Plasmon-enhanced absorption by optical phonon in cermets.

M. Gadenne[*a],

P. Gadenne[**], V. Podolskiy[***], P. Sheng[****] and V.M. Shalaev[***]

*Université P. et M.Curie, 75252 Paris Cedex 05, France.
**Université de Versailles Saint-Quentin, 78035 Versailles, France
***Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA
****Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

ABSTRACT

Cermet is mixture of nano-sized metallic grains and insulating matrix. When concentration in metal is large enough, the conducting particles are strongly interacting between each others. As predicted by V.Shalaev [1] for fractal metallic clusters and experimentally verified [2], in the vicinity of the percolation threshold, the local electromagnetic field can be very large because of plasmon resonance in the metallic grains which may happen in a wide spectrum of frequencies. In this enhanced field region, the micro-crystallites of the matrix are immersed in these huge fields. In the spectral range of the optical phonon of the matrix there can be a very large absorption band because of the possible coupling between phonon of the matrix and resonance of the metallic grains. We experimentally observe this huge absorption in gold alumina cermets. The theoretical model is in good agreement with experimental results.

Keywords : inhomogeneous media, percolation, phonon, enhanced electromagnetic field, infrared absorption.

1. INTRODUCTION.

So called "Cermets" have been regarded first as a solid state mixture of "Ceramic" and "Metal" grains, constituting an inhomogeneous medium. The electromagnetic response of these inhomogeneous media made of metallic inclusions in an insulating matrix have been studied for a long time, but some points of their behavior are still difficult to analyze. In particular, infrared absorption remains much larger than expected.

A lot of investigations are done in the visible and near infrared range to explain optical properties. In this range, the properties are found to be mainly related to the plasmon resonances of the metal constituting the conducting grains. Recently it has been shown that the electromagnetic field may be locally strongly enhanced close to the metallic clusters because of localization of plasmons. It is well known that the value of the resonance frequency strongly depends on the geometry of the grains and clusters (spherical, elliptical, thin films...).

By using a special Atomic Force Microscope (A.F.M) equipped with a conducting tip, we are able to measure the local resistivity of the sample at the same time of recording the AFM image. Looking at resistivity images performed on cermet samples at or above the percolation threshold with this conducting tip A.F.M., we are able to extract, at the sample surface, the metallic grains connected to the infinite cluster which is responsible of the conducting path. As expected, we notice a very tortuous morphology of these conducting clusters which can be regarded as fractals. In that case of disordered nano-sized metallic structures, it has been found that plasmons are present in a very wide frequency range. Because of disorder, these plasmon resonances are localized resulting in giant local enhanced electromagnetic fields, so called "hot spots". Then, we can conclude that giant enhanced fields should also take place in cermets. As a consequence, it is particularly interesting to look at the interactions between the metallic clusters and the insulating matrix, which is locally affected by the presence of the hot spots. Because the insulating matrix is mainly transparent, the interesting spectral range for it is the region of absorption by phonons which is in middle infrared. We then will look at optical properties in the case of materials close to percolation threshold, when the geometry of the clusters becomes self similar, and spread out investigations in a wider spectral range, up to middle infrared.

---

[a] paga@ccr.jussieu.fr, L.O.S. Université P. et M.Curie, 75252 Paris Cedex 05, France.

Next section will be devoted to a summary of the main theoretical ideas concerning enhanced electromagnetic field close to metallic clusters. Then we shall describe the practical works performed on some inhomogeneous media . Finally we shall give an example of confrontation between the theoretical model and the infrared experimental results.

2. THEORETICAL APPROACH

The studied material is a composite with metallic nano-scaled grains embedded in an insulating matrix. To look at their optical behavior, the samples are thin films deposited on transparent substrate. In such a case, we shall see that the sample may be macroscopically insulating or conducting according to metallic concentration and thickness of the film, [3].

The theory [1,4], done to predict the behavior of these nano-composites in the vicinity of the threshold, shows up that plasmon modes are localized near the metallic grains in very small area called "hot spots" .(By an other way these hot spots have been experimentally observed in the visible range, with A.F.M. set-up [2]). Close to percolation threshold the structure is very complicated and ramified in samples. The tortuous architecture of the clusters promotes capacitance interactions as well as ohmic conduction and the distribution of size and shape of the metallic oscillators is very wide. As the value of resonance frequency depends a lot on the metallic grains structure, the electromagnetic resonance may happen in a large spectrum of frequencies from U.V. to infrared range. So, there is accumulation of energy in the hot spots, able to resonate at any frequency, and creating huge local electromagnetic field, much larger than the applied field of the wave.

