Long-wavelength absorption of cermets

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(Received 25 November 1987)

Cermets are inhomogeneous materials composed of small metal spheres randomly distributed in a host dielectric. A theory is presented for the electromagnetic absorption at very long wavelength. The most important quantity is the magnetic permeability μ, even for nonmagnetic systems.

INTRODUCTION

There are numerous applications for materials which can absorb electromagnetic radiation at very long wavelength ($\lambda \sim 1$ cm). Homogeneous materials are generally unsuitable: nonmagnetic insulators do not absorb at long wavelength, and metals reflect rather than absorb most of the radiation. Cermets are inhomogeneous materials which are composed of small metal spheres which are randomly distributed in a host dielectric. Some are good absorbers of long-wavelength electromagnetic radiation. The metal spheres absorb the radiation. The random location of the spheres causes the radiation to scatter back and forth inside the cermet, thereby getting multiple passes at the metal spheres. This physical model is intuitively attractive. Here we provide a mathematical model for calculating the rate of absorption.

Most existing theories of the optical properties of cermets are variations or extensions of two older theories: those of Maxwell Garnett[1] (MG) and Bruggeman.[2] The latter is now called the "effective medium theory" (EMT). These two theories are still the most widely used and seem the most successful when compared with experiment. Both of them are based on Mie scattering, which is the scattering of electromagnetic radiation from a sphere. The easiest discussion of Mie scattering is due to Heister.[3] More recent theories are also based upon Mie scattering.[4-7]

The Maxwell Garnett theory applies to cermets when the metal spheres are not touching. These theories contain a number of parameters which are defined as follows. ϵ_1 is the dielectric constant of host, usually taken to be real; ϵ is the complex dielectric constant of metal; $\bar{\epsilon}$ is the effective complex dielectric constant of cermet; f is the fraction of volume occupied by spheres. In terms of these parameters, the MG theory for $\bar{\epsilon}$ is

$$\frac{\bar{\epsilon}-\epsilon_1}{\bar{\epsilon}+2\epsilon_1}=f\frac{\epsilon-\epsilon_1}{\epsilon+2\epsilon_1} \; . \tag{1}$$

This formula can be solved to obtain $\bar{\epsilon}$.

The EMT of Bruggeman applies to a two-phase material. There is a fraction f of dielectric constant ϵ and a fraction $(1-f)$ of dielectric constant ϵ_1. It is similar to MG when f is small. However, when f is larger, then many of the spheres touch. One can no longer state that

the spheres are surrounded by a material with ϵ_1. Instead, one states that both materials are surrounded by an effective medium whose dielectric constant $\bar{\epsilon}$ is given by

$$f\frac{\epsilon-\bar{\epsilon}}{\epsilon+2\bar{\epsilon}}+(1-f)\frac{\epsilon_1-\bar{\epsilon}}{\epsilon_1+2\bar{\epsilon}}=0 \; . \tag{2}$$

This formula treats both constituents of the cermet on an equal basis. The metal spheres with ϵ have a volume fraction f, while the host material with ϵ_1 has a volume fraction $(1-f)$. Equation (2) is a quadratic equation for $\bar{\epsilon}$. One chooses the root which has $\mathrm{Im}\bar{\epsilon}>0$.

Both MG and EMT are based upon the electric-dipole moment induced on the sphere. Recent theories in Refs. 4–7 have included higher multipoles and nonspherical shapes.

Stroud and Pan in Ref. 4 have extended Bruggeman theory to include the magnetic-dipole terms which are important at long wavelength. Their theory yields a formula of the form

$$\sum_i f_i \left| \frac{\epsilon_i-\bar{\epsilon}}{\epsilon_i+2\bar{\epsilon}}+\tfrac{1}{30}(\omega R_i/c)^2(\epsilon_i-\bar{\epsilon}) \right| =0 \; , \tag{3}$$

where f_i is the volume fraction of constituent, and dielectric function ϵ_i and R_i is the radius of the grain size. In the static limit where $(\omega R/c)\ll 1$ this reduces to the EMT theory. However, at intermediate frequencies, the second term in brackets can be much larger than the first. For example, when ϵ_i describes a metal with $\epsilon=1-(\omega_p/\omega)^2$ then the second term becomes $\sim -(\omega_p R/c)^2$ which need not be small as $\omega \to 0$. However, at wavelengths where the lifetime τ obeys $\omega\tau \ll 1$ then $\epsilon \approx 1-(\omega_p\tau)^2[1-i/(\omega\tau)]$ and the magnetic-dipole term becomes small. Stroud and Pan treat the magnetic-dipole terms as contributions to the dielectric function $\bar{\epsilon}(\omega)$. However, we think this is a mistake.

