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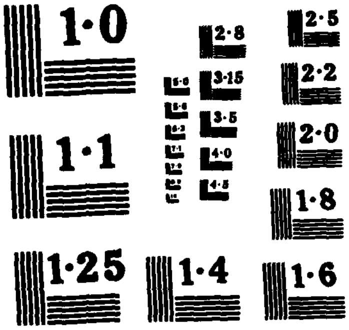
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Composite Materials, Thin Films, Theory, Multiple Scattering Theory of Optical Properties, Optical Properties of Non-Homogeneous Materials

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

A theoretical model is formulated that predicts the optical properties of non-homogeneous materials (cermets). It has been found that correlation effects due to the formation process of cermets, quantum size corrections, and renormalized corrections are essential ingredients of a realistic theory for the optical properties of cermets. This is particularly true in the high concentration regime of the metallic minority constituent (when concentration of the metal exceeds 10% volume fraction). The First Smoothing Approximation was used in the

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20. ABSTRACT CONTINUED

multiple scattering calculation in the context of the random continuum and distinct metallic island models for cermets. The T-Matrix renormalized calculation applied to the distinct metallic island model for cermets was found to give the best predictive theory. This model predicted the frequency and height of the observed resonance in the imaginary part of the index of refraction with a high degree of precision for a wide regime of concentration and materials.

Additional Keywords: Thin films.

MULTIPLE SCATTERING THEORIES FOR OPTICAL PROPERTIES OF COMPOSITE MATERIALS

FINAL REPORT

DR. MANUEL GOMEZ RODRIGUEZ

JUNE 15, 1981 TO MAY 15, 1985

U.S. ARMY RESEARCH OFFICE

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UNIVERSITY OF PUERTO RICO
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Appendix I (Copies of Publications):

1. M. Gómez, et al, Corrections to the Optical Properties of Cermets I. Quantum Size Effects, Ferroelectrics Letters, (5 EMF Conference) Vol. 54, 223-226, (1984).

2. M. Gómez, et al, Corrections to the Optical Properties of Cermets II. Application of the Quantum Size Effects to a Real Cermet, Ferroelectric Letters, (5 EMF Conference) Vol. 54, 227-230, (1984).

3. M. Gómez, et al, Corrections to the Optical Properties of Cermets III. Multiple Scattering Corrections, Ferroelectric Letters, Vol. 2, No. 1-4, 17, (1984).

4. M. Gómez and L. Fonseca, Multiple Scattering Renormalized T-Matrix, Theory to the Dielectric Constant of Non-Homogeneous Thin Films, Proceedings of the Sixth International Conference on Thin Films, Thin Solid Films, (accepted for publication), (1984).

5. M. Gómez, et al, Multiple Scattering Theories Including Correlation Effects to obtain the Effective Dielectric Constant of Non-Homogeneous Thin Films, Proceedings of the Third Latin American Symposium on Surface Physics, Small Particles and Thin Films, (accepted for publication), (1985).

BRIEF OUTLINE

In this project a theoretical model was formulated to predict the optical properties of non-homogeneous materials (cermets). This task has now been fully completed. Our calculations and the model have corroborated our original prediction that correlation effects due to the formation process of cermets, quantum size corrections, and renormalized corrections, are essential ingredients to give a realistic theory for the optical properties of cermets. This is particularly true in the high concentration regime of the metallic minority constituent (more than 10% volume fraction of the metallic constituent). The results of this work have been published in six papers.(See Appendix I).

The principal findings which are presented and elaborated in the published articles can be summarized as follows:

1. For cermets with island radiuses under 100A, the dielectric constant of the metallic constituent must be calculated using a quantum formalism. For radiuses that are between 100 and 50A the formalism developed by D. M. Wood and N. W. Ashcroft and the one developed by A. Kawabata and R. Kubo give similar results except for a geometrical factor, while for islands of radius under 50A, the Wood and Ashcroft formalism must be used. The structure found in the Wood and Ashcroft model must be smoothed by averaging the dielectric constant with a log-normal distribution of radiuses before it can be used in calculating the dielectric properties of cermets.
2. Using the Random Continuum Approach and doing a multiple scattering calculation in the First Smoothing Approximation, a dielectric constant for cermets was obtained. The resulting dielectric constant improved the zeroth-order non-correlated model of Bruggeman by reducing the intensity of the resonance of the complex index refraction, thus, achieving a better agreement with experimental results.

3. A better effective dielectric constant was obtained when the First Smoothing Approximation was improved by developing a renormalized procedure that used a T-Matrix formalism. With the renormalized approach, the resonance peak of the refractive index was shifted to the correct position in the spectrum, thus obtaining excellent agreement with the experimental results. This calculation was performed taking MG as the zeroth-order approximation dielectric constant since it is based on a model that sees cermets as distinct island embedded in a dielectric medium.

LIST OF PUBLICATIONS

M. Gómez, et al, Corrections to the Optical Properties of Cermets I. Quantum Size Effects, Ferroelectrics Letters, (5 EMF Conference) Vol. 54, 223-226, (1983).

M. Gómez, et al, Corrections to the Optical Properties of Cermets II. Application of the Quantum Size Effects to a Real Cermet, Ferroelectric Letters, (5 EMF Conference) Vol. 54, 227-230, (1983).

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M. Gómez, et al, Multiple Scattering Theories Including Correlation Effects to obtain the Effective Dielectric Constant of Non-Homogeneous Thin Films, Physical Review B (accepted for publication), (1985).

LIST OF PRESENTATIONS

1. "Corrections to the Optical Properties of Cermets". M. Gómez, G. Rodrîguez, and L. Fonseca; 5th European Meeting on Ferroelectricity, Spain, 1983.
2. "Multiple Scattering Theories for the Prediction of the Optical Properties of Cermets". M. Gómez; Jerusalem University, Israel. 1984.
3. "Multiple Scattering Renormalized T-Matrix Theory to the Dielectric Constant of Non-Homogeneous Thin Films". Sixth International Conference on Thin Films, M. Gómez and L. Fonseca; Stockholm, Sweden, 1984.
4. "Multiple Scattering Theories Including Correlation Effects to Obtain the Effective Dielectric Constant of Non-Homogeneous Thin Films". Third Latin American Symposium on Surface Physics, Small Particles and Thin Films, M. Gómez et al; San José, Costa Rica, 1984.
5. "Multiple Scattering Theory Including Correlation Effects for the Optical Effective Dielectric Constant of Non-Homogeneous Films". III Taller de Fîsica de Superficies, M. Gómez, et al; Mexico, 1985.

PARTICIPATING SCIENTIFIC PERSONNEL AND DEGREES AWARDED

This project provided support for a successful Master's thesis and for the Ph.D. thesis of the first student to graduate from the new Ph.D. program in Chemical-Physics, a joint interdisciplinary undertaking of the Physics and Chemistry Department of the University of Puerto Rico. It has also supported two undergraduate students in research projects. Of these students, one has been admitted to the Ph.D. program in Chemical Physics and the other has entered the M.S. of the Physics Department. Luis Cruz, the undergraduate student that has entered the M.S. program received the distinction of being the most outstanding graduating student of the College of Natural Sciences of the University of Puerto Rico at the 1985 Commencement Ceremony. Gerardo Rodríguez the student who received the M.S. degree under this project is currently doing his Ph.D. at Cornell University under Dr. A. Sievers in the field of optical properties of condensed matter.

<u>List of Participating Scientific Personnel</u>:

1. M. Gómez Rodríguez, Dept. of Physics, University of Pueto Rico, Río Piedras, PR 00931.
2. G. Rodríguez received his M.S. degree in May 1983.
3. L. Fonseca received his Ph.D. degree in Chemical-Physics in November 1984. His dissertation work was part of this project and his stipends as a graduate research assistant were financed by the Army Research Office.
4. A. Velázquez received his B.S. degree in July 1984.
5. L. Cruz received his B.S. degree in May 1985.

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APPENDIX I

Ferroelectrics, 1984, Vol. 54, pp. 223-226
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CORRECTIONS TO THE OPTICAL PROPERTIES OF CERMETS. I. QUANTUM SIZE EFFECTS

MANUEL GOMEZ, GERARDO RODRIGUEZ†, and LUIS FONSECA
Physics Department, University of Puerto Rico, Río Piedras, Puerto Rico; †Present address: Cornell University, Ithaca, NY

Abstract The dielectric constant of metallic grains in real cermets is obtained using the formalism developed by Wood and Ashcroft, and the resonance structure derived from this formalism is smoothed out by using a log-normal distribution to average the dielectric constant over grain sizes. The results from the quantum theory for the metallic inclusions in Au/Al_2O_3 cermet are compared with Drude's results against experimental data using mean field theory to obtain the effective medium dielectric constant of the cermet.

INTRODUCTION

Cermets are special types of composite materials made of two constituents, one metallic and the other dielectric, possessing a granular structure where the typical diameter of the grains is of the order of a 100 A. Given the small size of the microstructure, it is always possible to describe its infrared and visible optical properties in terms of an effective medium dielectric constant.

Mean field theories that express the effective dielectric constant of the cermet in terms of the known parameters of the constituents have been developed. The best known effective medium theories are the Maxwell-Garnett[1] and the Bruggeman[2] theories. Most of the mean field theories perform calculations using for the metal constituent a bulk dielectric constant that is corrected by an effective mean free path due to surface scattering of the electrons at the grain's boundaries.

Our objective is to develop a more realistic dielectric constant for the metallic grains that take into account quantum size effects (QSE). The quantum corrected dielectric constant of the metal will be susbtituted into the Bruggeman theory and the results compared with experimental data for real cermets.

This work is presented in two parts. First part describes the theoretical model used to consider quantum effects. Second part (following paper) describes the procedure to smooth out the discrete structure appearing in the QSE calculations and compares the effective medium dielectric constant of the Au/Al_2O_3 cermet calculated using QSE and Drude's model (D) against experimental data. Final conclusions appear in the second article.

Quantum Size Effects

Due to the sizes of the metallic grains the bulk dielectric constant of the metal must be corrected for size effects before being used in the mean field calculations. Traditionally the D constant together with the interband terms is used and the mean free path is corrected for grain boundary collisions. Unfortunately this correction is not justified for smaller particles since it does not fully take into account size effects.

