

Plasmon-enhanced absorption by optical phonons in metal-dielectric composites

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Abstract. – It is shown that in cermets, with metal percolating clusters in a dielectric host, the metal plasmon modes can strongly couple to the dielectric vibrational modes, optical phonons. In metal-dielectric percolation composites, the plasmon modes are capable of strong accumulation of the electromagnetic energy in small nanometer-sized areas, “hot spots”. The local fields in the hot spots can be very large, leading to enhanced absorption by optical phonons of the dielectric. In our experiments, strongly enhanced absorption by the coupled plasmon-phonon modes has been observed in Au-Al₂O₃ percolation composites.

Optical properties of a metal-dielectric composite are significantly different from those of constituents forming the composite [1–3]. At low metal concentrations in the composite, small metal nanoparticles (grains) are randomly distributed in the dielectric host; with the increase of the metal filling factor p , coalescence between the grains results in irregularly shaped metal clusters, which are self-similar under scale transformation, *i.e.*, the clusters are fractal [4]. The size of these metal fractals increases with p and at the percolation threshold $p = p_c$ a continuous conducting channel between the ends of the sample (“infinite” fractal cluster) is formed [2, 4]. At the percolation, the insulator-conductor phase transition occurs in the composite (in this case, referred to as the percolation composite).

Recently, it was theoretically predicted and verified in experiments that plasmon modes in percolation composites are localized in small (typically, nanometer-sized) areas, “hot spots” [5]. The resonant frequencies of the plasmon modes strongly depend on the local structure of clusters in the area where the modes are localized. The scale-invariant geometry of a percolation composite results in a large variety of shapes and sizes of the resonating structures (from the size of the particle to the size of the infinite cluster). The variety of the structures supporting localized plasmon excitations results, in turn, in an unusually broad spectral range covered by the resonant plasmon modes, from the near UV to the far-infrared (IR) [5, 6]. This is in sharp contrast with the plasmon modes of individual metal particles and compact metal

structures (including bulk and surfaces) that typically lie in the visible or near-UV parts of the spectrum.

The electromagnetic energy is accumulated in the hot spots associated with the localized plasmon modes, leading to large local fields, with the intensity exceeding the applied field by four to five orders of magnitude. This makes possible strong enhancement of a number of optical processes in the extremely broad spectral band [5, 6]. Remarkably, the local-field enhancement associated with the plasmons occurs within a rather large interval of metal concentrations near the percolation threshold. This is because in the visible, near-, and mid-infrared spectral ranges the displacement current dominates the Ohmic current, so that the physical contact between the particles and clusters in composites is not of critical importance. As a result, the broadband local-field enhancement in metal-dielectric composites is a robust effect [5, 6]. Toward the longer wavelengths, however, the concentration range where the enhancement occurs shrinks [5, 6].

In ref. [5, 6], the localization of plasmon modes in percolation composites was attributed to the Anderson localization in disordered systems. This was done by mapping the problem of plasmon modes, that can be described in terms of the Kirchhoff Hamiltonian [5, 6], to the quantum-mechanical Anderson problem. Recently, it was shown in [7] that the problem of the field distributions in percolation composites can be reduced to Efetov's nonlinear σ -model [8], which provides a direct link to the theory of Anderson localization.

In the present paper we address the problem of the enhanced infrared absorption in metal-dielectric composites that has been extensively studied both theoretically and experimentally [9]. Despite all the efforts and accomplishments the problem still remained not fully explained. A number of physical mechanisms was suggested to explain the effect, including clustering of metal particles (see [9] and references therein) and Breit interactions between electrons [10]. In all these models, however, the composite absorption was assigned entirely to metallic particles, whereas the absorption by a dielectric host was neglected. Below we show that the mid-infrared plasmon modes can strongly couple to the optical phonons of the dielectric host leading to the enhanced absorption.

As theory [5, 6] predicts, the largest local fields in percolation composites occur in dielectric gaps between the metal clusters supporting plasmon modes. Therefore, even very small absorption in the dielectric can be dramatically enhanced because of the large local fields associated with the plasmons. In particular, the mid-infrared absorption by optical phonons of the dielectric can be dramatically enhanced, provided that the metal plasmon modes are excited in the same spectral range, which is possible in the composites.