The enhanced local field takes place in the gap between two grains or two edges of metal just where the insulating matrix is. Most of the studies of infrared properties of percolative media consider the metal as the only responsible of the large observed absorption, whatever the proposed mechanism. Of course the insulator is generally not or weakly absorbing in visible and near infrared. However, a great number of matrices are molecular solids and have crystal collective oscillations in the mid infrared called optical phonon. This is obvious when looking at the dielectric function, the real part of which can become negative with a not so small absolute value, during imaginary part has a bump.

Consequently, as the enhanced local fields takes place in the insulator, between the metal clusters supporting plasmon modes, even small absorption in the dielectric can be enhanced because of the huge local fields due to plasmon modes. This is logical explanation for the large optical absorption in the whole infrared range around percolation threshold. Moreover, in particular, if the plasmon modes are excited in the same mid infrared range as the optical phonon of the matrix, which is possible because of the wide spectrum of resonance frequency, the transfer of energy is then observed as losses in this range and optical absorption in the phonon band must be enhanced.

Following the development in [1, 4, 5]for calculating the dielectric function of the mixture we find the expression

$$\varepsilon'' = p\varepsilon_m{}'' \frac{\left\langle \left| E(r) \right|^2 \right\rangle_m}{\left| E_o \right|^2} + (1-p)\varepsilon_d{}'' \frac{\left\langle \left| E(r) \right|^2 \right\rangle_d}{\left| E_o \right|^2}$$

where $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$ and $\varepsilon_d = \varepsilon'_d + i\varepsilon''_d$ are respectively the dielectric functions for metal and dielectric components and the angular brackets $\langle ... \rangle_m$ and $\langle ... \rangle_d$ denote the spatial averaging over the metal and the dielectric, respectively. In this expression the local field $E(r)$ is much larger than the applied field E_o and the ratios G_m and G_d represent local field enhancement in the imaginary part ε'', directly connected to optical absorption. Even in the second term related to the dielectric, enhancement happens because the imaginary part of dielectric function is no longer negligible in the phonon range. The calculation of the enhancement is given in reference [5,6] and leads to the following expressions :

$$G_m = \frac{\left\langle \left| E(r) \right|^2 \right\rangle_m}{\left| E_o \right|^2} \approx \left(\frac{\left| \varepsilon_m{}' \right|}{\varepsilon''_m} \right) \left| \frac{\varepsilon_d}{\varepsilon_m} \right|^{\frac{t}{t+s}}$$

$$G_d = \frac{\left\langle \left| E(r) \right|^2 \right\rangle_d}{\left| E_o \right|^2} \approx \left(\frac{a}{\xi_A} \right) \left(\frac{\left| \varepsilon_m{}' \right|}{\varepsilon''_m} \right) \left| \frac{\varepsilon_m}{\varepsilon_d} \right|^{\frac{v}{t+s}}$$

where t, s, and v are respectively the percolation critical exponents for conductivity, dielectric function, and percolation correlation length for three D materials.

ξ_d is the Anderson localization length corresponding to the plasmon resonance of individual grain ($\varepsilon_m = -\varepsilon_d$) and a is the size of this grain.

The capital result to be pointed out from these expressions is the following :

Even a small ε'' can lead to significant absorption when G_d is large enough, which is the case in mid infrared when $\left|\varepsilon'_m\right| >> \varepsilon''_m$. For the same reason, G_m is large also.