For islands of sizes smaller than 100 A a quantum treatment is needed. We will introduce the Wood and Ashcroft[3] formulation in calculating quantum size effects for small metallic particles. We summarize the salient points of their theory. The induced current produced by the applied field is calculated expanding the density matrix in terms of the perturbing field. The Liouville equation is then solved using the Linear Response Theory in the Random Phase Approximation, and then simplified within the Diagonal Response Approximation that is equivalent to assume that the electron system is homogeneuos, and only responds to the wave vector of the applied field.

In the region of interest for the optical properties of cermets ($0.2\mu m<\lambda<20\mu m$) the long wave length limit applies and it is possible to expand the expression for the dielectric constant obtained from the induced current in powers of the ratio between the frequency of the applied field and the plasma frequency. This yields a dielectric constant expression in terms of the matrix elements of the momentum of the electron along the applied field.

The grains in cermets usually have completely undefined shapes but since the wave lengths of interest to this work are considerably larger than the grain sizes, we can again follow the approach of Wood and Ashcroft and assume the grains to be cubic in form. The field is then taken to lie in the direction normal to one of the box faces. Then all that is needed is the spectrum of an electron in a one-dimensional quantum box. To take into account the effect of a finite electron relaxation times, the adiabatic switching-on term is replaced by an effective relaxation time τ. Within the Mermin scheme[4] the dielectric function for the metallic particles can then be written as,

$$\mathrm{Re}\,\varepsilon(x) = 1 + \frac{4^4}{\pi^4} \frac{a}{a_0} \sum_{m=1}^{m_c} m^2 (m_c^2 - m^2) \times$$

$$\sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2-(x^2+\Gamma^2)][1-(-1)^{m+m'}]}{\Theta}$$

$$\mathrm{Im}\,\varepsilon(x) = \frac{4^4}{\pi^4} \frac{a}{a_0} \frac{\Gamma}{x} \sum_{m=1}^{m_c} m^2 (m_c^2 - m^2) \times$$

$$\sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2+x^2+\Gamma^2][1-(-1)^{m+m'}]}{\Theta} \qquad (1)$$

, where

$$\Theta = \Delta^3 \{(\Delta^2 - x^2 + \Gamma^2)^2 + 4x^2 \Gamma^2\}; \quad \Delta = m'^2 - m^2$$

$$x = 2h\omega\, ma^2/h^2\pi^2; \quad \Gamma = hm_c{}^2/\tau\varepsilon_f; \; m_c = \mathrm{INT}(K_f a/\pi)$$

ε_f is the Fermi energy, K_f the Fermi wave number, a the size of the grains, and a_0 the Bohr radius.

Figure 1 compares the dielectric constant calculated using the QSE as expressed in Eq. (1), with that calculated using D model. In the calculation of the D model the size of the silver

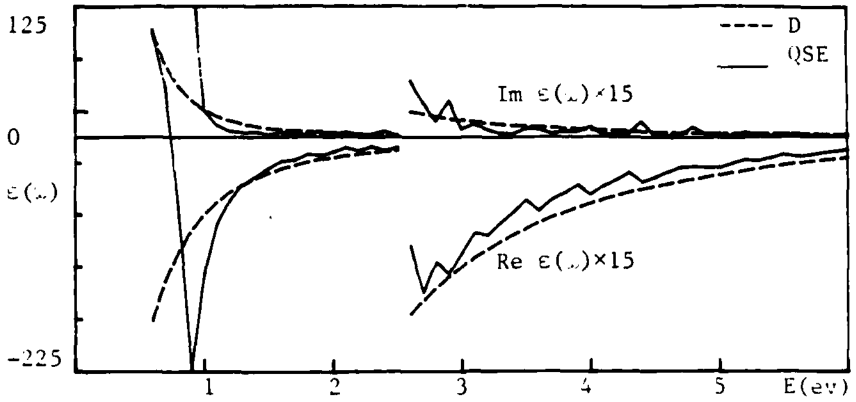

FIGURE 1 Dielectric constant of Ag metallic grains calculated using D model and QSE for a 30 A grain.

particles are taken to be 30 A and no interband contributions have been included. D model was corrected for size effect using an effective relaxation time that corrects the bulk result with grain boundary scattering. The multiple peaks appearing in the QSE calculations are due to the discrete energy spectrum of an electron in a box. In the next part of this work (following article) we will discuss the application of QSE to real cermets.

ACKNOWLEDGEMENT

This work was supported by the Army Research Office through Grant #DAAG-29-81-G0010.

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Ferroelectrics, 1984, Vol. 54, pp. 227-230
0015-0193/84/5401-0227$18.50/0

CORRECTIONS TO THE OPTICAL PROPERTIES OF CERMETS. II. APPLICATION OF THE QUANTUM SIZE EFFECTS TO A REAL CERMET

MANUEL GOMEZ, GERARDO RODRIGUEZ†, and LUIS FONSECA
Physics Department, University of Puerto Rico, Río Piedras,
Puerto Rico; †Present address: Cornell University, Ithaca, NY

Abstract See Part I (preceding paper).

Application of the QSE to a Real Cermet

We will apply the Quantum Size Effects (QSE) result described in Part I to the calculation of the optical properties of real cermets and compare the results with those obtained using Drude's model. In these calculations interband contributions to the dielectric constant of the metal grains will be fully taken into account. Experimentally the resonances observed in the dielectric constant of an isolated metal grain due to QSE are not observed in the effective dielectric constant of a real cermet. The disappearance of these peaks is due to the fact that the metallic grains in a real cermet do not have a unique size, but instead have a distribution of sizes. For this reason the dielectric constant obtained from the QSE calculations for one isolated particle was averaged over a distribution that realistically represented variation in size in actual cermets.

The histogram of the size distribution is skewed and actually, a log-normal distribution is usually used to fit the experimental results[1]. Averaging the dielectric constant of one metallic grain with a log-normal distribution function an effective dielectric constant for the metallic grains in the cermet is obtained and the result is shown in Figure 1.

As seen from the figure the effect of taking the average is to smooth out the quantum structure of a single particle when using the QSE approximation.

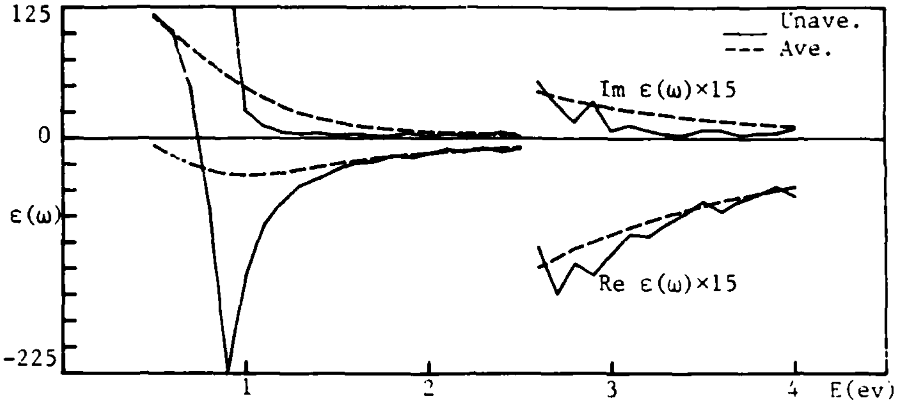
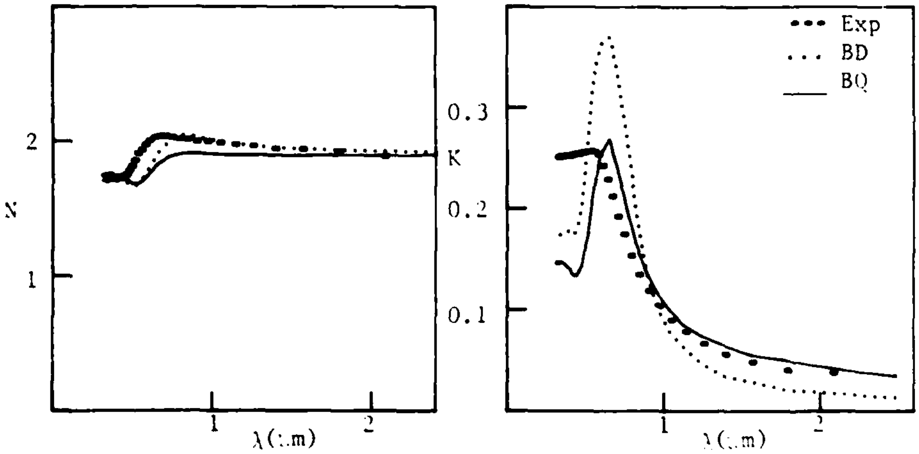


FIGURE 1 Unaveraged and averaged quantum dielectric constant of Ag metallic grains for a grain distribution with average radius of 30 A and a geometrical standard deviation of 1.3



FIGURES 2a and 2b Experimentally obtained real and imaginary parts of the index of refraction for Au/Al_2O_3 (90% Al_2O_3) cermet compared with BD and BQ models using 20 A average radius and a limited mean free path of 10 A.

Small metallic inclusions in cermets are known to grow by coalescence of smaller inclusions which difuse on the substrate, as a result, a significant number of imperfections are trapped within the metallic grain during the formation process. The effect of these imperfections is considered introducing a restricted mean free path which is smaller than the bulk mean free path when applying the QSE calculation.

We now compare with experimental data the results obtained when the QSE dielectric constant is introduced into the calculation of the effective dielectric constant of the cermet. The theoretical calculations will be compared with the measured refractive index for the Au/Al_2O_3 cermet obtained by Craighead[2]. This experimental data was selected because it is made on cermet with metallic grains of average radiuses less than 50 A, and consequently, the QSE method should contribute significantly to the complex refractive index.

