_{\perp} + \epsilon_b(1 - F_{\perp})}{\epsilon_a(F_{\perp} + p) + \epsilon_b(1 - F_{\perp} - p)} \end{aligned} \right. \quad (4)$$

where  $F_{\perp}$  and  $F_{\parallel}$  are respectively the non degenerated and the degenerated values of the effective depolarization tensor  $\mathbf{F}(A_{\parallel}, A_{\perp})$  taking into account the effect of the substrate that will be detailed below. Up to now, all the components of any depolarization tensor ( $A_a, A_b, A_{\parallel}$  and  $A_{\perp}$ ) depend only on the shape of the ellipsoid. For a general ellipsoid (axis  $a, b, c$ ), the depolarization factors are given by [16, 17] :

$$A_{\alpha} = \frac{abc}{2} \int_0^{\infty} \frac{dq}{(q + \alpha^2) f(q)} \quad (\alpha = a, b, c) \quad (5)$$

with  $f(q) = \{(q + a^2)(q + b^2)(q + c^2)\}^{1/2}$ . The integral cannot be evaluated in closed form, but extensive tabulations are available [18, 19]. When the general ellipsoid degenerates into a prolate or oblate spheroid with rotation axis  $c$ , we have

$$\begin{cases} A_c = \frac{1-e}{2e^3} \left( \text{Log} \frac{1+e}{1-e} - 2e \right) & \text{with } e = \sqrt{1 - a^2/c^2} \text{ (prolate) ,} \\ A_c = \frac{1+e}{e^3} (e - \text{Arctg } e) & \text{with } e = \sqrt{a^2/c^2 - 1} \text{ (oblate) respectively :} \end{cases} \quad (6)$$

and for the degenerate values :

$$A_{a,b} = (1 - A_c)/2. \quad (7)$$

The well known variations of  $A$  with the axis ratio are shown in figure 3.

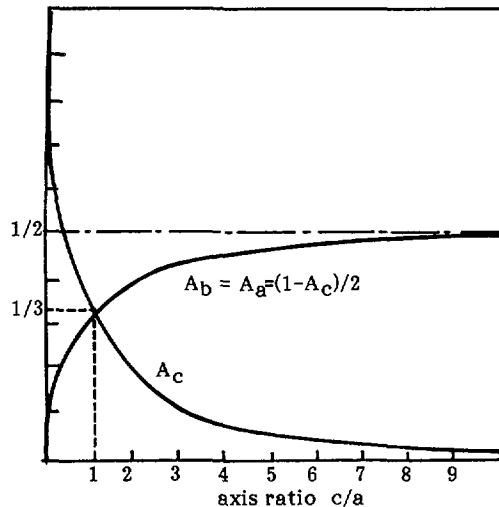


Fig. 3. — Geometrical factors for a spheroid.

These expressions are determined by solving the Laplace equation  $\Delta\Phi = 0$  in an ellipsoidal coordinate system with the assumption that the external medium (the effective medium in the problem treated here) is isotropic. In fact, this is never the case, except for spherical isotropic inclusions in 3D medium, and the above calculation requires some discussion. This is not a purely academic problem : the shape of the ellipsoid, and then the depolarization factor value, has a direct influence on the position, width and the amplitude of the surface plasmon modes in

the metallic inclusions. Moreover, in the mean field theory of Bruggeman, the critical percolation concentration  $p_c$ , which determines the metal — non-metal transition, is exactly equal to  $A$ . It is then necessary to evaluate the influence of the anisotropy on the depolarization factor.

All previous results are based on the validity of the Laplace equation in a charge free region. The problem is somewhat more complicated for an anisotropic external medium defined by a tensorial DF  $\varepsilon$  where the absence of electric charges does not involve the validity of Laplace's equation [20]. The volume charge density  $\rho$  is related to the electric displacement  $\mathbf{D}$  and the potential  $\Phi$  by

$$\rho = \nabla \cdot \mathbf{D} = -\nabla \cdot (\varepsilon \cdot \nabla \Phi) = -\varepsilon \cdot \nabla \cdot \nabla \Phi = -\left[ \varepsilon_{xx} \frac{\delta^2}{\delta x^2} + \varepsilon_{yy} \frac{\delta^2}{\delta y^2} + \varepsilon_{zz} \frac{\delta^2}{\delta z^2} \right] \Phi, \quad (8)$$

where the coordinate system is such that the axes are along the principal axes of the tensor  $\varepsilon$ . We can see here that, except if  $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$  (isotropic medium),  $\rho = 0$  does not involve  $\Delta \Phi = 0$ . Nevertheless, a solution can be obtained by changing from a cartesian coordinate system to a new coordinate system parallel to the principal axes of  $\varepsilon$ , such that the Laplace equation holds in the outer medium [21]. For a homogeneous external field along the  $z$  axis, the potential far from the inclusion boundary is given by :

$$\Phi_0 = -E_0 \varepsilon_{zz}^{-1/2} z', \quad (9)$$

so that, if we define the new coordinate system by :

$$x' = x(\varepsilon_{xx})^{-1/2}, \quad y' = y(\varepsilon_{yy})^{-1/2}, \quad z' = z(\varepsilon_{zz})^{-1/2}, \quad (10)$$

the external field is also homogeneous. We can already notice that in the new coordinate system, the axes of the ellipsoid change into :

$$\begin{cases} a' = a \varepsilon_{xx}^{-1/2}, \\ b' = b \varepsilon_{yy}^{-1/2}, \\ c' = c \varepsilon_{zz}^{-1/2}, \end{cases}$$

so that the ellipsoidal inclusion apparently changes into another ellipsoid with different axes.