In conclusion, the theory predicts that in a percolative sample absorption is larger than individual absorption by bulk metal and dielectric in same proportion, especially when there are optical phonons in dielectric

3. EXPERIMENTAL WORK.

3.1 Deposition techniques and characterizations.

Experimental results are obtained in Au-Al2O3 cermet thin films prepared by co-sputtering onto optically polished intrinsic silicon substrates. [6]

To study their morphology, some thin films are sputtered simultaneously on copper microscopy grids previously covered with amorphous silica so that the crystallization remains the same as the crystallization in the samples deposited on silicon covered by spontaneous oxide. The size of the elementary gold grains varies between 4 and 12 nm as shown on figure (1) representing a Transmission Electronic micrograph of a gold-alumina cermet film (thickness d = 40 nm). One can notice that there are several grains in the thickness. Consequently the apparent concentration in metal on this image is larger than the actual one in the sample.
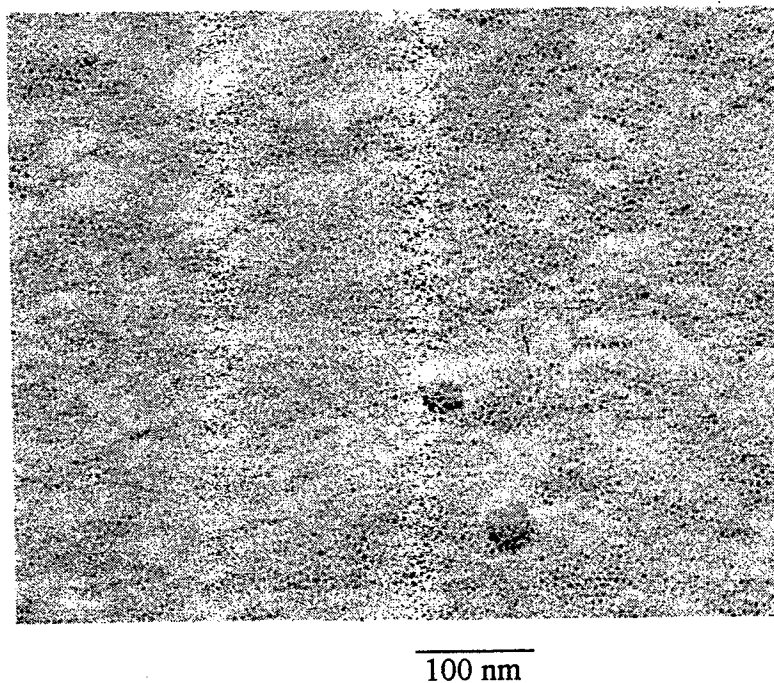
Au-Al2O3 cermet   p = 0.23 d= 40 nm

100 nm

Figure 1: TEM image of a Au-Al2O3 cermet film
Thickness d = 40 nm, gold volumic filling factor p = 0.23

It is possible to get various concentrations by varying the number of small metal pellets laid on the target. With alumina matrix, the plasma is pure argon. The concentration in metal has been predicted by several preliminary measurements

(Rutherford back-scattering and electronic microprobe techniques) either on optical samples or on thicker samples deposited onto copper disks. The metal filling factor varies linearly with the number of pellets laid on the target. In the sample presented on figure (1) the actual measured filling factor is $p = 0.23$.

During deposition, the D.C. resistance of the film is measured in situ [6]. Sputtering can be stopped at any time and any conduction when the aimed resistance is reached. No special cooling or heating of the substrates is performed. The films, studied here, are thin enough to suppose their composition macroscopically homogeneous along their thickness.

The thickness is measured afterwards by X-rays interference on very thin films or with a profilometer on thicker films (d > 50 nm).

The deposition conditions (output power of the supply, argon flux pressure) are carefully maintained so that the deposition rate and the composition are reproducible in agreement with calibration.

It is essential to be very careful with the conditions of preparation, as the composition and thickness of this kind of material are strongly dependent on them and, therefore, the physical properties.