The very important term from magnetic dipoles is actually a contribution to the magnetic susceptibility of the medium $\bar{\mu}(\omega)$. The complex magnetic susceptibility causes the absorption of electromagnetic radiation at long wavelength. Here we develop a theory for calculating this quantity in cermets.

Other types of theories are bounds on $\bar{\epsilon}$ of the type given in Refs. 8–10. Although these bounds are useful at visible wavelengths, they are not useful at very long

wavelengths. The application of these bounds at long wavelengths usually shows that $\epsilon_1 < \bar{\epsilon} < \epsilon$ which is not much help.

One way to distinguish these theories is to examine their behavior in the limit that the light frequency ν goes to zero. The dc limit of MG and EMT are given for the range of concentration below the percolation threshold where $\bar{\epsilon}$ is real, as follows:

$$\bar{\epsilon} = \epsilon_1(1+2f)/(1-f) \quad \text{for MG} ,$$

$$\bar{\epsilon} = \epsilon_1/(1-3f) \quad \text{for EMT} .$$

These two formulas have the same behavior at small f but predict quite different values for the critical concentration where $\bar{\epsilon}$ diverges. Doyle[11] has solved the problem exactly for a lattice of spheres and has shown that the approach to critical behavior is better described by a logarithm

$$\bar{\epsilon} = \epsilon_1[1-3f_c\ln(1-f/f_c)] .$$

The critical concentration for percolation differs for each crystal structure but has typical values of $f_c \approx 0.7$. The above formula is very accurate for sc lattices, and approximately accurate for other lattices.[11-14] These exact results for lattices suggest that the EMT and MG theories are not accurate near the percolation threshold.

MAGNETIC SUSCEPTIBILITY

Commercial absorbers for long-wavelength radiation are always composed of magnetic powders such as ferrites and ferromagnetic materials. Therefore, it seemed worthwhile to examine the role of the magnetic susceptibility in long-wavelength absorption. In the limit that $(\omega R/c) \ll 1$, then from Mie scattering one finds for the induced electric (α_E) and magnetic (α_M) polarizabilities of a sphere of susceptibilities ϵ and μ in a medium of susceptibilities ϵ_1 and μ_1:[3]

$$\alpha_E = R^3 A(\epsilon,\epsilon_1) ,$$

$$\alpha_M = R^3 A(\mu,\mu_1) ,$$

where A has the form

$$A(\beta,\beta') = \frac{[(2\beta+\beta')j_1(z)-\beta'\sin(z)]}{2[(\beta-\beta')j_1(z)+\beta'\sin(z)]} ,$$

where j_1 is the spherical Bessel's function, and $z^2 = \epsilon\mu(\omega R/c)^2$. In the limit of long wavelength, z is small and it is convenient to use the expansion

$$\alpha_E = R^3\left[\frac{\epsilon-\epsilon_1}{\epsilon+2\epsilon_1}+\frac{3}{10}\left(\frac{\omega R}{c}\right)^2\mu\epsilon_1\left(\frac{\epsilon}{\epsilon+2\epsilon_1}\right)^2+\cdots\right] ,$$

(4)

$$\alpha_M = R^3\left[\frac{\mu-\mu_1}{\mu+2\mu_1}+\frac{3}{10}\left(\frac{\omega R}{c}\right)^2\epsilon\mu_1\left(\frac{\mu}{\mu+2\mu_1}\right)^2+\cdots\right] .$$

This formula has the symmetry between ϵ and μ which has been noticed by previous workers.[13,14] In these ex-

pressions both ϵ and μ can be complex susceptibilities. The absorption cross section for a single sphere is

$$\sigma_a = \frac{4\pi\omega}{c}\text{Im}(\alpha_E+\alpha_M) .$$

In ferrites, ϵ is real and μ is complex. Then the first term of α_M is the most important of the four shown in (4).

For multidomain ferromagnets one has $B = \mu H$ where μ is typically about 30. Then the second term in α_M is the largest of the four shown in Eq. (4). This term is the same as that considered by Stroud and Pan[4] when $\mu = \mu_1 = 1$. However, for a ferromagnet in a nonmagnetic host ($\mu_1 = 1$, $\mu \gg 1$) the shape factor of $[\mu/(\mu+2\mu_1)]^2$ increases the absorption by a factor of 9 over that found by Stroud and Pan.

For magnetic spheres which are also conducting, one has to define both an effective dielectric permeability $\bar{\epsilon}$ and magnetic permeability $\bar{\mu}$. The effective wave vector for light propagation is $k^2 = \bar{\epsilon}\bar{\mu}(\omega/c)^2$. The two permeabilities seem to be independent, and are calculated separately. This conclusion is probably our major physical result. The major components of the local electric and magnetic fields are perpendicular even in random systems. Local variations in the microscopic fields can point in other directions. However, the effective permeabilities $\bar{\epsilon}$ and $\bar{\mu}$ come from the major components of the fields. Since the electric and magnetic fields are perpendicular, the local fields and susceptibilities are averaged separately.