We now consider the problem of an ellipsoidal inclusion of isotropic DF  $\varepsilon_2$  immersed in an anisotropic dielectric with tensorial DF  $\varepsilon_1$ , to which an external electric field is applied in the direction of one of the principal axes ( $a$ ). In the new coordinate system defined above, the Laplace equation holds and equation (5) becomes :

$$\begin{aligned} A_a^* &= \frac{a' b' c'}{2} \int_0^\infty \frac{dq}{(q + a'^2)^{3/2} (q + b'^2)^{1/2} (q + c'^2)^{1/2}} = \\ &= \frac{abc}{2} (\varepsilon_1)_{xx} \int_0^\infty \frac{dq}{(q(\varepsilon_1)_{xx} + a^2)^{3/2} (q(\varepsilon_1)_{yy} + b^2)^{1/2} (q(\varepsilon_1)_{zz} + c^2)^{1/2}} \quad (11) \end{aligned}$$

and similar expressions for the other mean values  $A_b$  and  $A_c$ . For inclusions in an anisotropic medium, the depolarization tensor depends both on its shape and on the anisotropy of the outer medium. The integral expressions (11) have analytic solutions when  $b'^2 = a'^2$ , i.e.  $b^2/(\varepsilon_1)_{yy} = a^2/(\varepsilon_1)_{xx}$ . Except for unprobable specific cases, this occurs for spheroids ( $b = a$ ) immersed in a uniaxial anisotropic medium ( $(\varepsilon_1)_{yy} = (\varepsilon_1)_{xx}$ ). Whatever the inclusion shape may be, the complex effective depolarization factor  $A_c^*$  can be written under one of the

equivalent forms :

$$A_c^* = \frac{1 - e^*}{2 e^{*3}} \left( \log \frac{1 + e^*}{1 - e^*} - 2 e^* \right) \text{ (pro.) } \text{ or } \frac{1 + e^*}{e^{*3}} (e^* - \text{Arctg } e^*) \text{ (obl.)} \quad (12)$$

with

$$e^* = \sqrt{1 - \frac{(\varepsilon_1)_{zz} b^2}{(\varepsilon_1)_{yy} c^2}} \quad \text{or} \quad e^* = \sqrt{\frac{(\varepsilon_1)_{zz} b^2}{(\varepsilon_1)_{yy} c^2} - 1}. \quad (13)$$

It can be seen from the complex expression of the eccentricity  $e^*$  that the anisotropy flattens the ellipsoidal inclusion (i.e. increases the depolarization factor) along the direction of high  $\varepsilon_1$  values and elongates it along the other. If we now turn back to the effective medium theories, this will lead to a shift of the plasmon mode frequencies toward the sphere resonance frequency.

### 3. The effective medium theories revisited.

If we consider ellipsoidal inclusions aligned along the same direction in a 3D system, or spherical and ellipsoidal particles with the rotational axis perpendicular to the films, deposited on a substrate (2D system), the effective dielectric tensor and the ellipsoidal inclusion have, by nature, parallel axes and the above formalism applies. The unit cells which allow the determination of  $\varepsilon_e$  are now immersed in an anisotropic medium of DF  $\varepsilon_e$  which modifies their apparent eccentricity and thus the effective value  $\varepsilon_e$  itself : in the anisotropic case, all the EMT become self-consistent. We will now point out this anisotropic effect with in the frame work of the most commonly used 3D theories (the Maxwell Garnett theory and the self-consistent theory of Bruggeman) and the 2D theory of Yamaguchi. These theories will be briefly outlined.

**3.1 THE GENERALISED MAXWELL GARNETT THEORY.** — If we introduce the anisotropic effect in the MGT, expression (1) becomes a tensorial self consistent expression of the form

$$\frac{\varepsilon_e - \varepsilon_b \cdot 1}{\varepsilon_b \cdot 1 + A^*(\varepsilon_e - \varepsilon_b \cdot 1)} = p \frac{\varepsilon_a - \varepsilon_b \cdot 1}{\varepsilon_b \cdot 1 + A^*(\varepsilon_a - \varepsilon_b \cdot 1)} \quad (14)$$

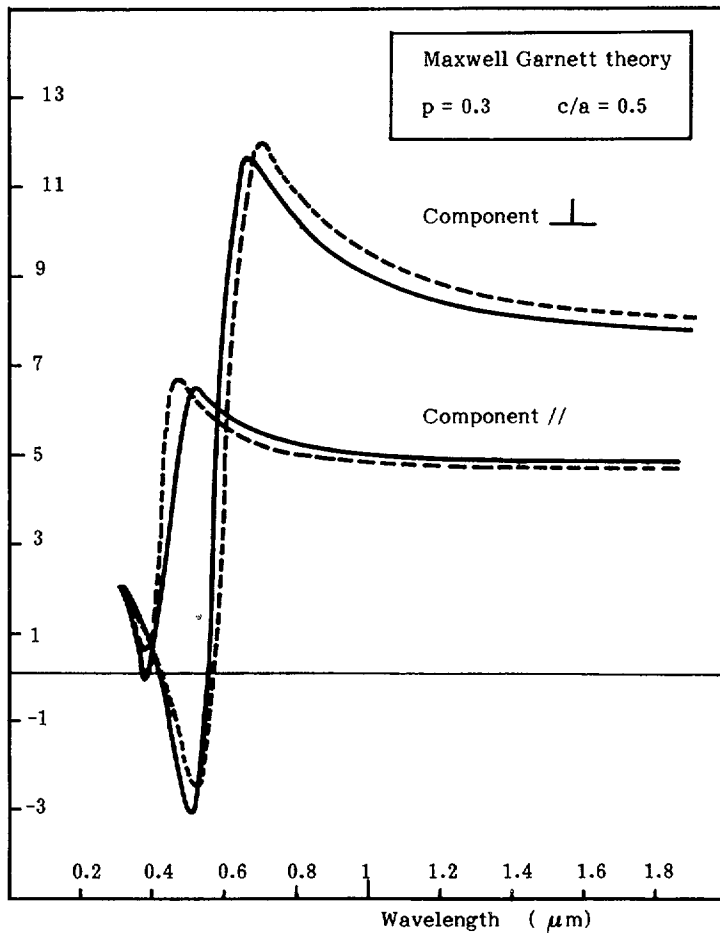
where the eigenvalues of  $A^*$ , determined by equations (12) and (13), depend on  $\varepsilon_e$ . This implicit system of non-independent equations is numerically solved using a forced convergence procedure. The two distinct components of  $\varepsilon_e$  ( $\parallel$  and  $\perp$  to the rotational axis of the ellipsoid) are shown in figure 4, and compared to the classical prediction of the MGT. (Matrix and inclusion can be permuted to model dielectric inclusions in a metallic host.)