As the TEM images are difficult to analyze and seems to present larger concentration in metal than really, when the studied film is not thin enough to have only one grain in the thickness, it is not very easy to follow conducting path in a sample close to percolation threshold. To characterize more carefully the films we have performed some observations with an Atomic Force Microscope called "Resiscope"[8, 9]. With this set-up we work in Contact Mode (CM). Both tip and cantilever are conducting. A bias voltage (about 1 V) is applied between tip and sample. The film is scanned line by line with the x-y displacement of the piezoelectric tube whereas the applied force (around 10 nN) is held constant by the z-translation of the sample. The resulting current is put in an amplification / conversion device and gives an instantaneous image of the local tip / sample contact resistance. As the substrate is intrinsic silicon, the conducting paths take place in the sample only towards the edge of the film where is the output contact
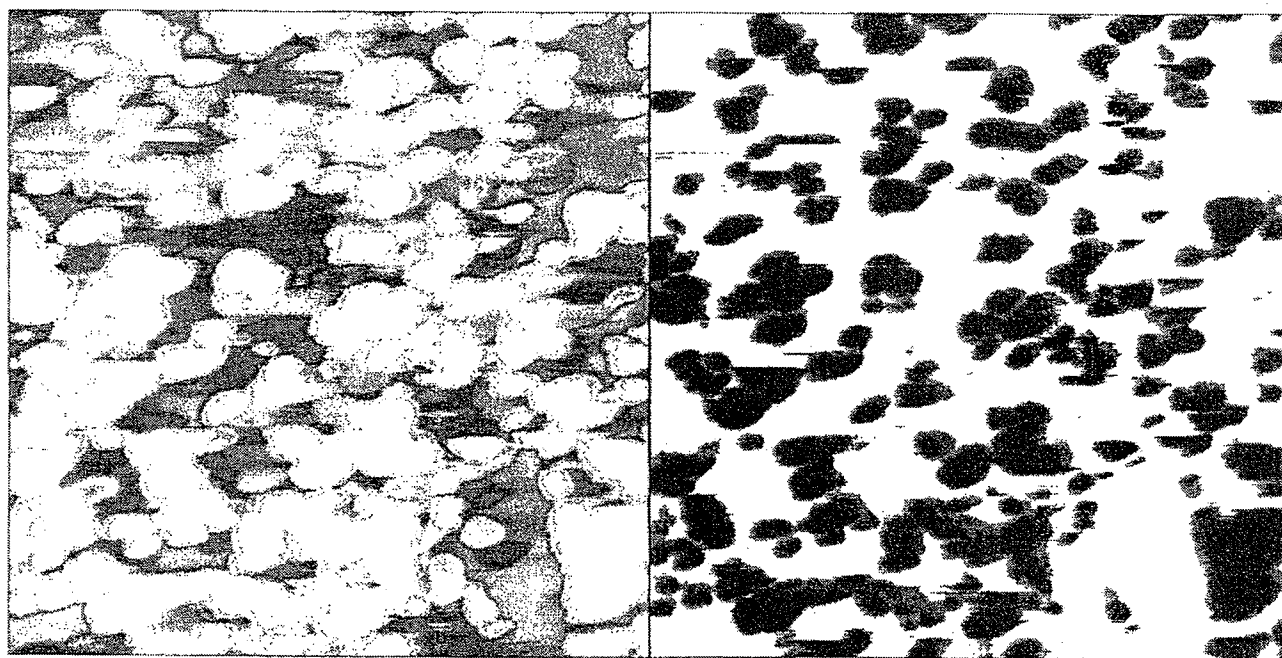
(a)   Without conducting clusters   (b)   Conducting clusters
Density of conducting clusters: 40.1%
Figure 2 : Electrical image of the Au-Al2O3 cermet, performed with the Resiscope set-up

With this set-up, we are able to get simultaneously cartography of both the topography and the electrical features of the sample. The range of contact resistance to be explored is very wide (10^{2} to $10^{11}\Omega$) with a commercial tip and cantilever (N-doped silicon coated with P-doped diamond Nano-sensors DCT). High values of resistance are observed because of the small tip size and therefore small tip / sample contact area. All the measurements are performed at room temperature in the ambient atmosphere.

On figure (2a,b) we show an electrical image of the same gold alumina nano-cermet as the TEM observed sample, with filling factor p = 0.23, and thickness d = 40 nm. The topography does not point out any particular features. On the contrary, on electrical image , the tortuous clusters are obvious. To show the conducting clusters in a better way we have separated them (b) from the insulating area (a).The dark area in figure 2b (small D.C.resistance) correspond to connected grains through out the sample to the electrical contact put on the edge of the film. This path can be hidden in the thickness of the film if the surface is locally covered with insulator, as the tip is in contact with the surface. But nevertheless it belongs to the percolating cluster (backbone). The distribution of the dark grains corresponds to a section of the backbone close to the surface of the film. One can observe that the metallic grains may interact strongly in capacitance and ohmic paths in very intricated geometry. Moreover interactions may happen also in the direction of the thickness. This observation justifies the use and the test of the previous theory explained in section 2.