Figures 2a and 2b compare the experimentally measured complex refraction index for Au/Al_2O_3 cermet, with the Bruggeman's theory using Drude's model (BD) and Bruggeman's theory using the QSE correction (BQ). The average radius used for the calculations was 20 A, and the value for the *limited mean* free path was 10 A. As can be observed from the figure the BD model gives good results for the real part of the index of refraction but exaggerates the magnitude of the observed resonance in the imaginary part of the index of refraction (K). The BQ model greatly improves on the BD for K by reducing the magnitude of the peak and approximating much better the actual values of K in the infrared region of the spectrum. The BQ model gives a smaller value for the real part of the index of refraction N than the BD model.

CONCLUSIONS

The classical approach to the theory of the optical properties of cermets has traditionally used Drude's model to obtain the complex dielectric constant of the metallic component corrected by an effective relaxation time that taken into account surface scattering, but fails to consider quantum effects. This approach is found to work when the radius of the metallic inclusions are larger than 100 A. We have shown that when the radiuses of the metallic grains are smaller than a 100 A QSE become an important correction to the effective dielectric constant of the metallic grains, when calculating the optical properties of cermets. QSE predicts discrete absorbtion peaks (see Part I) that are not observed experimentally in the optical measurements of cermets. Micrograph of dielectric rich cermets shows that the metallic inclusions obey a log-normal size distribution. When the results for the QSE for metallic grains are averaged over this type of distribution the absorbtions are smoothed out yielding an average single particle with a smooth complex dielectric constant, thus, explaining why no structure is observed experimentally.

The ability to reproduce the experimentally observed optical properties of cermets are considerably improved when the dielectric constant of the metallic constituent is corrected for Quantum Size Effects.

We will develop a multiple scattering correction to the effective dielectric constant of the cermet in a following paper.[3]

ACKNOWLEDGEMENT

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CORRECTIONS TO THE OPTICAL PROPERTIES OF CERMETS. III. MULTIPLE SCATTERING CORRECTIONS†*

MANUEL GOMEZ, LUIS FONSECA, and GERARDO RODRIGUEZ†
Physics Department, University of Puerto Rico, Río Piedras, Puerto Rico; †Present address: Cornell University, Ithaca, NY

(Received for publication November 25, 1983)

Abstract Improvements to the theory of the optical properties of real cermets are made by performing multiple scattering corrections to the effective medium dielectric constant. A multiple scattering model that considers correlation effects between metallic grains in a systematic way is discussed. The results using both mean field and multiple scattering theories are compared against experimental data for Au/Al_2O_3 and Ag/MgO cermets.

INTRODUCTION

Search for adequate theoretical models that will effectively predict the optical properties of composite materials is a problem that has been studied for many years[1,2] but no satisfactory solution to the problem has yet been found.

Cermets are special types of composite materials made of two constituents, one metallic and the other dielectric. The characteristic cermet possesses a granular structure where the typical diameter of the grains is of the order of a 100 A. Given the small size of the microstructure of the typical cermet it is always possible to describe its infrared and visible optical properties in terms of an effective medium dielectric constant.

Mean field theories have been developed that express the effective dielectric constant of the cermet in terms of the known parameters of the constituent, to wit, the radius of the grains, relative volume concentration, and dielectric constant of the two constituents. The best known and most basic effective medium theories are the Maxwell-Garnett[1] and the Bruggeman[2] theories. These theories assume the electrostatic field approximation

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†Communicated by Professor J. Gonzalo

*This paper was informally presented at the Fifth European Meeting on Ferroelectricity (EMF 5) Benalmadena, Spain, September 1983 spherical shapes or other similar geometric structure for the grains and a completely random microstructure. Many modifications of these theories have been developed, correcting for different shape factors[3], island size distributions[4], and effective depolarization factors[5]. Some attemps have been made to include in an indirect way correlation effects between the grains in the microstructure by considering coating effects[6] or, in some few cases, by introducing a correlation function for the microstructure[7].

The objective of this work is to briefly discuss a method that explicitly takes into account correlation between metallic grains and corrects for multiple scattering effects in calculating the effective dielectric constant of the cermet.

Multiple scattering correction will be compared with Bruggemann's model against experimental data for a Ag/MgO. For Au/Al_2O_3 cermet the metallic grain sizes are significantly smaller than 100 A and the model shall be used together with quantum size effects[8] and compared with mean field theories and experimental data to demonstrate that these corrections provide a better fit with the results obtained from optical measurements of real cermets.

Multiple Scattering Correction

Standard method for growing cermet films such as sputtering and co-evaporation produces a film growth process dominated by diffusion and coalescence phenomenas. Due to these mechanisms the positions of adjacent grains are strongly correlated with a gradual decrease in the correlation between grains as the distance between them increases. As a first approximation for grain-grain correlation an exponential type of correlation function can be utilized. A more careful development of a theory for correlation effects in cermets worked out by our group corroborates that the exponential approximation is an excellent one[9]. The validity of mean field theories strongly depends on the assumption that the metal grains are totally uncorrelated. Since this is not the case for real cermets, we have removed this restriction and constructed a multiple scattering theoretical model that effectively takes into account these correlations.

The fluctuations in the dielectric constant due to the microsctructure are taken to be deviations from an average dielectric constant that we will take to be Bruggeman's mean field result. That is

$$\varepsilon(\vec{r},\omega) = \varepsilon_0(\omega) + \delta\varepsilon(\vec{r},\omega) \tag{1}$$

, where $\varepsilon_0(\omega)$ is the Bruggeman's value for the dielectric constant of the cermet and $\delta\varepsilon(\vec{r},\omega)$ is the fluctuation due to the microstructure.

Our theory uses a perturbation expansion of the propagating electric field in the cermet expressed as a power series of the fluctuating part of the dielectric constant.

Starting from the electric field equation

$$\nabla \times \nabla \times \vec{E} - (\omega/c)^2\mu\varepsilon\vec{E} - \mu^{-1}\nabla\mu \times \nabla \times \vec{E} = 0 \tag{2}$$

This equation should be approximated and expressed in terms of the fluctuating part of the dielectric constant as:

$$\nabla \times \nabla \times \vec{E} - K_0{}^2\vec{E} = K_0^2\ (\delta\varepsilon/\varepsilon_0)\ \vec{E} \tag{3}$$

, where K_0 is the effective propagation constant in the Bruggeman's medium. Then the field equation may be written as an integral equation. Using the operator form,

$$G = G_0 + G_0VG \tag{4}$$

, where G and G_0 are the Green's tensors associated with the field

$\vec{E}$ and the field in the Bruggeman medium respectively. V is the perturbation term due to the fluctuations $\delta\varepsilon$.

An average is then performed to obtain a macroscopic field equation keeping only terms involving pair correlation functions of the fluctuating part of the dielectric constant and using the so called First Smoothing Approximation (FSA)[10,11].

$$\langle G\rangle = G_0 + G_0 \langle VG_0V\rangle \langle G\rangle \tag{5}$$

The equation obtained is an infinite series corresponding only to scattering processes where two point correlations are involved. Diagramatically

$$\langle G\rangle = - + -\bullet-\bullet- + -\bullet-\bullet-\bullet-\bullet- + \cdots \tag{6}$$

, where symbol - represents G_0, $\bullet$ is V, and the diagram $\bullet-\bullet$ contains the pair correlation function $\langle\delta\varepsilon(\vec{r}_1)\delta\varepsilon(\vec{r}_2)\rangle$.

Following the procedures used by F. Karal and J. Keller[12] a plane wave solution is then assumed for the macroscopic field in the equation resulting from the FSA and the effective dielectric constant corrected for multiple scattering effect is then obtained. To get the final result, the pair correlation function was chosen to be an exponential decay type as we pointed out above, and

$$\langle\delta\varepsilon(\vec{r}_1)\delta\varepsilon(\vec{r}_2)\rangle = \Delta\, e^{-r/L} \tag{7}$$

, where L is the correlation length, $r = \vec{r}_2 - \vec{r}_1$, and Δ was chosen as the square of the standard deviation of the fluctuations.

The final result expresses the effective dielectric constant of the composite in terms of the dielectric constant obtained using Bruggeman model and the correlation length L. The region of interest for the optical properties of cermets lies between 0.5ev and 4.0ev in the electromagnetic spectrum, in this range the final result should be expressed as:

$$\varepsilon = \varepsilon_0 + \frac{\Delta}{2\varepsilon_0}\left\{\frac{2}{3} + \frac{1+ia}{a^2} + \frac{2a^2}{1-i2a} - \left[\frac{1}{a} + \frac{1+a^2}{a^3}\right]\cot^{-1}\frac{1-ia}{a}\right\} \qquad (8)$$

, where $a^2 \equiv \varepsilon_0 w^2 L^2/c^2$.

Application of Multiple Scattering Corrections to Real Cermets

We will now apply the developed multiple scattering corrections theory (M) to perform the calculation of the optical properties of real cermets and compare the results with those obtained using Bruggeman's theory (B). The predictions of both theoretical models B and M will be compared against experimental data obtained by H. Craighead[13] for the real (N) and imaginary part (K) of the index of refraction.

Figures 1a and 1b show the experimental results for Ag/MgO cermet with a concentration of 80% of the dielectric constituent compared with B and M models. The dielectric constant of the metallic grains is an important parameter included in the B and M models. In that cermet we have calculated it using Drude's model corrected by a restricted mean free path due to impurities and defects into the metallic grains. Interband contributions are also taken into account. Another important parameter in the M model is the correlation length that was 125 A in that calculation.

As can be observed from the figures, N obtained using M model reproduces B model when $\lambda<1\mu m$ but predicts lower values for larger wavelengths that are also obtained with the experimental data. B model predicts higher values for the imaginary part of the index of refraction K than those obtained experimentally in all the region of interest but M model performs a very good fit with the experimental data in almost all the region. Only a slight difference is found around 0.6μm. In Figure 1 the best fit, to date, is found between experiment and theory for this cermet.