Taking into account the effect of the anisotropy does not deeply affect the absolute value of  $\varepsilon_e$  but, as expected, shifts the two absorption peaks toward the plasmon mode frequency of the sphere, indicating a significant modification of the apparent shape of the inclusion. In the example presented here (Au-Al<sub>2</sub>O<sub>3</sub>,  $p = 0.3$ ,  $c/a = 0.5$ ), the new position corresponds to an effective axis ratio reduced by more than a factor 2.

**3.2 THE MEAN FIELD THEORY OF BRUGGEMAN.** — More drastic effects are expected with this theory, if we consider the particular signification of the depolarization factor  $A$ . It has been demonstrated a long time ago that the static percolation threshold  $p_c$  is exactly equal to  $A$  and the physical meaning of  $A$  may be quite different whether the concentration  $p$  is close or far from  $p_c$ . Each modification of the effective value of  $A$  may deeply affect the predictions of this theory. We can distinguish two situations. We have mentioned that, for spheroidal inclusions,

the degenerated values of  $A^*$  are related to the non-degenerated one by equation (7) so that we can determine two concentration regions where  $p$  falls between  $p_{c\perp}$  and  $p_{c\parallel}$  (i.e.  $A_{\perp}$  and  $A_{\parallel}$ ), leading to an extremely anisotropic medium, metallic in the direction of  $A_{\parallel}$ , for example, and dielectric in the other directions. This is represented by regions C and D on the  $A$ - $p$  diagram of figure 5. These regimes are typical of the Bruggeman theory. In the other regions, A and B, the effective medium is very similar to those predicted by the MG theory and the anisotropic effect qualitatively equivalent.

In the example given in the previous section, an axis ratio equal to 0.5 gives a depolarization factor equal to 0.527 along the axis of rotation and 0.236 along the other two axes, so that for a concentration  $p = 0.3$ , the effective medium is dielectric in a direction parallel to the axis of rotation, metallic along the other two axes (region C).



a)

Fig. 4. — Real (a) and imaginary (b) part of the effective dielectric function of Au-Al<sub>2</sub>O<sub>3</sub> cermet modelled by the classical (---) and generalised (—) Maxwell Garnett theory. The absolute values are not affected but the absorption peaks are shifted toward the plasmon mode frequency of the sphere.



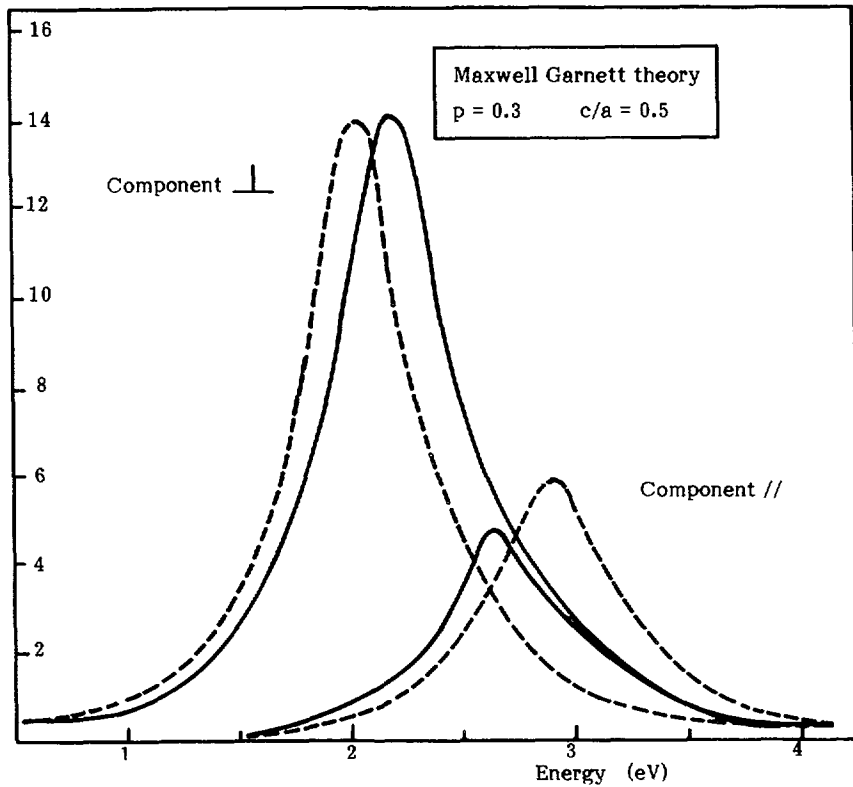


Fig. 4b.