3.2 Optical properties in the middle infrared range (2.5-40 μm)

Optical measurements of reflectivity and transmittivity over the spectral range (between 2.5 and 40 μm) have been performed on the double beam spectrophotometer Perkin-Elmer(580B) equipped with a V-W set-up to get absolute reflection measurements. We claim that no scattered light has been observed.

In the study of the optical properties one can either observe the rough data of reflectance R and transmittance T versus wavelength, or calculate the relative complex dielectric function and the optical absorption by solving the Fresnel equations. [10]

3.2.1 Study of reflectance R, transmittance T

According to theory, looking at mid infrared optical properties of solid state material when considering an insulating sample, the reflectance R has to decrease with wavelength while transmittance T has to increase. In a conducting material the behavior is opposite.

But in the present work, the samples, being thin films, may show up a drastic change in electrical and optical properties depending on whether they are conducting (on the metallic side) or insulating (on the dielectric side). In the intermediate region one observes a second order phase transition occurring when the sample comes from insulating regime to conducting one, as soon as one first conducting path connects one side of the sample to the opposite one, at the percolation threshold. When the metallic and insulating grains are randomly distributed on a surface, they are called 2D samples, which hides in some way the third dimension (the thickness perpendicular to the substrate) of the films. When the metallic and insulating grains are distributed at random in the same way along the three directions of space, they are 3D. We focus here on these 3D samples,

However, because the used samples are mainly thin films, the three directions cannot be treated in the same way. The direction perpendicular to the substrate, along the thickness of the film, is always much smaller than the two others and even smaller than the wavelength of the light or of the same order of magnitude. This point has to be emphasized, because it is the origin of one very simple result [3], which is not often taken into account. For 2D samples, which are made of a planar distribution of metallic and insulating (often vacuum) grains, the percolation occurs when a sufficient part p of the total surface is covered by metal. In fact, the concentration p is the proportion of the total volume occupied by metal or filling factor. The percolation transition occurs then for a critical value $p = p_{c2D}$ of the metal concentration. This is also the case for true 3D random mixture of insulating and conducting grains, i.e. when the three directions are equivalent and of same order of magnitude. The size of the sample can then be taken as "infinite" compared to the elementary grain size. The percolation transition occurs here for a critical value $p = p_{c3D}$ of the metal concentration. These metal concentrations critical values p_{c2D} and p_{c3D} are not universal: they depend on morphology.

On the contrary, thin cermet films cannot be regarded neither as 2D nor as true 3D samples, because the thickness is of order of few hundreds of nanometers at most, and the two other directions are of order of millimeters at least. At the beginning of the deposit, as long as the thickness is given by the elementary grain size, which is of order of ten to twenty nanometers, the samples have to be regarded as 2D samples. By increasing the amount of deposited material, grains are growing not only in the first substrate plan, but also along the thickness direction. The main consequence is that the DC electrical current has no longer to stay in the substrate plane and can find new connections between the opposite sides of the sample by using the third direction. The percolation transition can then occur easier just by introducing these new connection ways. As a consequence of this, percolation threshold in thin 3D inhomogeneous films depends on two different parameters which are not independent from each other :

♦   for a given finite thickness d, the percolation transition occurs for some metallic concentration $p_c(d)$,

◆ for a given concentration p belonging to the range $p_{c3D} < p < p_{c2D}$, the percolation transition occurs for some film thickness $d_c(p)$.
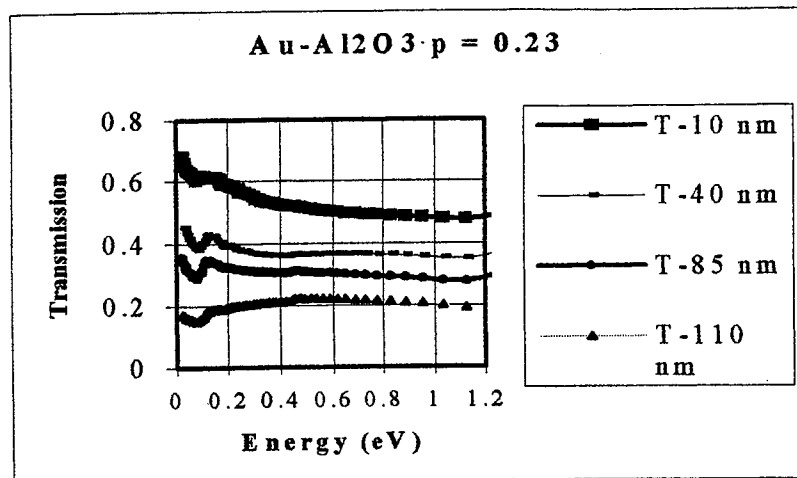