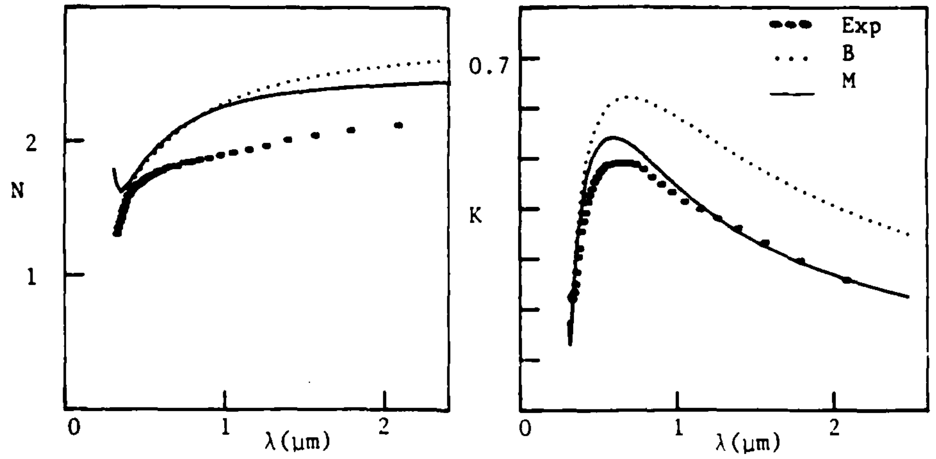

FIGURE 1a and 1b Experimental real and imaginary parts of the index of refraction for Ag/MgO (80% MgO) cermet compared with B and M models using a restricted mean free path of 5 A and a correlation length of 125 A.

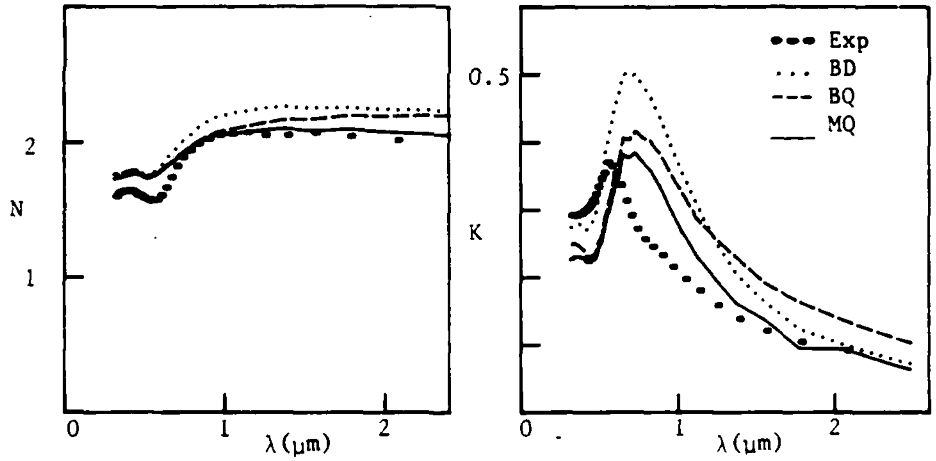

FIGURE 2a and 2b Experimental real and imaginary parts of the index of refraction for Au/Al_2O_3 (84% Al_2O_3) cermet compared with BD, BQ and MQ with 80 A correlation length, 30 A average radius and limited mean free path of 10 A.

Figures 2a and 2b compare the theoretical models with experimental results for the Au/Al_2O_3 cermet with 84% volume fraction of the dielectric constituent. In this cermet the metallic grains are smaller than 100 A and quantum corrections to the dielectric constant of the metallic grains become important[8]. To obtain the best results with the multiple scattering model using quantum size corrections (MQ), the restricted mean free path was taken to be 10 A, and the correlation length to be 80 A. In the figures we compare Bruggeman model using Drude's dielectric constant with interband contributions for the metallic grains (BD), Bruggeman with quantum size corrections (BQ) and MQ against experimental data. The BD model again predicts a higher peak in K than the one observed experimentally and the values obtained for this model are always larger than the experimentally observed ones for both N and K. The BQ results improved on the BD model fitting much better the experimental N and K. The MQ model greatly improves on the BD and BQ models by narrowing and decreasing the peak for K and giving better agreement with the experimental result in the region $0.8\mu m < \lambda < 2.5\mu m$ while coinciding with the BQ model for smaller wavelength.

CONCLUSION

The processes that involve the cermet formation make that the position of adjacent grains are strongly correlated. A multiple scattering theory that takes into account these correlation effects in a systematic way is needed to predict the optical properties of cermets.

A multiple scattering expression for the effective dielectric constant of a cermet is developed as a correction to the Bruggeman mean field theory and used to predict the values of the effective index of refraction of real cermets.

Comparison against the experimental data shows that the theory considerably improves the Bruggeman's model. When the sizes of the metallic grains of the cermet are smaller than 100 A, quantum size corrections become important and it must be considered together with scattering corrections, then the best fit between experiment and theory is obtained.

Multiple scattering effects are important when the volume fraction of the metallic constituent in the cermet is greater than 10% and grain-grain correlations become significant. Work is in progress to further improve the multiple scattering theory by taking into account renormalization effects within the T-Matrix formalism.

ACKNOWLEDGMENT

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PAPER TO APPEAR IN THIN SOLID FILMS, 1985

MULTIPLE SCATTERING RENORMALIZED T-MATRIX THEORY TO THE DIELECTRIC CONSTANT OF NON-HOMOGENEOUS THIN FILMS.

Manuel Gómez and Luis Fonseca. Physics Department, University of Puerto Rico, Río Piedras, Puerto Rico.

I. INTRODUCTION

The inhomogeneous media of granular metal films have been extensively studied because of their importance to technological applications[1]. The optical property of films composed of random arrays of metallic grains embedded in a dielectric matrix (cermet) have been studied for their spectral selectivity which make them promising selective surfaces[2].

In the range of the visible and near infrared regions of the spectrum where the wave length of the incident light is large compared to the radiuses of the metallic grains, the effect of the microstructure is averaged and the film behaves as an effective homogeneous medium. Several theoretical models have been proposed to obtain the effective dielectric constant of cermets in terms of the dielectric constant of the constituents and parameters describing the microstructure, such as island radiuses, relative concentrations of the constituents, and the shape of the islands. Two basic and widely used models are the Maxwell-Garnett (MG) and the Bruggeman (B) models[3]. The MG model is asymmetric, since it considers the cermet as composed of spheres of the less abundant constituent embedded in a matrix of the most abundant material. The effective dielectric constant is then obtained by performing a volume average over the local fields. While the B model is symmetric since it considers the two constituents materials as spheres embedded in an effective medium, a volume average is also performed to obtain a self-consistent expression for the effective dielectric constant. In both theories a resonance in the spectral response of the cermet is obtained, but neither agrees with the experimentally measured complex dielectric constant. For example, comparison between the experimentally obtained imaginary part of the effective index of the refraction and the MG model reveals that the theoretical resonance is too high and narrow and in many cases blue shifted with respect to experimental results. Several papers, like those of Granqvist[4] show that the magnitude and position of the resonance is a strong function of the inclusions' shape. Corrections to the dielectric constant of metallic grains for size effects have been extensively used to reduce the magnitude of the resonance, but they fail to produce enough red shift and broadening to explain experimental data.

II. THE THEORY

We consider the cermet as a random array of metallic grains embedded in a dielectric matrix. The spatial fluctuation of the dielectric constant can be envisioned as consisting of a constant dielectric constant ε_0 (e.g. the dielectric constant of the more abundant material or a judiciously select mean value dielectric constant) and a stochastic term $\delta\varepsilon$ that accounts for the spatial fluctuations of the dielectric constant, i.e.

$$\varepsilon(\vec{r}) = \varepsilon_0 + \delta\varepsilon(\vec{r})$$

With this expression the field equations for the propagating electromagnetic field can be separated into a non-stochastic and a stochastic fluctuating term. The fluctuating term will be considered as the perturbing potential responsible for the scattering processes. The resulting field equations cannot be solved exactly and approximation methods must be used.

The First Smoothing Approximation (FSA)[5,6] considers only the contribution of two point correlations to the multiply scattered field. This approximation has previously been applied to obtain the effective dielectric constant of a general random medium[7] and more recently to cermets[8]. Our recent work for cermets showed that the FSA approximation corrects the magnitude of the resonance but fails to predict a significant spectral shift, suggesting that renormalization corrections to the scattering terms must be included in order to obtain better agreement with experiments. In order to apply renormalization techniques[8], the T-matrix multiple scattering of an individual grain, is redefined as the new renormalized potential symbolically represented by $\otimes$, and responsible for scattering processes in the medium. A new Green's function is then generated by taking into account multiple scattering effects from these new single scatterer potentials in the absence of correlation. These Green's function associated with $\langle\vec{E}\rangle$ and represented diagramatically by —— then defines an effective medium, that because it is uncorrelated, we will call the zeroth order effective medium characterized by a dielectric constant $\bar{\varepsilon}_0$. In terms of the new renormalized Green's function and potential an averaged field equation, that takes into account pair correlation functions, is written to yield the Renormalized First Smoothing Approximation (RFSA),

$$\langle\vec{E}\rangle = \langle\vec{E}_0\rangle + \sum_{\alpha,\beta\neq\alpha} \underset{\alpha\qquad\beta}{\overset{\frown}{\otimes\!-\!\!-\!\!-\!\otimes}} \langle\vec{E}\rangle \quad , \tag{1}$$

where $\langle\vec{E}_0\rangle$ is the statistically averaged field propagating in the uncorrelated medium and $\langle\vec{E}\rangle$ the effective total field. The second term in the r.h.s. part of this self-consistent equation represents scattering processes where the effective total field $\langle\vec{E}\rangle$ is scattered by pairs of correlated islands α and β located respectively at $\vec{r}_i$ and $\vec{r}_j$. In order to apply this formalism an explicit mathematical representation of the diagram in the second term of the r.h.s. of eqn. (1) must be obtained. Peterson and Ström[9] developed a formalism to obtain the T-matrix from an array of n-scattering objects with well defined spatial coordinates. Their formalism is an extension to multiple number of scatterers of that developed by Waterman[10] for a single scatterer. In Waterman's formalism the T-matrix for a single scatterer is obtained expanding all the local fields in terms of Spherical Harmonics, and Bessel or Hankel functions. The term describing this double scattering process in Peterson and Ström's formalism is given by:

$$\otimes\!\!-\!\!\!-\!\!\!-\!\!\otimes \rightarrow R(\vec{r}_j)\, T^{\alpha}\, \sigma(\vec{r}_i-\vec{r}_j)\, T^{\beta}\, R(\vec{r}_j-\vec{r}_i)\, R(-\vec{r}_j) \quad , \qquad (2)$$

where T^{α}, T^{β} are the single scatterer T-matrices of islands α and β, respectively, expressed with their center in the origin of the coordinate system. The formalism then translates the particle through matrices R and σ to their correct position $\vec{r}_i$ and $\vec{r}_j$. Expressions for T^{α} are described in several articles[9,10] and expressions for matrices R and σ can be found in Peterson and Strom's article. Using eqn. (2) the field equation can now be expressed as:

$$\langle\vec{E}(\vec{r})\rangle = \langle\vec{E}_0(\vec{r})\rangle + 1/V^2 \sum_{\alpha,\beta\neq\alpha} \iint g(\vec{r}_i,\vec{r}_j)\, R(\vec{r}_j)\, T^{\alpha}\, \sigma(\vec{r}_i-\vec{r}_j) \times$$
$$\times\; T^{\beta}\, R(\vec{r}_j-\vec{r}_i)\, R(-\vec{r}_j)\, \langle\vec{E}\rangle\, d\vec{r}_i\, d\vec{r}_j \quad , \qquad (3)$$

where $g(\vec{r}_i,\vec{r}_j)$ is the two-point correlation function and V is the volume of the film. Considering the spheres as impenetrable and the medium as isotropic exponential correlation functions can be defined as:

$$g(\vec{r}_i,\vec{r}_j) = \Theta(r-2a)\, \exp\left[-\left|\vec{r}_i - \vec{r}_j\right| / L\right] \quad ,$$

where Θ is the Heaviside function and L the correlation length. To simplify the calculation we assume all the metallic grains to be spherical in shape and of equal radiuses which allow us to write $T^{\alpha}=T^{\beta}$ and make them diagonal matrices. Assuming a microscopic volume we can change $(1/V^2)\Sigma$ by δ^2, where δ is the density of islands in the cermet. The field $\langle\vec{E}\rangle$ and $\langle\vec{E}_0\rangle$ will be expanded in terms of the basis functions $\{\mathrm{Re}\vec{\psi}_n(K_0\vec{r})\}$ that are solutions to the Helmholtz equation described by Waterman[10]. The $\vec{\psi}_n$ are known as the elementary fields and K_0 is the propagation constant of the electromagnetic wave in the zeroth order effective medium. In terms of this base the fields can be expressed as:

$$\langle \vec{E}_o \rangle = \sum_n d_n \, \mathrm{Re}\vec{\psi}_n(K_o\vec{r}) \quad \text{and} \quad \langle \vec{E}(\vec{r}) \rangle = \sum_n X_n \, \mathrm{Re}\vec{\psi}_n(K_o\vec{r}) \quad .$$

While the total effective field $\langle \vec{E} \rangle$ in the second term of the r.h.s. is expanded in a base centered at one of the correlated islands:

$$\langle \vec{E} \rangle = \sum_{n'} B_n \, \mathrm{Re}\vec{\psi}_n[K_o(\vec{r}-\vec{r}_j)] \quad .$$

Substituting these expansions for the fields in eqn. (3) and performing the integration over the relative coordinate between the correlated islands we obtained :

$$\sum_n X_n \, \mathrm{Re}\vec{\psi}_n(K_o\vec{r}) = \sum_n d_n \, \mathrm{Re}\vec{\psi}_n(K_o\vec{r}) + \delta^2 \sum_n M_n \int B_n \, \vec{\psi}_n[K_o(\vec{r}-\vec{r}_j)] \, d\vec{r}_j \quad . \qquad (4)$$

Matrix elements M_n contains all the correlations effects and can be written in terms of the elements of the single scatterer T-matrices. Since the wave length of incident radiation relevant to our problem is $\lambda > .3$ µm and the radiuses of islands for typical cermets are of the order of .01 µm, the long wave limit can be utilized, thus reducing the expansion of the electric fields to the first few terms. In this long wave limit only the first six terms of these matrices are necessary, that correspond to a dipolar approximation.

To perform the integral over the $\vec{r}_j$ coordinate we must use the properties of the translation matrices σ[11] to translate the $\vec{\psi}_n$ from position $\vec{r}_j$ to the origin,

$$\vec{\psi}_n \, [K_o(\vec{r}-\vec{r}_j)] = \sum_{n'} \sigma_{n'n}(K_o\vec{r}_j) \, \mathrm{Re}\vec{\psi}_{n'}(K_o\vec{r}) \quad , \qquad (5)$$

and all terms in eqn. (4) are now written in the same orthogonal base and is equivalent to the following set of scalar equation:

$$X_n = d_n + \sigma^2 \sum_{n'} \int M_{n'} \, B_{n'} \, \sigma_{nn'} \, d\vec{r}_j \quad .$$

Since we are in the long wave limit where the electromagnetic wave tends to average the microstructure at the scale of island sizes we can assume that the wave propagates in the effective medium as a plane wave. The coefficient d_n can be written in terms of K_0, while the coefficient representing $\langle \vec{E} \rangle$ can also be expressed in terms of the effective propagation constant K of the correlated medium as:

$$d_n = d_n^{\circ} \exp[i\vec{K}_0 \cdot \vec{r}] \quad \text{and} \quad X_n = X_n^{\circ} \exp[i\vec{K} \cdot \vec{r}] \quad \text{and} \quad B_n = X_n^{\circ} \exp[i\vec{K} \cdot (\vec{r} - \vec{r}_j)] \quad .$$

In terms of these expressions the field equation now becomes:

$$X_n^{\bullet} \exp[i\vec{K} \cdot \vec{r}] = d_n^{\circ} \exp[i\vec{K}_0 \cdot \vec{r}] + \delta^2 \sum_{n'} M_{n'} X_{n'} \int_{|\vec{r} - \vec{r}_j| > a} \exp[i\vec{K} \cdot (\vec{r} - \vec{r}_j)] \, \sigma_{nn'}(K_0 \vec{r}_j) \, d\vec{r}_j .$$

Following the procedure described by Varadan et al.[12] we can use the scalar Helmholtz operator in the zeroth order approximation to simplify the above equation and reduce the volume integral to a surface integral:

$$X_n^{\circ} = \sum_{n'} M_{n'} X_{n'}^{\bullet} I_{nn'} \quad , \tag{6}$$

where

$$I_{nn'} = \delta^2/(K^2 - K_0^2) \int_{|\vec{r}| > a} \{\sigma_{nn'}(-K_0 \vec{r}) \, \partial \exp(i\vec{K} \cdot \vec{r})/\partial r - \exp(i\vec{K} \cdot \vec{r}) \, \partial \sigma_{nn'}(-K_0 \vec{r})/\partial r\} \, ds \quad .$$

Eqn. (6) represents a system of homogeneous coupled equations with unknown coefficients. Solving the associated secular equation we obtained a new dispersion relationship that takes into account pair correlations in the scattering medium. In terms of the dielectric constants this expression can be expressed as:

$$\varepsilon = \bar{\varepsilon}_0 \, (1 + 2Fk^2 \bar{\varepsilon}_0)/(1 - Fk^2 \bar{\varepsilon}_0) \quad , \tag{7}$$

where ε is the new effective dielectric constant in the correlated medium of the film obtained from the RFSA model, k = ω/c is the propagation constant of the electromagnetic wave in vacuum, and F contains all the effects due to correlations between islands and can be expressed as:

$$F = 22/50 \, f^2 \exp(-2a/L) \, (L^2 + 2aL) \, [(\varepsilon_r - 1)/(\varepsilon_r + 2)]^2 \quad ,$$

where (a) is the radius of the inclusions, (f) the relative concentration of metal, and ε_r is the ratio of the dielectric constants of the metallic islands and the external medium.

III. RESULTS AND DISCUSSION

The result obtained in eqn. (7) permits the calculation of the complex effective dielectric constant of cermets taking into account correlation effects, in terms of basic physical parameters obtainable from experimental data. When a metal concentration is small the correlation length tends to vanish and we recover from eqn. (7) the zeroth order approximation $\bar{\varepsilon}_0$, the effective dielectric constant for the uncorrelated effective medium. To apply the dispersion relationship the MG model is used for the zeroth order dielectric constant. Conceptually MG model is compatible with the T-matrix formalism, in addition, Varadan et al., have shown that in the limit of no correlation the T-matrix calculations yields the MG result[12]. For the dielectric constant of the metallic islands both Drude's model (D) with relaxation time τ corrected for size effect and the Quantum Size Effect model (QSE)[13] will be used, both calculations are corrected for the interband contributions.

Fig. 1 shows the real and the imaginary part of the refraction index for Ag/MgO 80% MgO cermet. In this case the τ used in the Drude model is adjusted to give the best fit to the experimental resonance by the MG model. Then using the same dielectric constant for the metal constituent, the RFSA calculations shifts and broadens the peak improving the MG calculation and giving a much better fit to experimental data obtained from H. Craighead work[14]. Fig. 2 shows the same experimental data, but now the D model has been substituted for the QSE model in the calculation for the metallic dielectric constant. In this case a more realistic τ gives the best fit to experiment by the RFSA model but the peak is now narrower. The corresponding mean free path for the

τ used in this figure is 10A. Values of up to 5A had to be used by Craighead to obtain the best fit with the MG theory to his experimental data. We have also applied the model to other cermets such as Ni/Al_2O_3 obtaining a very good fit with experimental data with metallic concentrations of up to 54%.