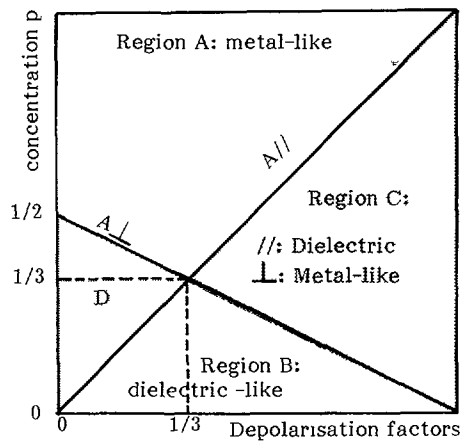
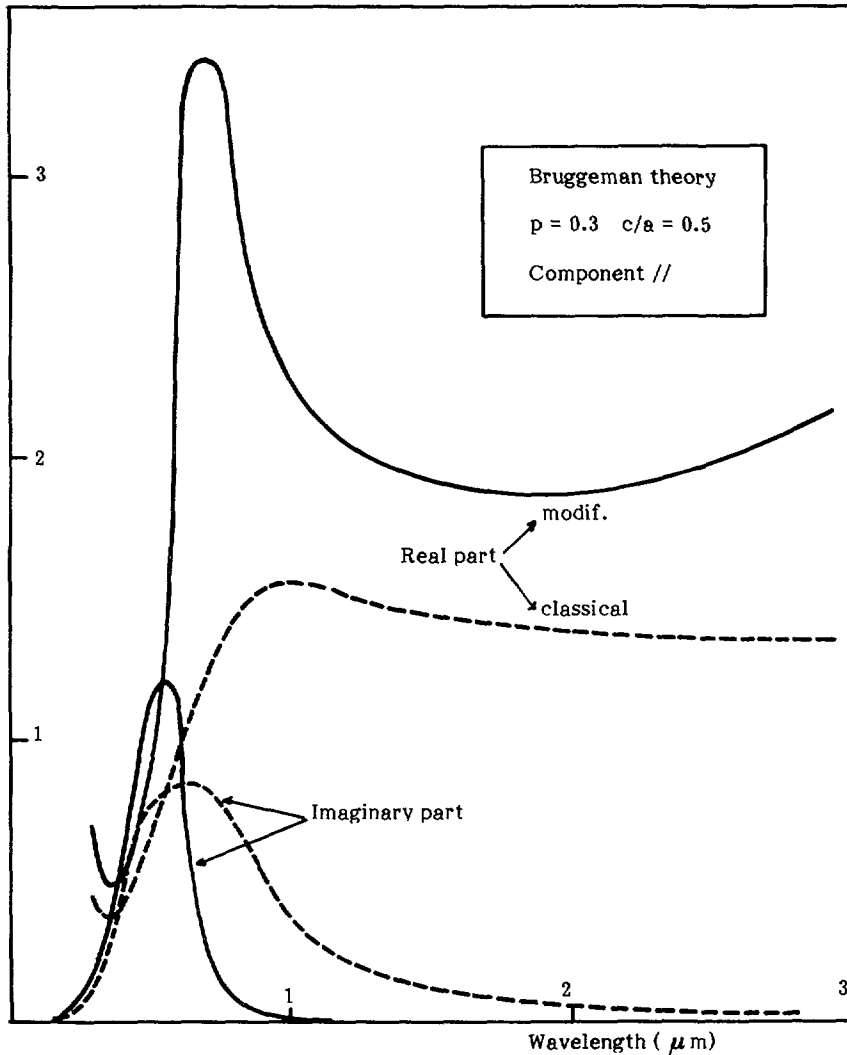


Fig. 5. — The  $A$ - $p$  diagram showing the four different regions modelled by the Bruggeman theory. Region A and B correspond to the media modelled by the Maxwell theory in the metallic and dielectric configuration. Regions C and D are specific of the Bruggeman approach.

The tensorial equation for the BR theory is

$$p \frac{\epsilon_a \cdot 1 - \epsilon_e}{\epsilon_e + A_a^*(\epsilon_a \cdot 1 - \epsilon_e)} + (1 - p) \frac{\epsilon_b \cdot 1 - \epsilon_e}{\epsilon_e + A_b^*(\epsilon_b \cdot 1 - \epsilon_e)} = 0. \quad (15)$$

Figures 6 present the classical and modified predictions of the Bruggeman theory in two different characteristic regions. As expected, the influence of the anisotropic effect is quite



a)

Fig. 6. — (a, b) The theory of Bruggeman in the extreme anisotropic configuration. The effective medium is dielectric-like along the axis of rotation of the oblate inclusions (Fig. 6a), conducting along the other two directions (Fig. 6b). It implies a shift of the percolation threshold value with the frequency together with significant modification of the dielectric function (Au-Al<sub>2</sub>O<sub>3</sub>). (c) The Theory of Bruggeman in the dielectric configuration. We find again the mode contraction around the sphere plasmon frequency.