Figure 3 : Transmission of Au-Al2O3 films with same filling facto p = 0.23 and various thickness

On figure (3) we show transmission of several films all of the same filling factor p = 0.23 but of different thickness. The thinner film is then below percolation threshold, the thickest one is above (conducting), the intermediate is very close to the threshold. As expected, we observe that the general slopes of transmission curves are

◆ increasing with energy for conducting film (DC resistance $\approx 40\ \Omega$),
◆ decreasing for insulating film (d = 10 nm, DC resistance > 20 MΩ).

But it is impossible to miss the bump in the transmission at the exact abscissa of the bump in the curve relative to pure alumna that corresponds to the optical phonon of alumna. In these samples, alumna is composed of non ordered micro-crystallites and so, it is not possible to separate the different structures as it could be the case for well crystalline alumna phonon. The experimental results only show the envelope of the phonon absorption, but we already note in these transmission curves that absorption by phonon is quite large in cemets.

3.2.2 Study of the complex dielectric function

To investigate more accurately we calculated the complex dielectric function $\varepsilon'+i\varepsilon''$ for every sample. To compare with theory we represent optical absorption ε''/λ versus energy. Let us notice once more that all these samples have the same filling factor in gold and that the only difference is the thickness and consequently morphology.
We obtain the curves of figure (4).

In this presentation, optical absorption now is an intrinsic characteristic of the material, taking into account the actual morphology of the material. For comparison, we have put the optical absorption of pure alumna, measured on sample elaborated exactly in the same conditions as cermet samples. The expected bump is obvious at the right place corresponding to absorption due to optical phonon in alumna. It is not possible to separate the different structures of the phonon because alumna is micro crystalline, as we told previously. But resolution is already accurate. Looking at the amplitude of the bump, we observe that it is much larger than expected with alumna. For instance, the difference between maximum and mean value of optical absorption, concerning sample just at percolation threshold (d = 40 nm) is almost 3, while it is less than 0.5 for pure alumna in the same spectral range. For this reason, it is not possible to pretend that the bump in absorption is only due to alumna alone. Moreover looking at the amplitude of the bump it seems that it depends on the vicinity of the threshold, since it is larger for the intermediate samples than for the really conducting and really insulating ones.

Au - Al2 O 3   p = 0.23

Legend:
- eps2/1 110 nm
- eps2/1-85 nm
- eps2/1-40 nm
- eps2/1-10 nm
- eps2/1am Al2O3

Y-axis: Optical absorption
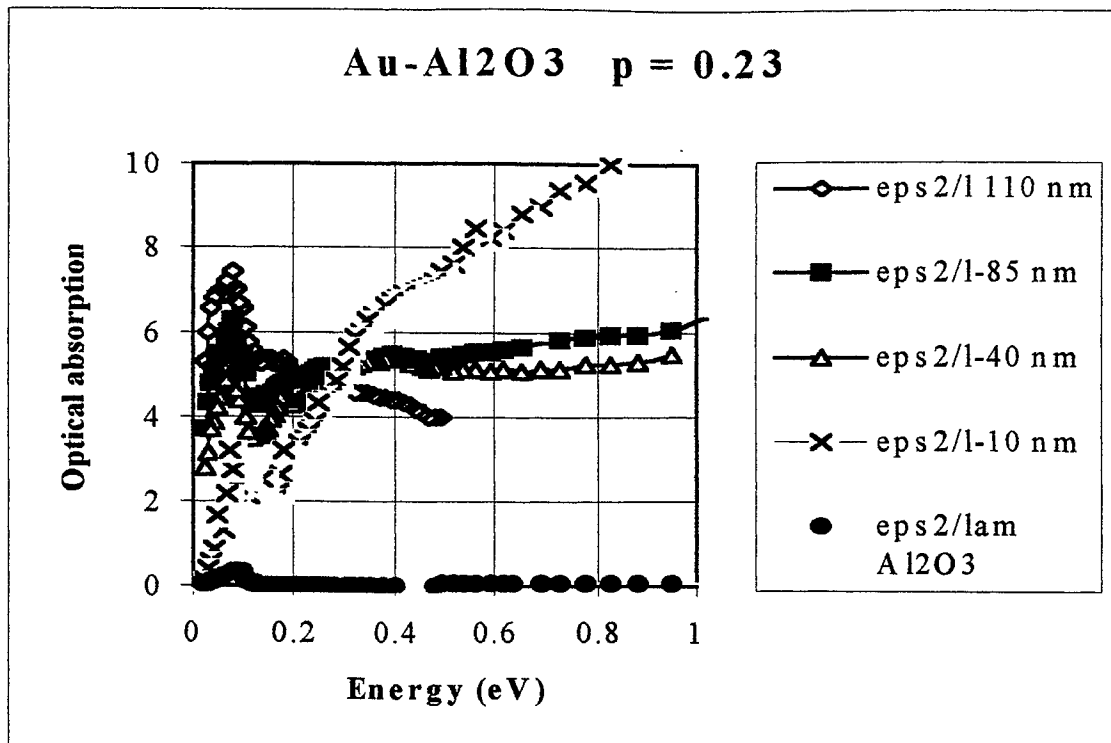X-axis: Energy (eV)