IV. CONCLUSIONS

We have extended our FSA model calculations, that take into account correlation effects among metallic islands in cermet films, to include renormalized corrections and have shown that correlation effects are important in the broadening and shifting the resonance peak to obtain better fit with experimental results. The results of this and other recent work[8] leads us to conclude that correlation effects and multiple scattering corrections make important contributions to the optical properties of cermet materials and need to be included in theories with predictive value. Eqn. (7) is restricted to spherical shapes and long wave limit, but the formalism, as presented here, can be extended to include other island shapes and to permit corrections for higher multipolar contributions to the field equation that may become important when the metal concentration increases and island proximity may make these consideration important. The proposed dispersion relation depends strongly on the models used for the zeroth order dielectric constant and used for dielectric constants of the metallic grains. Other zeroth order models for the effective medium dielectric constant are being studied as possible starting points for the application of the dispersion relationship presented in this paper. These new calculations might permit the use of a longer τ that correspond to more realistic mean free path. Recently other models have been proposed for $\bar{\varepsilon}_0$ that should help moderate the height and broaden the resonance with a larger τ[15].

V. ACKNOWLEDGMENT

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SUMMARY

A multiple scattering theory to obtain the effective dielectric constant for a granular metal film is developed considering correlation effects. A renormalization procedure is applied to obtain a field equation within a Renormalized First Smoothing Approximation (RFSA), using Tmatrix formalism. From the field equation a dispersion relation is obtained that is expressed in terms of the dielectric constant of the metal corrected for size effects, the relative concentration of the constituents, the radius of the inclusions and a correlation length. Using the Maxwell-Garnett model for the dielectric constant of the uncorrelated medium, the multiple scattering theory shows that correlation effects moves the resonance in the imaginary part of the index of refraction predicted by the Maxwell-Garnett model toward lower frequencies and broadens it. Comparison of the RFSA with experiments shows better fit than previous theories.

FIGURE CAPTION

Figure 1:

The real part n_1 and the imaginary part n_2 of the refractive index as a function of the wavelength is drawn for an Ag/MgO 80% MgO cermet. Solid line is the result of RFSA calculation, dashed lines that of the MG model and dots represent the experimental results from H. Craighead[14]. This figure is obtained using the D model with $\tau = 2.14 \times 10^{16}$ sec for the dielectric constant of the metallic grains in both MG and RFSA curves. The radius of the islands is taken as 80A and L=6 islands.

Figure 2:

The real and imaginary parts of the refractive index are drawn for the same cermet of figure 1. This figure is obtained using QSE[13] with a restricted mean free path of 10A for the dielectric constant of the metallic grains in both MG and RFSA curves. The island radius is 125A and L=6 islands.

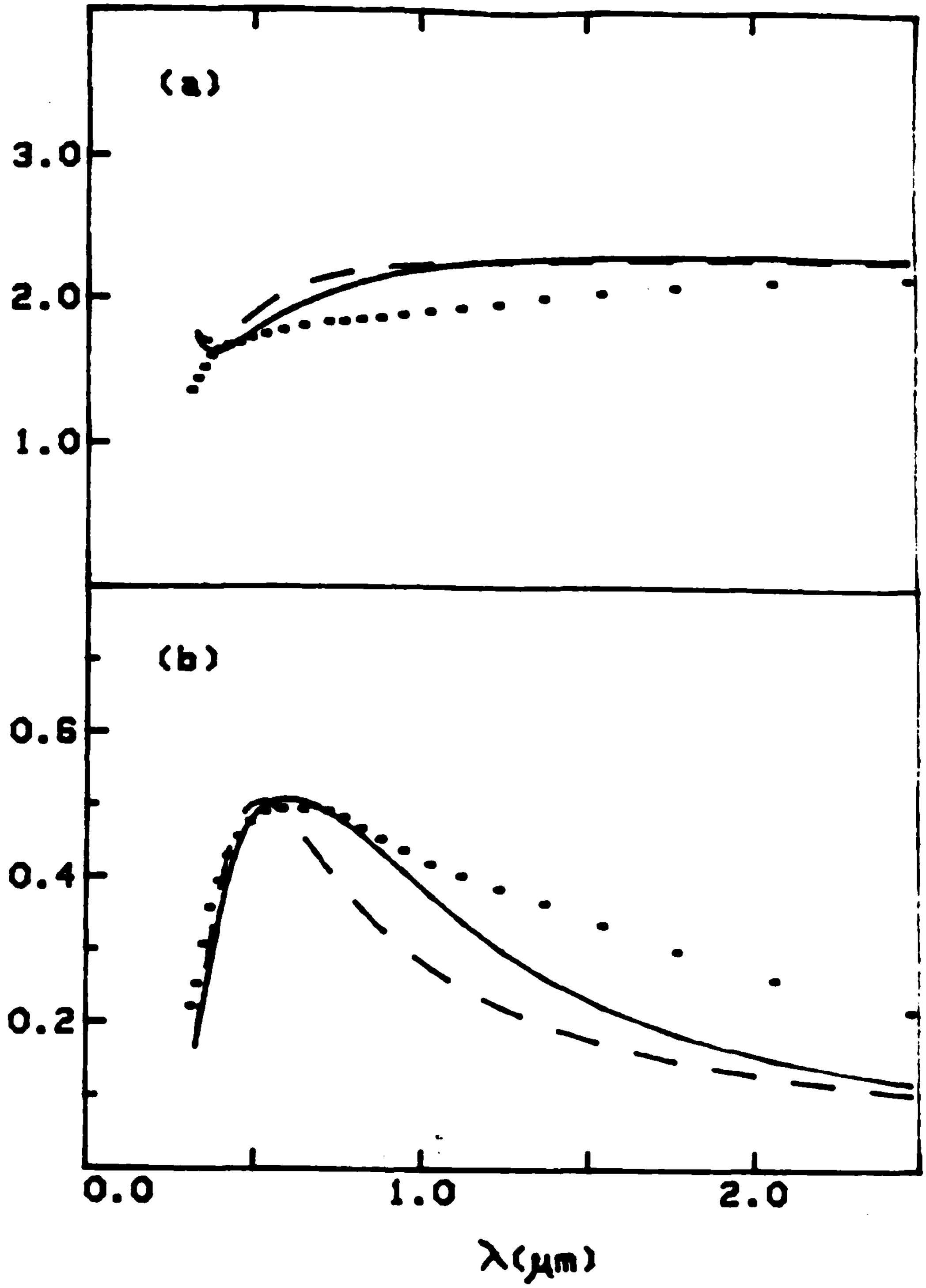

Figure 1

M. Gómez and L. Fonseca

Multiple Scattering Renormalized T-matrix Theory to the Dielectric Constant of Non-homogeneous Thin Films

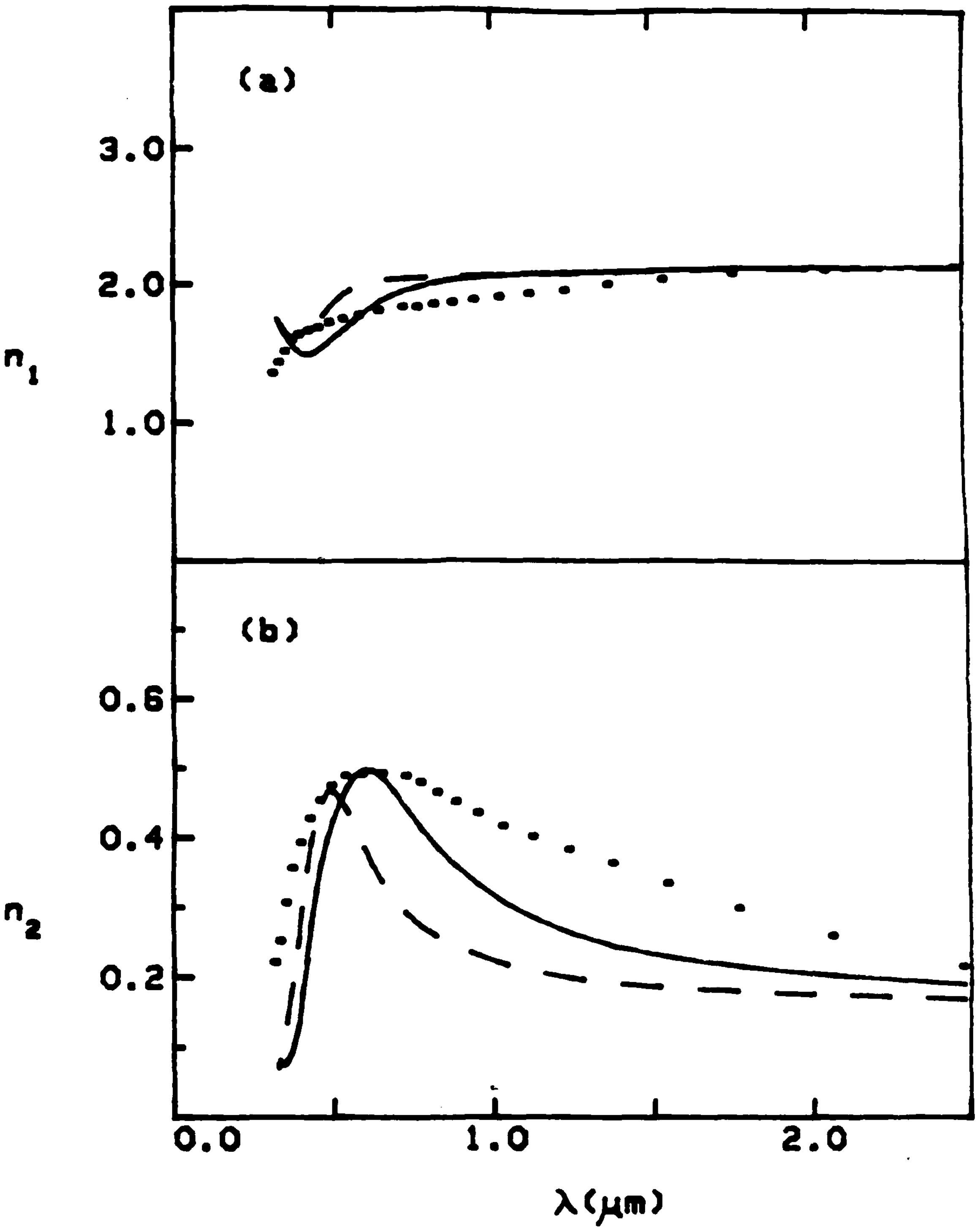

Figure 2

M. Gómez and L. Fonseca

Multiple Scattering Renormalized T-matrix Theory to the Dielectric Constant of Non-homogeneous Thin Films

PAPER TO APPEAR IN THE PROCEEDINGS OF THE THIRD LATIN AMERICAN SYMPOSIUM
ON SURFACE PHYSICS, SMALL PARTICLES AND THIN FILMS

SAN JOSE, COSTA RICA

Multiple Scattering Theories Including Correlation Effects to Obtain the Effective Dielectric Constant of Non-Homogeneous Thin Films.*

Manuel Gómez, Luis Fonseca†, Gerardo Rodríguez††, Angel Velázquez and Luis Cruz. Department of Physics. University of Puerto Rico. Río Piedras, Puerto Rico.