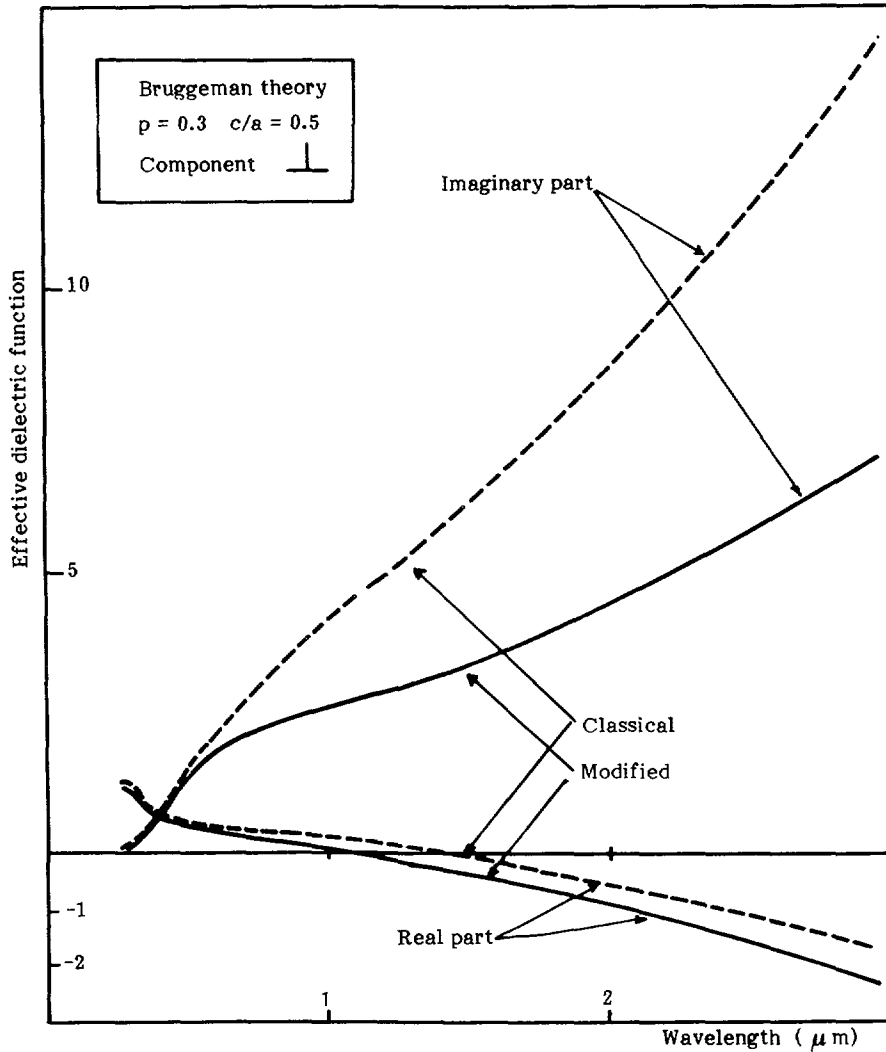


Fig. 6b.

sensitive. As already mentioned, for a concentration  $p = 0.3$  and an axis ratio  $c/a = 0.5$ , the medium lies in region C, the component perpendicular to the rotational axis  $c$  is metal-like and dielectric like along the axis of rotation. The anisotropy elongates the oblate ellipsoid, reduces the depolarization factor in the direction of  $c$  ( $A_c^*$  now fluctuates between 0.4 and 0.44, these values correspond to an effective ratio  $c/a \approx 0.8$ ) and increases  $A^*$  in the other two directions ( $0.28 < A_{a,b}^* < 0.29$ ). The ellipsoid tends to a sphere, the mean values of  $A^*$ , and so the percolation threshold in this theory, become closer to  $p$ , so that the conductivity of the metallic components decreases and the polarizability of the dielectric one increases (Figs. 6a, b). In this connection, it is worth noting that the percolation threshold now depends on the frequency. Far from the resonance region,  $A^*$  decreases with  $\omega$ , involving a gradual increase of the polarizability in the infrared region. As a consequence, this modified theory cannot determine more critical exponents for the conductivity  $t$  and the polarizability  $s$  of anisotropic inhomogeneous media, than when the anisotropic effect is neglected, which leads to the static

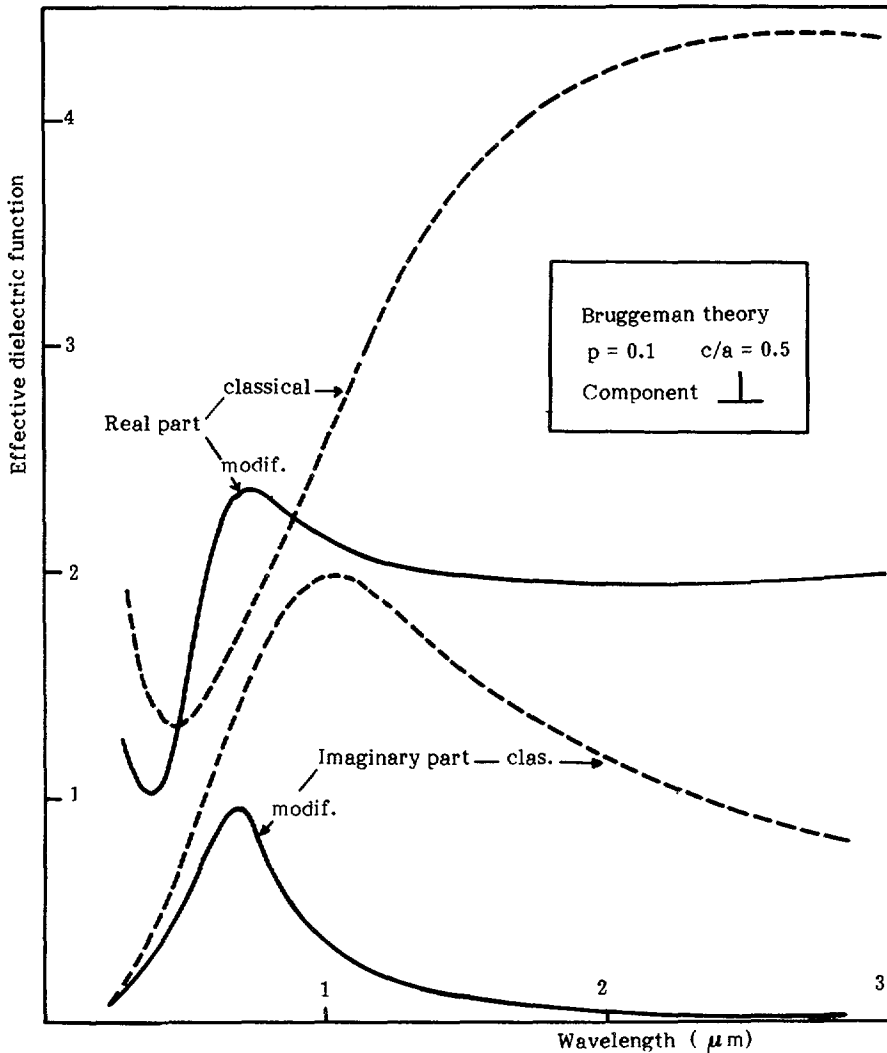


Fig. 6c.