Although it is, indeed, very important to advance our understanding of the enhanced IR absorption in composites and explore a new related effect, we believe that the proposed mechanism of the plasmon-phonon coupling goes beyond this. The significance of the studied effect also lies in the fact that the local evanescent field, similar to those used in the near-field optical microscopy, can be employed for strongly enhancing optical phonons and thus opening the way to "visualize" localized phonon modes in insulators. The feasibility of this development could inspire new experimental studies and, eventually, lead to novel means for studying the phonons.

Below we first outline the developed theory showing that the light absorption due to the combined plasmon-phonon excitations in metal-dielectric composites can significantly exceed the individual absorptions by the metallic and dielectric components (and by their sum). Then we present results of our experimental studies of the enhanced absorption in Au-Al₂O₃ cermetts.

The absorption coefficient α can be expressed in terms of the imaginary part of the *effective* dielectric constant ϵ'' as $\alpha = k\epsilon''$, where $k = 2\pi/\lambda$ is the light wave vector. As follows from

the optical theorem applied to metal-dielectric composites, the quantity ϵ'' can, in general, be represented as

$$\epsilon'' = p\epsilon_m'' \frac{\langle |\mathbf{E}(\mathbf{r})|^2 \rangle_m}{|E_0|^2} + (1-p)\epsilon_d'' \frac{\langle |\mathbf{E}(\mathbf{r})|^2 \rangle_d}{|E_0|^2}, \quad (1)$$

where $\epsilon_m = \epsilon_m' + i\epsilon_m''$ and $\epsilon_d = \epsilon_d' + i\epsilon_d''$ are the dielectric constants for the metal and dielectric components, and the angular brackets, $\langle \dots \rangle_d$ and $\langle \dots \rangle_m$, denote the spatial averaging over the dielectric and metal, respectively. The field factors in (1) represent enhancement of the absorption in metallic and dielectric parts of the composite. Because of the high local fields, $E(\mathbf{r}) \gg E_0$, resulting from plasmon excitation, this enhancement can be large for both components of the composite. It is also clear from (1) that even a small ϵ_d'' (ignored in previous considerations) can lead to significant absorption, provided that the field enhancement in the dielectric component is strong.

In the mid-infrared, where optical phonons can be excited, the dielectric function ϵ_d of a dielectric can be well approximated by the following expression (see, for example, [11]):

$$\epsilon_d = \epsilon_\infty + \sum_j f_j \frac{\Omega_j^2}{\Omega_j^2 - \omega^2 - i\omega\gamma_j}, \quad (2)$$

where ϵ_∞ stands for the high-frequency dielectric constant; f_j , Ω_j , and γ_j are the oscillator strength, the frequency, and the damping of the j -th transverse optic mode, respectively.

For the dielectric function of a noble metal in the infrared part of the spectrum, one can use the Drude model

$$\epsilon_m = \epsilon_0 - (\omega_p/\omega)^2 / [1 + i\Gamma/\omega], \quad (3)$$

where ϵ_0 is contribution due to interband transitions, ω_p is the plasma frequency, and Γ is the plasmon relaxation rate.

Now, given ϵ_d and ϵ_m , we can calculate the field enhancement and absorption in both metal and dielectric components, by applying the approach suggested in [5,6].

As shown in refs. [5,6] the average intensity of the local field $E = E(\mathbf{r})$ in the dielectric component of a composite is enhanced by the following factor:

$$G_d = \langle |E/E_0|^2 \rangle_d \sim (a/\xi_A) (|\epsilon_m'|/|\epsilon_m''|) |\epsilon_m/\epsilon_d|^{\nu/(t+s)}. \quad (4)$$

In eq. (4), indices t and s are the percolation critical exponents for the conductivity and dielectric constants, respectively, and ν is the critical index for the percolation correlation length, $\xi \sim |p - p_c|^{-\nu}$; for 3D systems, the indices are given by $\nu \approx 0.89$, $t \approx 2.05$, and $s \approx 0.76$ [2]. The scale ξ_A in (4) represents the Anderson localization length, in the special case of $\epsilon_m = -\epsilon_d$, corresponding to the plasmon resonance of individual grains; a is the size of the grains ($a \sim 10$ nm). Typically, ξ_A/a ranges from 1 to 10 [5].