Figure 4 : Optical absorption of the same samples calculated from the experimental results

These remarks lead to testing the theory presented in section 2.

4. COMPARISON BETWEEN EXPERIMENTAL RESULTS AND THEORETICAL MODEL.

To calculate the dielectric function of the composite according to theory, we need the optical parameters of alumna and gold. For alumna, we have used a two oscillators model $\varepsilon_d = \varepsilon_\infty + \sum_j f_j \dfrac{\Omega_j^2}{\Omega_j^2 - \omega^2 - i\omega\gamma_j}$ where ε_∞ stands for the high frequency dielectric function limit, f_j is the oscillator strength, Ω_j is the eigen-frequency and γ_j is the damping of the jth transverse optic mode. These parameters have been chosen according to our measurements performed on sputtered alumina deposited in the same conditions:

Ω_1 = 670 cm-1, Ω_2 = 370 cm-1, $\gamma1 = \gamma2$ = 280 cm-1 ε_∞ = 2.56, f_1 = 1.8 and f_2 = 2.5 .

For gold, as the simulation takes place in the mid infrared range, a Drude formula $\varepsilon_m = \varepsilon_o - \dfrac{\left(\dfrac{\omega_p}{\omega}\right)^2}{1 + i\dfrac{\Gamma}{\omega}}$ has been chosen

to determine optical constants of gold with the following values : $\varepsilon_o = 7$, $\omega_p = 9.2$ ev and $\Gamma = 0.06$ ev.

For critical exponents we use 3D values. The pre-factors c_1 and c_2 are chosen to provide the best fit to experimental data (c_1 = 0.16 and c_2 = 2) which is in good agreement with the predictions of the model [1, 4] where it is shown they have to be in the range of 1.