mean field exponents  $s = t = 1$  [22]. (The effective dielectric function in the infrared region was shown to follow a Drude function with an effective polarizability  $P_e$  and an effective plasma frequency  $\omega_{pe}$ . In the Bruggeman equation one can then distinguish the wavelength dependent and independent terms, whose solutions lead to the determination of the scaling laws :  $P_e = \epsilon_b p^{*-s}$  and  $\omega_{pe}^2 = \omega_p^2 p^{*t}$  with  $s = t = 1$ , where  $\epsilon_b$  is the dielectric function of the dielectric inclusions and  $\omega_p$  the plasma frequency of the metallic ones.  $p^*$  is the reduced concentration defined by  $p^* = (p - p_c)/p_c$  with  $p_c = A$  in the Bruggeman theory. This procedure is no longer suitable as  $A$  depends on  $\omega$  and all the terms in the Bruggeman decomposition are wavelength dependent.)

Figures 6c, d present the same situation as that described with the MG theory (same axis ratio  $c/a = 0.5$  but  $p = 0.1$ ). The effective medium is dielectric-like in every direction (region B). We observe the shift of the absorption peaks toward the plasmon mode frequency of the sphere corresponding to the apparent modification of the shape of the spheroid, but in

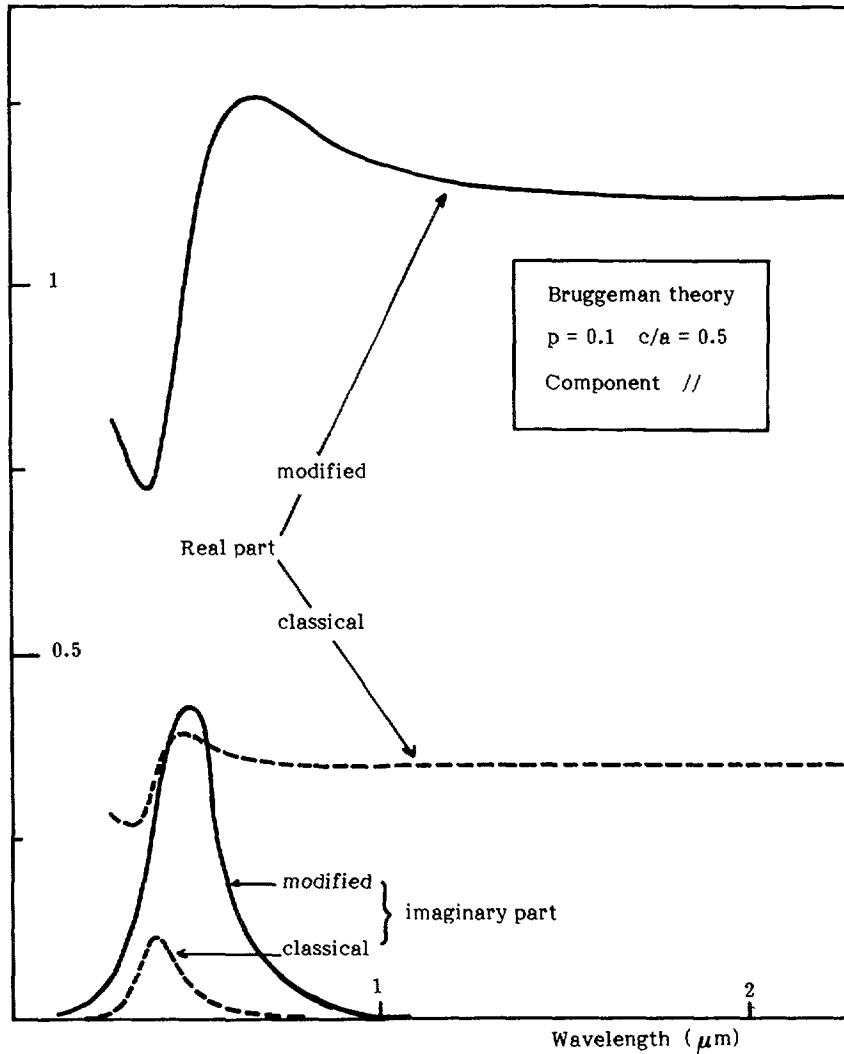


Fig. 6c'.

contrast to the MGT, the absolute value of  $\varepsilon_e$  is deeply affected, due to the apparent modification of the reduced concentration  $p^* = (p - p_c)/p_c$  (with  $p_c = A^*$ ).

**3.3 THE 2D THEORY OF YAMAGUCHI.** — No spectacular effects have to be expected from the classical 2D theories which are based on the same principle as the theory of Maxwell Garnett, namely the theory of Yamaguchi *et al.* and the theory of Bedeaux and Vlieger. We will focus our attention on the first approach which can be analytically solved whereas the second one, which takes into account the actual morphology of the film, needs an image and does not present a general formulation.