In the mid-infrared, the dielectric constant for a metal is much larger than the one for a dielectric, $|\epsilon_m| \gg |\epsilon_d|$. Also, as follows from (3), for frequencies exceeding the plasmon relaxation rate, *i.e.*, for $\omega \gg \Gamma$, we have $|\epsilon_m'| \gg \epsilon_m''$. Thus, according to (4), in the infrared part of the spectrum, the field enhancement G_d (and thus absorption) in the dielectric component can be very large.

As shown in [5], the average field enhancement in the metallic component of a composite, G_m , is estimated as

$$G_m = \langle |E/E_0|^2 \rangle_m \sim (|\epsilon_m'|/|\epsilon_m''|) |\epsilon_d/\epsilon_m|^{t/(t+s)}. \quad (5)$$

According to (5), the absorption enhancement, G_m , in a metallic component of the composite can be also large at $\omega \gg \Gamma$ when $|\epsilon_m'| \gg \epsilon_m''$.

It is interesting to note that the absorption by a metal component of the composite does not depend on ϵ''_m . This is because the resonant field enhancement is determined by the quality factor, which is proportional to $|\epsilon'_m|/\epsilon''_m$, and thus, in the expression for metal absorption, $\alpha_m \propto \epsilon''_m G_m$, the factor ϵ'' cancels out. Therefore, the absorption is independent of the plasmon relaxation rate Γ (see (3)). Different metal clusters in the composite have randomly shifted levels and resonate at different frequencies, which results in rapid relaxation of the light-induced polarization, with the rate independent of the plasmon lifetime Γ^{-1} . This effect is similar to the Landau damping in the sense that the finite width and the imaginary part of the dielectric function (and absorption) are independent of dissipation.

Now we note that, as follows from (4) and (5), the absorption enhancement in a dielectric component can be much larger than in the metallic component, $G_d \gg G_m$. By comparing $\epsilon''_d G_d$ and $\epsilon''_m G_m$, we also see that the absorption in the metal-dielectric composite can be dominated by the dielectric component (even at $\epsilon''_d \ll \epsilon''_m$), provided that $(a/\xi_A)|\epsilon_m/\epsilon_d|^{(\nu+t)/(t+s)} \gg \epsilon''_m/\epsilon''_d$.

By combining now (1) with (4) and (5) and approximating $|\epsilon'_m|$ by $|\epsilon_m|$, we ultimately obtain the following expression for the imaginary part of the effective dielectric function, $\epsilon'' = G_d \epsilon''_d + G_m \epsilon''_m$:

$$\epsilon'' = c_1 (a/\xi_A) \epsilon''_d (|\epsilon_m|/\epsilon''_m) |\epsilon_m/\epsilon_d|^{\nu/(t+s)} + c_2 |\epsilon_m|^{s/(t+s)} |\epsilon_d|^{t/(t+s)}. \quad (6)$$

In eq. (6) we introduced the adjustable coefficients c_1 and c_2 , which are needed because the scaling formulas (4) and (5) are, indeed, estimates rather than exact equations. If these estimates are good, then the constants c_1 and c_2 are anticipated to be of the order of one.

As follows from eq. (6), the absorption in a percolation metal-dielectric composite ($\alpha = (2\pi/\lambda)\epsilon''$) can be much stronger than the individual absorptions by the bulk dielectric and metal; moreover, the composite absorption can also be much greater than the metal absorption in a dielectric with no optical phonons. This, indeed, occurs due to the strong plasmon-phonon coupling in the composite material.

Below we describe results of our experimental studies and compare them with the theoretical predictions above.

Reflectance and transmittance measurements are performed with a Perkin Elmer 580 B grating spectrophotometer, in the range from 2.5 to 30 microns. This double-beam spectrophotometer is equipped with a *V-W* set-up to perform absolute reflection measurements. By solving the Fresnel equations, as described in [12], for a thin film on a silicon substrate and using the Newton-Raphson method, we determine the complex dielectric function of Au-Al₂O₃ cermets, for the whole spectral range. This, in turn, allows us to determine the optical absorption, ϵ''/λ .

The samples used in our experiments are Au-Al₂O₃ cermet thin films deposited by radio-frequency co-sputtering onto optically polished intrinsic silicon wafers (for details, see [13]). As TEM micrographs show, the size of gold grains varies between 4 nm and 12 nm. The metal filling factor p depends only on the composition of the target, consisting of an alumina disk on which small gold cylinders are regularly arranged in a hexagonal array. The number of small metallic plates determines the composition. The filling factor p is measured by nuclear and electronic microprobe analysis. A rotating substrate holder allows the homogeneous planar composition. The DC resistance is measured *in situ*, during the deposition, so that it is possible to prepare samples very close to the percolation threshold. The filling factor in our experiments is given by $p = 0.23 \pm 0.01$.