We have tested the model in the case of the sample that is the closest to percolation threshold and we see(figure 5) that agreement is quite good.
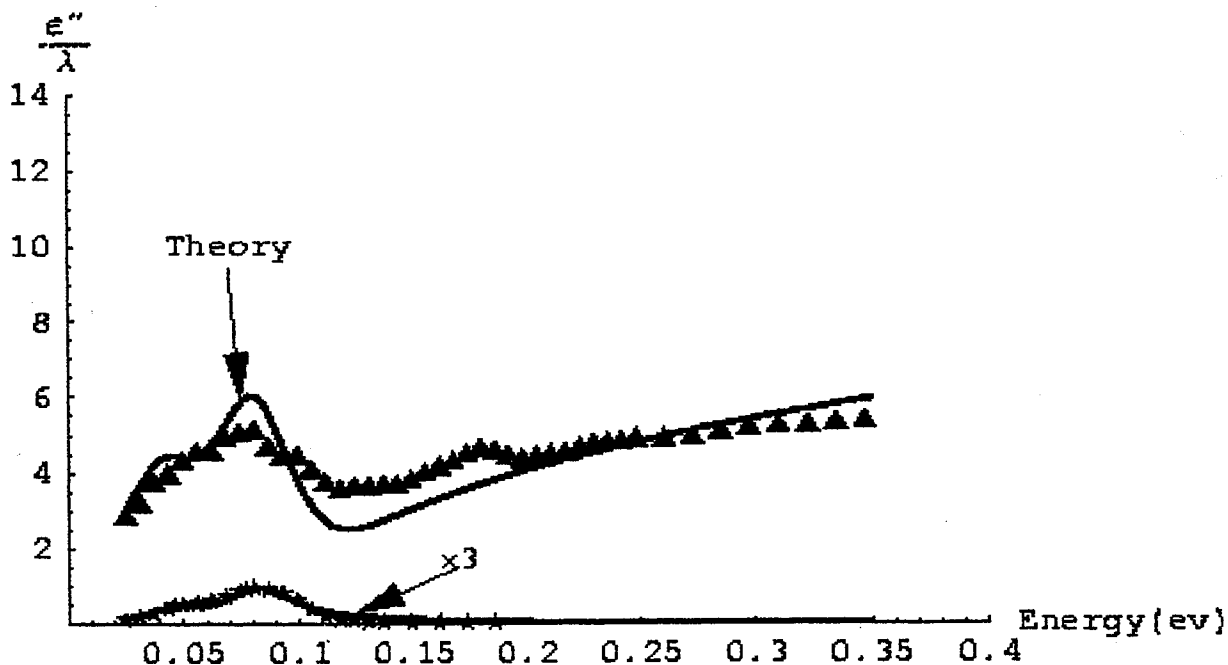

Figure 5 : confrontation between experimental and theoretical results. .Optical absorption of alumina has been multiplied by 3 to be visible.

The general value of absorption is right. As for the slope there is a light difference between experiment and model. Perhaps it is due to the fact the 3D critical exponents of percolation are taken to do calculation. There is a supplementary small bump close to 0.18 eV in energy, probably due to some amount of native silica because of the substrate. In the range of the optical phonon of alumina the magnitude of enhancement is well described. In the calculation the double structure is more obvious although it is already visible in the measurements. Anyway, absorption is much larger than in pure alumina.

5. CONCLUSION

The theory describes well both the enhancement of absorption and the spectral behavior in the case of sample very close to the percolation threshold (d = 40 nm in our case). No other mixture theory could provide a correct description in this spectral range. By using cermets, we have shown that is possible to strongly couple the electromagnetic field enhanced at the hot spots location close to the metallic grains with the vibration modes of the insulator embedding the metal. We have developed a model able to give a reasonable account of the unexplained optical high absorption in the middle infrared range for cermets close to the percolation threshold : the absorption by optical phonons is largely enhanced in regard to pure alumna.
To develop this new model, we have had to take into account the fractal structure of the metallic clusters in strong interaction and to calculate the local field enhancement and the local insulator absorption enhancement factors. This means another time, that effective medium models are not able to give a reasonable account of optical properties of cermets, at least in the percolation range.

AKNOWLEDGMENTS

REFERENCES

[1]V.Shalaev et al. Phys.Rev.B **57**,13265 (1998)

[2] S. Grésillon et al. P.R.L. **82**, 4520 (1999)

[3] M.Gadenne et al. Physica A **157**, 344 (1989)

[4] A.K.Sarychev andV.M.Shalaev, Physics Reports **335**, 275 (2000)

[5] M.Gadenne et al. EuroPhysics Letters **53**,(3) 364 (2001)

[6].M.Gadenne et al. Thin Solid Films, **221**, 183 (1992)

[7]P.Gadenne et al Mat. Res. Soc. Symp. Proc. vol **237**, (1992)

[8] F.Houzé, R.Meyer, O.Schneegans and L.Boyer,Appl.Phys.Lett. **69,** 1975 (1996)

[9] O. Shneegans, F. Houzé, R. Meyer and L. Boyer, Proc. of the 42nd Holm Conf. on Electrical Contacts 205 (1996)

[10]F.Abeles in Advanced Optical Techniques, ed. by A.C.S. van Heel (North Holland, Amsterdam), 144 (1967)

[11] Hand Book of physical constants of Solids, ed. by E.D.Palik (Academic Press, New York), (1985)

[12] T.S.Erikson et al Applied Optics **20**, 2742 (1981)

[13] Clerc et al .Phys. Rev. B 22 ,2489(1980)