As the Lorentz approach is no longer suitable in 2D to determine the local field polarising the inclusion, it has to be exactly calculated for a given distribution of spheroids on a substrate. Yamaguchi *et al.* account for the substrate effect by using the mirror image expedient. For a given inclusion, the local field is then the superposition of the applied field, the field of the

image-dipole and the field of all the other dipole and image couples. The dipoles are assumed to be distributed onto the nodes of a square array (interspacing  $d$ ). Even for spherical inclusions, the effective medium presents an appreciable anisotropy considering the particular form of the dipolar field and the orientations of the image dipole (Fig. 7).

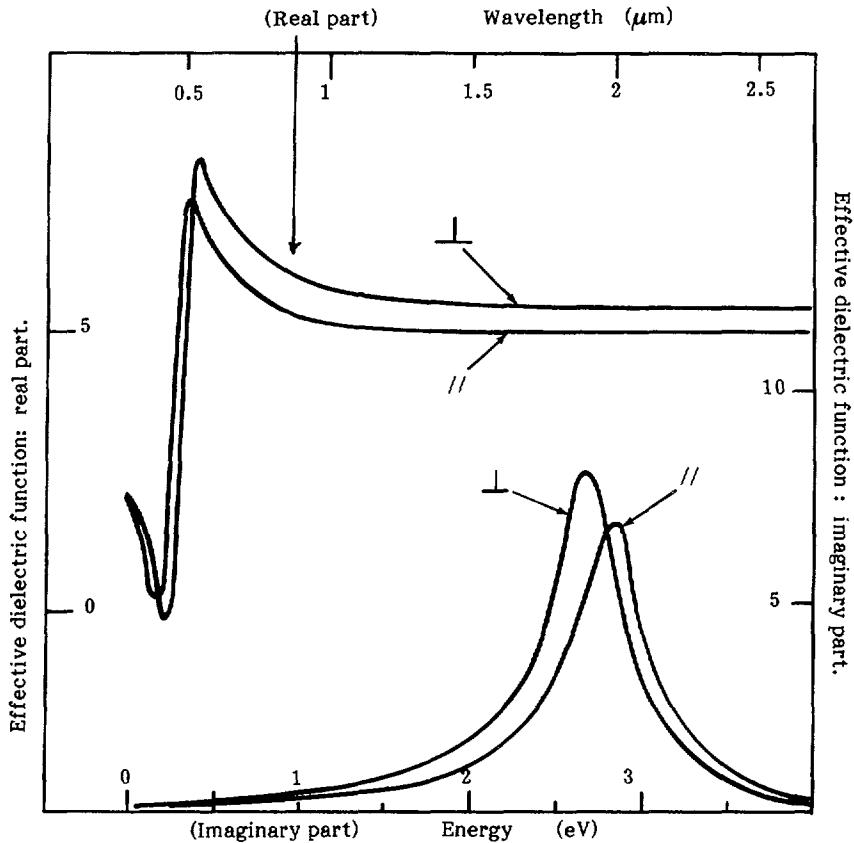


Fig. 7. — Prediction of the theory of Yamaguchi *et al.* for spherical gold inclusions deposited onto a glass substrate. The anisotropy arises from the 2D configuration.

When the field is parallel to the film, dipole and image-dipole are in opposite directions whereas they are in the same direction when the applied field is perpendicular to the substrate (Fig. 8). As a consequence, the substrate effect is minimized in the first case and increased in the second one. At least, the anisotropy may also be induced by the shape of the inclusions. In the case where the rotational axis of the spheroid is parallel to the substrate [23] or with oblique columnar structures [24], none of the components of the effective depolarization tensor is degenerated and they have to be numerically determined from equation (11). If this axis is perpendicular to the substrate, two mean values (parallel to the film) degenerate, the tensor is determined by the analytical expressions (6) et (7) and the anisotropic effect can be studied in a similar way as the above 3D theories (Fig. 1b).

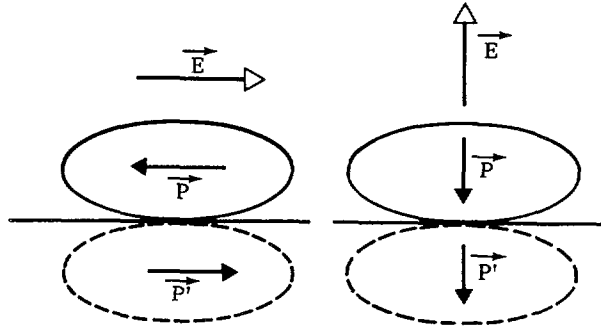


Fig. 8. — The influence of the image-dipole is different for the two directions of the applied field.

The effective depolarization tensor, as determined by Yamaguchi *et al.* has the following form :

$$\begin{cases} F_{\parallel} = A_{\parallel} - \frac{\gamma^2 \varepsilon_s - \varepsilon_a}{24 \eta^3 \varepsilon_s + \varepsilon_a} - 0.716 \frac{2 \varepsilon_a}{\varepsilon_s + \varepsilon_a} \frac{d_w}{2d}, \\ F_{\perp} = A_{\perp} - \frac{2 \gamma^2 \varepsilon_s - \varepsilon_a}{24 \eta^3 \varepsilon_s + \varepsilon_a} + 0.716 \frac{2 \varepsilon_s}{\varepsilon_s + \varepsilon_a} \frac{d_w}{d}. \end{cases} \quad (16)$$

$A_{\parallel}$  and  $A_{\perp}$  are the mean values of the geometric depolarization tensor in directions parallel and perpendicular to the substrate (Eqs. (6) and (7)),  $d_w$  is the mass thickness of the film,  $\gamma$  the axis ratio and  $\eta = \ell/h$ , where  $\ell$  is the distance between the dipole and the image-dipole and  $h$  the rotational axis. For adsorbate inclusions with the rotational axis perpendicular to the substrate,  $\ell = h$  and  $\eta = \ell$ . The second term in (16) represents the dipole-image contribution and the third term is the result of the summation over all the couples (dipole, image-dipole). This third term contributes less than 10 % to  $F_{\parallel}$  but can be preponderant in the perpendicular case. It can be seen that only the first two terms of  $F$  are affected by an apparent modification of the shape of the inclusion. In the following, we will neglect the variations of the second term. This approximation is valid for oblate spheroids ( $c/a < 1$ ). In this case the second term, representing less than 10 % of the total effective factor (only 5 % in the parallel case), is not greatly affected by a modification of  $A$  (see Fig. 3) and we avoid the questionable inversion of equations (6).