When one gradually increases the film thickness keeping the metal filling factor fixed, the composite transits from a 2D system (very thin film) to a 3D system (relatively thick film),

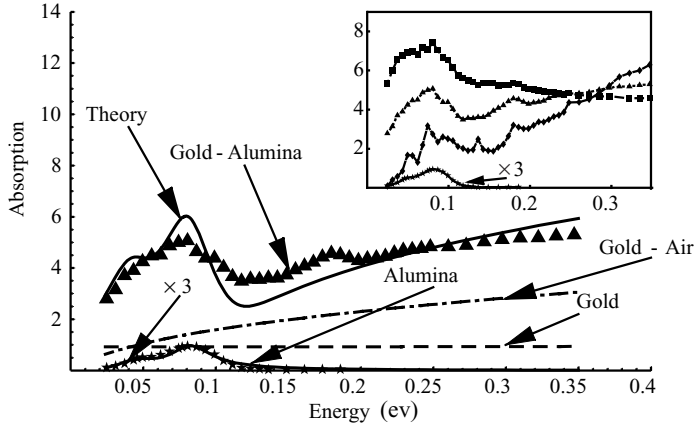


Fig. 1 – Absorption in polycrystalline alumina Al_2O_3 , percolation gold-alumina and gold-air films, and a pure gold film of thickness $d_m = pd_p$. For the pure alumina and for the percolation composites with gold nano-particles, the absorption per unit length is given by ϵ''/λ , whereas for the bulk gold film the corresponding absorption is represented by $A_m/(2\pi d_m)$, with A_m being the metal film absorptance (see the text for details; in the figure, λ and d_m are in microns). The stars are measurements of ϵ''/λ in alumina and the solid line is the 2-oscillator fit with eq. (2); all ϵ'' values are multiplied by 3. The triangles are measurements of ϵ''/λ in Au- Al_2O_3 cermet and the solid line is the result of theoretical calculations using eq. (6) with the same parameters as in Al_2O_3 (thickness: $d_p = 40$ nm, metal filling factor: $p = 0.23$). The dot-dashed line is absorption, ϵ''/λ , by gold-air percolation composite found from eq. (6) with $\epsilon_d = 1$. The dashed line is absorption, $A_m/(2\pi d_m)$, by bulk gold film of thickness $d_m = 9.2$ nm. Inset: Absorption, ϵ''/λ , in pure alumina (stars) and in gold-alumina films with same filling factor $p = 0.23$ but different thickness: below the percolation (diamonds: $d = 10$ nm), at the percolation (triangles: $d = d_p = 40$ nm), and above the percolation (squares: $d = 110$ nm).

which, as known, have different percolation thresholds [2, 13]. Our measurements of the DC resistance show that at $p = 0.23$ thin films, with thickness $d \approx 10$ nm, are far below the threshold, whereas relatively thick (3D) films, with $d \approx 100$ nm and more, are well above the threshold; the percolation was measured to occur at $d = d_p \approx 40$ nm. (The film thicknesses were measured by X-ray Kiessig fringes under grazing incidence.)

In fig. 1, we show results of our measurements of the optical absorption, ϵ''/λ , for pure alumina and for gold-alumina composite films.

For the polycrystalline aluminum oxide Al_2O_3 (alumina), our absorption is similar to that measured earlier in ref. [14], which is shown in the figure. The experimental data for pure alumina, as seen in fig. 1, is in excellent accord with the two-oscillator model used in our calculations. In this model for ϵ_d we set in (2) the following parameters: $\Omega_1 = 670$, $\Omega_2 = 370$, $\gamma_1 = \gamma_2 = 280$ (all quantities are given in the wave numbers, cm^{-1}), $\epsilon_\infty = 2.56$, $f_1 = 1.8$, and $f_2 = 2.5$, and all other f_j are equal to zero. For the dielectric function ϵ_m of gold, we used the Drude formula (3) with the following parameters: $\epsilon_0 = 7$, $\omega_p = 9.2$ eV and $\Gamma = 0.06$ eV [11].