Introduction

Cermets are inhomogeneous materials consisting of immisibles mixtures of insulators and metals. Extensive work has been performed to develop theoretical models which will correctly predict the optical properties of cermets when the bulk dielectric constant of the constituents is known experimentally. When the concentration of the dominant constituent is less than 98% the material develops a distinct resonance which is not characteristic of either one of the constituents. The prediction of this resonance has been the goal of all theories developed for the optical properties of cermets materials.

Two basic and widely used models are the Maxwell-Garnett (MG) and the Bruggeman (B) models[1]. The MG model is asymmetric, since it considers the cermet as composed of spheres of the less abundant constituent embedded in a matrix of the most abundant material. The effective dielectric constant is then obtained by performing a volume average over the local fields. While the B model is symmetric, since it considers the two constituent materials as spheres embedded in an effective medium, a volume average is also performed to obtain a self-consistent expression for the effective dielectric constant. In both theories a resonance in the spectral response of the cermet is obtained, but neither agrees with the experimentally measured complex dielectric constant. For example, comparison between the experimentally obtained imaginary part of the effective index of refraction and the MG model reveals that the theoretical resonance is too narrow and in many cases blue shifted with respect to experimental results.

The objective of this paper will be to show that corrections due to correlation between the position of the metallic islands, resulting from the formation process of the cermet, can move and broaden resonance obtained by the traditional mean field theories of Maxwell-Garnett and Bruggeman. In

†On leave from Escuela de Física, Universidad de Costa Rica.

††Present Address: Cornell University.

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order to perform this correction a multiple scattering theory has been developed that starts from an effective dielectric constant that is calculated assuming no correlation between the metallic islands and labeled in this work as the zeroth order approximation. Non-renormalized and renormalized theories will be discussed in which correlation effects are taken into account. Also corrections for size effects on the dielectric constant of the metallic grains will be studied.

Quantum Size Effects

In order to calculate the effective dielectric constant of cermets it is necessary, in general, to correct the bulk dielectric constant of the minority constituent for size effects. Normally the insulator has a dielectric constant that is essentially non-frequency dependent in the spectral range of interest, while the metallic constituent has a strong frequency dependence in the same region. When the metal is the minority constituent, its bulk dielectric constant must be corrected for size effects. Traditionally Drude's model together with experimentally obtained interband contributions is used to calculate the dielectric constant of the metal. In this procedure, the mean free path of the electrons in the metallic island is corrected for boundary scattering at the interface between the island and the external medium. Many researchers[2] have observed that in order to obtain a reasonably good fit between theory and experiment, it is necessary to use mean free paths that are considerably smaller than the ones attributed only to the size of the island. These corrections could be explained as the combination of boundary scattering at the metallic grains surface and scattering inside the island due to internal imperfections. The Drude theory with these corrections is satisfactory for metallic grains of more than 100A. However, when the size of the metallic particles become comparable to the electron wavelength, quantum corrections become mandatory if a realistic dielectric constant is going to be obtained.

To solve this problem several works have used the Quantum Box Method within the Random Phase Approximation to calculate the dielectric constant of the metallic particles. Kawabata and Kubo[3] have corrected the dielectric constant for size effects assuming that the spectrum of the quantum levels form essentially a continuum, while Wood and Ashcroft[4] carefully reworked the Quantum Size Method, fully taking into account the spectrum resulting from the box quantization and obtained a dielectric constant for the particles.

Recently this formalism has been applied by the authors of this article to real cermets in the region where the metallic inclusions in the cermets are smaller than 100A[5] and better results have been obtained for the dielectric constant than when Drude's model is used.

Figure 1 compares the imaginary part of the dielectric constant taking into account quantum size effects following Wood and Ashcroft (QSE) and Kawabata and Kubo model (KK) with the one calculated using Drude's model. In the calculation of the Drude's model the size of the silver particles are taken to be 30A and no interband contributions to the dielectric constant have been included.

The multiple peaks appearing in the QSE calculations are due to the discrete energy spectrum of an electron in a box. Experimentally the resonances observed in the dielectric constant of an isolated metal grain due to quantum size effect are not observed in the effective dielectric constant of a real cermet. The disappearance of these peaks is due to the fact that the metallic grains in a real cermet do not have a unique size, but instead have a distribution of sizes as can be verified by micrographs of the materials. For this reason the dielectric constant obtained from the QSE calculations for one isolated particle were averaged over a distribution that realistically represented variation in size in actual cermets. Averaging the dielectric constant of one metallic grain with a log-normal distribution function, an effective dielectric constant for the metallic grains in the cermet is obtained. This average QSE result is then used to calculate the effective medium dielectric constant using the B and MG mean field theories,

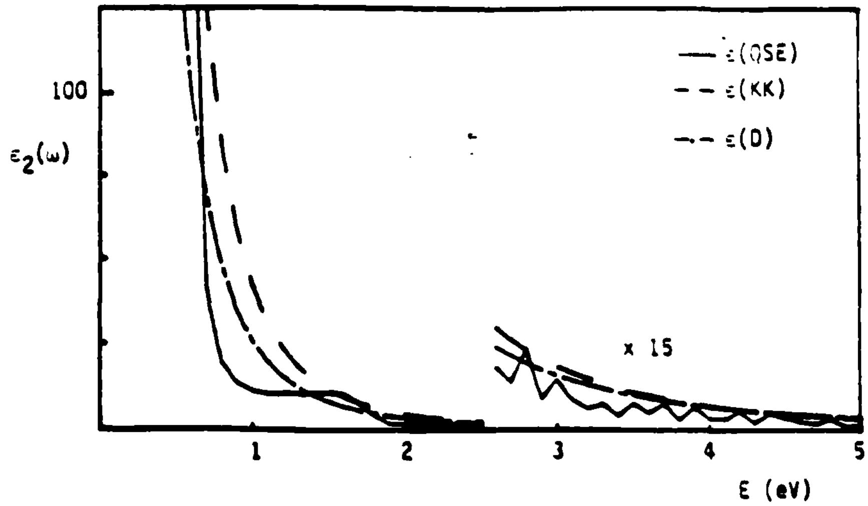

Figure 1. Comparison between the imaginary part of the dielectric constant as function of frequency of the QSE, D, and KK models.

and multiple scattering corrections theories. To take into account the effect of the imperfections we will introduce a restricted mean free path smaller than the bulk mean free path when applying the QSE calculation to obtain an effective complex dielectric constant.

Multiple Scattering Theory: The First Smoothing Approximation (FSA)

When thin films of cermets are grown by cosputtering or coevaporation methods, nucleation processes are responsible for the formation of metallic or dielectric islands in the matrix of the correspondingly more abundant constituent. Since the nucleation process is governed by the diffusion effects, relative island positions must be correlated. Thus the purpose of the multiple scattering calculations will be to correct the mean field theories for the contribution of the correlation to the effective dielectric constant of the medium.

The theory is based on the concept of a local dielectric constant that fluctuates around an average value ε_0 that is independent of position. In terms of operator formalism the field equation can be written in terms of a non-stochastic operator $H = \nabla \times \nabla \times - K_0^2$ and a stochastic term $H_1 = K_0^2 \; (\delta\varepsilon/\varepsilon_0)$. Where K_0 is the propagation constant of an average medium with constant ε_0 and $\delta\varepsilon$ is the fluctuating part of the dielectric constant. This field equation is

$$\vec{E} = \vec{E}_0 + Go \; H_1 \vec{E} \tag{1}$$

where $\vec{E}_0$ is the electric field that results from solving the non-stochastic operator and $\vec{E}$ is the resulting scattered field. Since we are in the presence of a random medium and we will assume that an effective medium dielectric constant can be defined, an average of this equation can be performed to obtain

$$\langle \vec{E} \rangle = \vec{E}_0 + G_0 \langle H_1 \vec{E} \rangle$$

where G_0 is the Green's function associated with $\vec{E}_0$. In order to be able to obtain useful values for the effective dielectric constant, the First Smoothing Approximation[6,7] will be used. Following the procedure of Karal and Keller[8] this approximation was used to obtain an effective medium dielectric constant ε_{eff}. To do this, it was necessary to assume a plane wave solution for the macroscopic field with an effective propagation constant

$$K^2 \equiv \omega^2/c^2 \;\; \varepsilon_{eff}$$

Previous work by the authors[9] indicate that the pair correlation can be expressed as an exponential relationship with a correlation length L. In the spectral range of interest the final dispersion relation becomes

$$\varepsilon_{eff} = \varepsilon_0 + \frac{\Delta}{2\varepsilon_0}\left\{ \frac{2}{3} + \frac{1+ia}{a^2} + \frac{2a^2}{1-i2a} - \left[\frac{1}{a} + \frac{1+a^2}{a^3}\right] \cot^{-1} \frac{1-ia}{a} \right\}$$

where $a^2 \equiv \varepsilon_0 \omega^2 L^2 / c^2$ and Δ is the square of the standard deviation of the fluctuation.

The new effective dielectric constant includes the averaged dielectric constant plus a term that is a function of the correlation length L. This calculation is conceptually based on the assumption that there is an averaged dielectric constant around which local fluctuations due to the metallic and dielectric islands occur, known as the Random Continuum Model. Since this is precisely the model that is described by the Bruggeman theory, we have chosen as the averaged dielectric constant ε_0 the one obtained from that theory.