The modifications introduced when substituting  $A^*$  in equations (16) are shown in figure 9. Only the parallel component is appreciably affected by the anisotropic effect, considering the relative amount of  $A$  in the effective depolarization factor  $F$ .

#### 4. Conclusion.

Most historical effective medium theories, initially developed for spherical inclusions, have been subsequently extended to ellipsoidal shapes. Except for the case of randomly oriented ellipsoids, the effective medium thus determined is anisotropic and the depolarization factors of the ellipsoidal inclusions, now immersed in an anisotropic medium, depend both of the shape of the inclusion and of the effective dielectric tensor  $\varepsilon_e$ . As a consequence, all the theories become self consistent and have to be numerically solved. This has been done in the particular cases where the effective dielectric tensor and the axes of the spheroids present the same symmetries. This is always the case in 3D systems but reduces our analysis to 2D systems with the rotational axis of the inclusions perpendicular to the substrate. The main result is that the anisotropy tends to minimize the eccentricity of the spheroid and thus, the

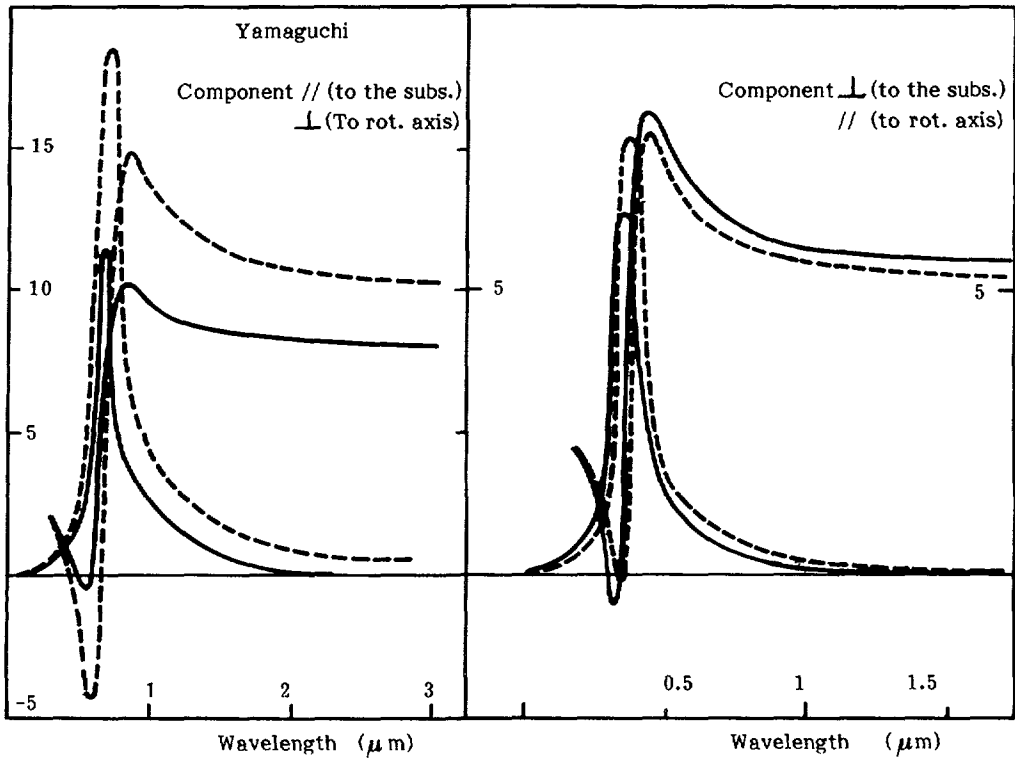


Fig. 9. — The anisotropic effect in the theory of Yamaguchi *et al.* (Au-granular,  $p = 0.3$ ,  $c/a = 1$ ). Only the absolute value of  $\epsilon_c$  is affected.

anisotropy itself. This affects more or less the absolute values of  $\epsilon_e$ , depending on the theory, and shifts the positions of the absorption peaks toward the intermediate position of the sphere resonance. This anisotropic effect has been experimentally observed in the 2D configuration and interpreted as a multiple-image effect introduced in the theory of Yamaguchi *et al.* [25, 26] (this effect leads to an enhancement of the anisotropy of the effective medium).

More drastic effects are predicted from the self consistent mean field theory of Bruggeman, due to the particular sense of the depolarization factor in this theory. It is well established that the static percolation threshold  $p_c$  is strictly equal to  $A$  in this theory. This result has been demonstrated for optical frequencies, where optical conductivity and polarisation follow power laws in the form of  $(p - p_c)^\alpha$ , with critical exponents equal to unity and  $p_c = A$ . We have shown here that this result is only valid for spherical inclusion ( $A = p_c = 1/3$ ). For ellipsoidal shapes,  $A^*$  depends on the anisotropy characterized by  $\epsilon_{e\parallel}/\epsilon_{e\perp}$  which is a function of the frequency and the percolation threshold now depends on the frequency.

When applied to anisotropic media, the simple effective medium theories have to be solved numerically. In addition to their classical restriction to low concentrations and long wavelengths (quasi-static approximation), the classical formulations are limited to quasi-spherical inclusions.



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