Calculations of the enhanced absorption are performed using (6), with ϵ_m and ϵ_d specified above. For the critical exponents in (6) we used the 3D values. (We cannot rule out, however, that the actual critical exponents for our quasi-3D systems can be somewhat different from those measured in conventional 3D systems [2].) The pre-factors c_1 and c_2 in (6) were chosen to provide the best fit to experimental data, namely, as $c_1(a/\xi_A) = 0.16$ and $c_2 = 2$. Taking into account that according to simulations and experiments of [5] the factor (a/ξ_A) is typically

in the range between 1 and 10, we conclude that both fitting coefficients, c_1 and c_2 , are of the order of one that indicates that the scaling formulas (4) and (5) estimate the enhancement well.

In fig. 1, we also show the absorption by a pure gold film, with the same amount of metal as in the composite, so that the thickness of the film is $d_m = pd_p \approx 9.2$ nm. Because of the skin effect and reflection, absorption by bulk metal is not given by ϵ''/λ , as in the case of a pure dielectric and a composite including metal particles of the *sub-wavelength* size. Instead, the absorption per unit length in a bulk metal film of thickness d_m ($\ll \lambda$) is given by A_m/d_m , where A_m is the film's absorptance [15]. In the limit of large ϵ_m that corresponds to our experimental situation $1/|\epsilon_m| \ll (\omega/c)d_m \ll 1/\sqrt{|\epsilon_m|}$, and the absorptance A_m is given by $A_m = (2\lambda/\pi d)\epsilon_m''/|\epsilon_m|^2$ [15]. Therefore, to compare with the absorption per unit length (divided by 2π) in the composite, ϵ''/λ , we also plot in fig. 1 the corresponding quantity $A_m/(2\pi d_m) = (\lambda/\pi^2 d_m^2)\epsilon_m''/|\epsilon_m|^2$, representing the absorption per unit length (also divided by 2π) in the bulk gold film.

The main conclusion following from fig. 1 is that the absorption in the alumina-gold composite is enhanced dramatically in comparison with both pure alumina and pure gold film. The observed enhancement occurs because of the plasmon-phonon coupling and it is in good qualitative agreement with our theoretical calculations. The theory describes well the main features of the observed effect: strong enhancement of the absorption and, approximately, its spectral dependence. Some discrepancy seen in the figure can occur because of the uncertainty in the values of the critical exponents mentioned above. Another possible reason is due to the size distribution of constituent elementary particles, roughly between 4 nm and 12 nm. In such small gold particles, the size effect can be important, leading to the modified values of the plasmon relaxation rate Γ , different for particles of different sizes.

We note that in contrast to metal-alumina composites, the alumina absorption did not change significantly in composites of alumina with other dielectrics not supporting plasmons. This proves that the observed enhanced absorption is directly related to the mid-IR *plasmons* rather than some other possible reasons, such as the alteration of alumina phonons in the composite, and defects or impurities. To emphasize the role of the second component, optical *phonons*, in the observed effect, in fig. 1 we also show that absorption by the gold-alumina composite significantly exceeds absorption by a gold-air composite, with the latter found from eq. (6) with $\epsilon_d = 1$. (Note that if we set in (6) $\epsilon_d = \epsilon_\infty = 2.56$, the absorption still remains significantly less than in the gold-alumina composite supporting optical phonons.)

To illustrate the robustness of the observed effect, we also show (in the figure's inset) the absorption detected in samples below and above the threshold. For all the composites, significant enhancement in absorption has been detected. In thin, below-threshold films ($d = 10$ nm), the absorption above 0.1 eV increases with the frequency at the rate which is somewhat less than the ω^2 -dependence predicted by theory for $p \ll 1$ [2, 4, 6]; the slower increase is not surprising because p in our case is not that small. The largest absorption occurs in thick samples, with $d = 110$ nm. According to estimations, at this film thickness the skin effect becomes important. It is shown in [16] that because of the skin effect, there is strong interaction between the electric and magnetic fields leading to the local magnetic fields in a composite film as large as the electric fields. As a result, absorption due to metal can be significantly increased. Due to the large density of states and hence the field strength in the dielectric gap region associated with the optical phonons, it is plausible that the further increase in absorption at the mid-infrared occurs in metal but is induced by the optical phonons.

In summary, the plasmon-phonon coupling results in strongly enhanced absorption in metal-dielectric composites near a percolation threshold. The absorption by the coupled plasmon-phonon modes can be much greater than the individual plasmon and phonon absorptions.

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