For MG theory, one uses an equation similar to (1) for each permeability

$$\bar{\epsilon} = \epsilon_1\{1+3fA(\epsilon,\epsilon_1)/[1-fA(\epsilon,\epsilon_1)]\} ,$$

$$\bar{\mu} = \mu_1\{1+3fA(\mu,\mu_1)/[1-fA(\mu,\mu_1)]\} .$$

(5)

For EMT one uses an equation similar to (2) for each permeability,

$$0 = \sum_i f_i A(\epsilon_i,\bar{\epsilon}) ,$$

$$0 = \sum_i f_i A(\mu_i,\bar{\mu}) .$$

Each of these equations is solved separately. Our procedure is different than that of Stroud and Pan. However, when one term dominates the absorption, the two theories for $n^2 = \bar{\epsilon}\bar{\mu}$ will be numerically similar for nonmagnetic powders. However, we assign the eddy-current term to $\bar{\mu}$ whereas they assign it to $\bar{\epsilon}$. We expect our theory to be more accurate for magnetic materials.

One use of cermets is for paints which absorb electromagnetic radiation. We calculated the amount of radiation absorbed by a thin film on a metal substrate. Figure 1 shows a theoretical calculation using Eq. (5) for $\bar{\epsilon}$ and $\bar{\mu}$. The absorptance is defined as $A = 1 - R$. The cermet had a thickness of 1 mm on an aluminum substrate. Iron spheres in the cermet had a packing fraction of $f = \frac{1}{3}$. Two different values are shown for the radius a of the spheres. The host dielectric constant is $\epsilon_1 = 2$. The
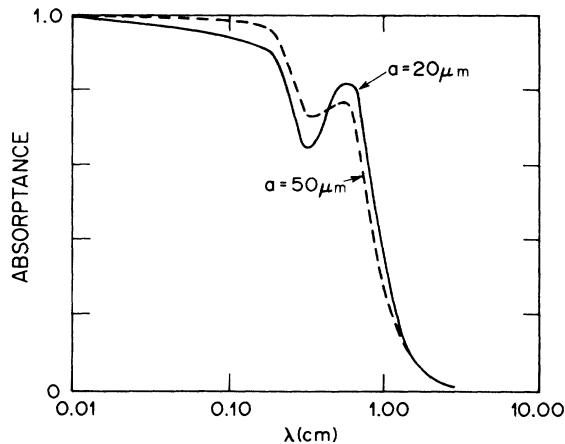
FIG. 1. The theoretical absorptance of a thin film of cermet painted on an aluminum substrate. The cermet is 1 mm thick, and contains iron spheres with a packing fraction $f = \frac{1}{3}$. Two values are shown for the radius a of the spheres. The absorptance is 1 minus the reflectance.

absorptance is about unity for wavelengths less than 1 cm, and falls to zero for longer wavelengths. The dip in the curve is an interference effect due to the finite thickness of the cermet. Nearly all of the absorptance comes from the magnetic permeability $\bar{\mu}$. The permeability of the iron was assumed to be real, so this is not magnetic absorption. The absorption comes from eddy currents associated with the magnetic susceptibility. Stroud and Pan in Eq. (3) assign this effect to $\bar{\epsilon}$, whereas we assign it to $\bar{\mu}$.

The falloff of the absorptance for $\lambda > 1$ cm is dictated by geometry. This phenomenon is understood by

remembering two formulas from optics:

$$R = \left| \frac{n-1}{n+1} \right|^2 ,$$

$$t \sim \exp(i2\pi dn / \lambda) .$$

The reflectance of the cermet depends upon the complex refractive index $n = (\bar{\epsilon}\bar{\mu})^{1/2}$. Large absorptance requires small reflectance, so n must be on the order of unity. The electromagnetic wave has a transmission factor t of getting through the film. Large absorptance occurs when the real part of the phase factor is larger than unity. Since n is of order unity, then large absorptance occurs when $\lambda \leq 2\pi d$, where d is the thickness of the cermet. Thus the wavelength at which the absorptance becomes small is primarily determined by the film thickness.

There have been several measurements on long-wavelength absorption in cermets. Heister's[3] work is pioneering. Reference 15 is for cobalt in Al_2O_3, Ref. 16 for silver in KCl, and Ref. 17 for iron in epoxy. The latter is notable because the experiments are in the microwave region with $\lambda \sim 1$ cm. References 15 and 16 present measurements in the infrared, and provide detailed comparisons to experiments. Reference 15 concludes that EMT is better, while Ref. 16 concludes that MG is better. Both could be right since they are investigating different systems.

ACKNOWLEDGMENTS

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