The theoretical predictions of both the Bruggeman and FSA models will now be compared with experimental data for Ag/MgO, 80% MgO, and Au/Al_2O_3, 84% Al_2O_3. Figures 2 shows the imaginary parts of the index of refraction of these cermets. For the calculation, as presented in the Fig. 2a, the dielectric constant of the metallic islands was obtained from Drude's model corrected for a restricted mean free path due to the size effects and due to impurities and defects. As observed, the Bruggeman model predicts higher values for the imaginary part of the index of refraction N_2, than those obtained experimentally, whereas the FSA model fits very well with experimental data in almost all the region in the case of Ag/MgO where the radius of the islands is of the order of 80A and restricted mean free path of 5A. In the case of Au/Al_2O_3, it was necessary to make quantum corrections in order to obtain the best fit, because the islands in this case are of the order of 30A. In this second case, the resonance in the imaginary part of N_2 is shifted towards longer wavelengths with respect to the experimental results.

Renormalized FSA Approximation (RFSA)

The results obtained using the QSE and multiple scattering corrections in the FSA approximation to the B model shows improvements on the predicted value for the imaginary index of refraction, but these corrections, although affecting the magnitude of the resonance, do not broaden or shift the resonance peak. This suggests that a renormalized approach to the multiple scattering calculation may be the correct path to obtain the necessary corrections to the position and width of the resonance peak. A renormalized procedure can be devised[7] starting from the field Eq. 1 and then using a T-matrix calculation for single spherical scatterers. Contrary to the case of the FSA approximation, the cermet is conceived here as spherical islands of the minority constituent embedded in a matrix of the dominant constituent. Each one of these spherical islands is then taken to be a scattering source from which the overall scattering wave for the random medium can be obtained. Since this model of cermet is consistent with the MG model, the whole procedure will be constructed on a zeroth order scattering dielectric constant $\bar{\varepsilon}_0$ that is obtained from a MG theory, thus assuming a non-correlated medium in which the spherical grains serve as scattering sources. Applying now the First Smoothing Approximation yields an equation that is formally equivalent to the FSA but renormalized and written in the following form

$$<\vec{E}> = \vec{E}_0 + G_0{}' <T\ G_0{}'T> <\vec{E}> \quad , \qquad (2)$$

where $G_0{}'$ is the renormalized Green's function associated with $<\vec{E}_0>$.

The second term in the r.h.s. part of this self-consistent equation represents scattering processes where the effective total field $<\vec{E}>$ is scattered by pairs of correlated islands α and β located respectively at r_i and r_j. In order to apply this formalism an explicit mathematical representation of the expression in the second term of the r.h.s. of Eq. (2) must be obtained. Peterson and Ström[11] developed a formalism to obtain the T-matrix for an array of n-scattering objects with well-defined spatial coordinates. Their formalism is an extension to a multiple number of scatterers of the one developed by Waterman[12] for a single scatterer. In Waterman's formalism the T-matrix for a single scatterer is obtained expanding all the local fields in terms of Spherical Harmonics, and Bessel or Hankel functions. The term describing this double scattering process in Peterson and Strom's formalism is given by

$$T\ G_0{}'T \quad \rightarrow \quad R(\vec{r}_j)\ T^{\alpha}\ \sigma(\vec{r}_i-\vec{r}_j)\ T^{\beta}\ R(\vec{r}_j-\vec{r}_i)\ R(-\vec{r}_j) \quad , \qquad (3)$$

where T^{α}, T^{β} are the single scatterer T-matrices of islands α and β, respectively, expressed with their center in the origin of the coordinate

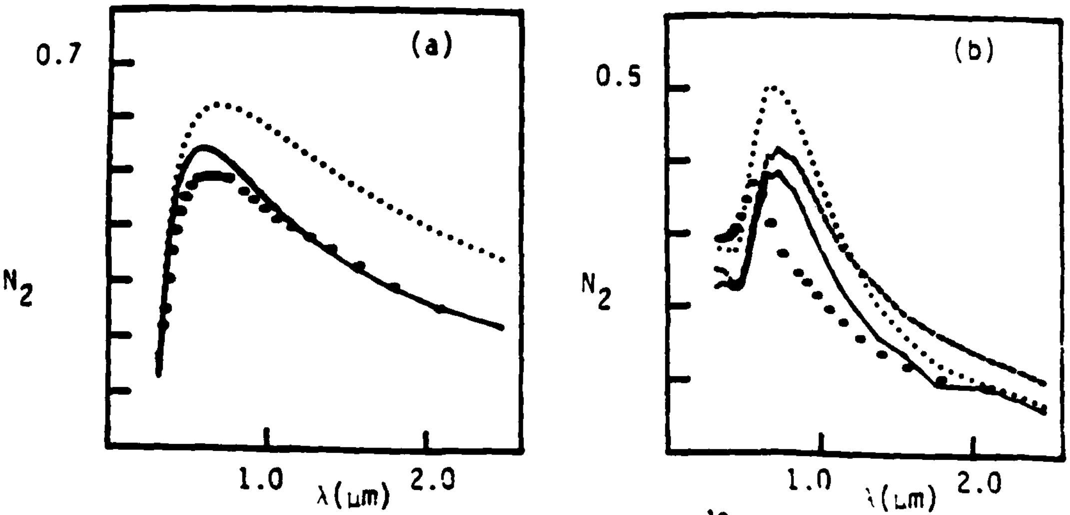

Figure 2. Comparison between experimental data [10] and calculations for N_2. (a) Ag/MgO (80%MgO) cermet compared with B (doted line) and FSA (dashed line) models with L=125A, and a restricted mean free path = 10A. (b) Au/Al$_2$O$_3$ (84% al$_2$O$_3$) cermet compared with BO (doted line), BO (dashed line) and FSAQ (solid line) models with L=80A, a=30A and the mean free path = 10A.

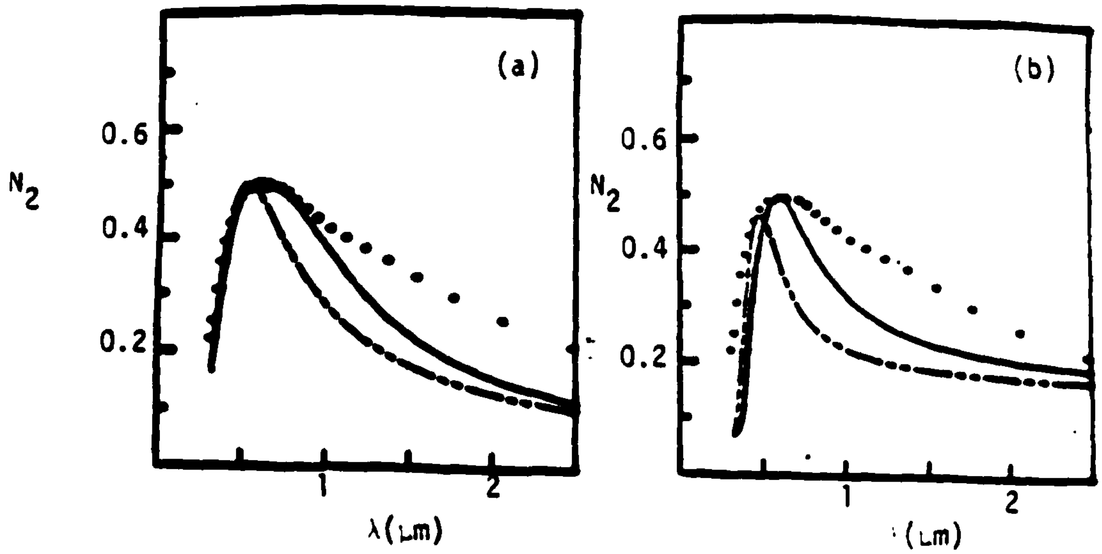

Figure 3. The imaginary part N_2 of the refractive index is drawn for an Ag/MgO 80% MgO cermet. Solid line is the RFSA calculation, dashed lines that of the MG model and dots are the experimental. (a) N_2 using the D model with $\tau = 2.14 \times 10^{-16}$s in both MG and RFSA. The radius of the islands is taken as 80 A and L= 6 islands. (b) N_2 using QSE with a restricted mean free path of 10 A for dielectric constant of the metallic grains in both curves. The island radius is 125 A and L same as (a).

system. The formalism then translates the particle through matrices R and σ to their correct position $\vec{r}_i$ and $\vec{r}_j$. Expressions for $\cdot T^{\alpha}$ are described in several articles[11,12] and expressions for matrices R and σ can be found in Peterson and Ström's article. Using Eq. (3) the field equation can now be expressed as

$$\langle\vec{E}(\vec{r})\rangle = \langle\vec{E}_0(\vec{r})\rangle + 1/V^2 \sum_{\alpha,\beta\neq\alpha} \iint g(\vec{r}_i,\vec{r}_j)\, R(\vec{r}_j)\, T^{\alpha}\, \sigma(\vec{r}_i-\vec{r}_j) \times \times\, T^{\beta}\, R(\vec{r}_j-\vec{r}_i)\, R(-\vec{r}_j)\, \langle\vec{E}\rangle\, d\vec{r}_i\, d\vec{r}_j \quad , \tag{4}$$

where g $(\vec{r}_i,\vec{r}_j)$ is the two-point correlation function and V is the volume of the film. We again consider an exponential decay type correlation function.

To simplify the calculation we assume all the metallic grains to be spherical in shape and of equal radius which allows us to write $T^{\alpha}=T^{\beta}$ and make them diagonal matrices. The field $\langle\vec{E}\rangle$ and $\langle\vec{E}_0\rangle$ will be expanded in terms of the basis functions $\{\mathrm{Re}\vec{\psi}_{\ell 2}(K_0\vec{r})\}$ that are solutions to the Helmholtz equation described by Waterman . K_0 is the propagation constant of the electromagnetic wave in the zeroth order effective medium. Substituting these expansions for the fields in Eq. (4) it is possible to reduce this expression to an equivalent set of scalar equation

$$X_n = d_n + \delta^2 \sum \int M_{n'}\, B_{n'}\, \sigma_{nn'}\, d\vec{r}_j \quad ,$$

where M_n contains all the correlation effects.

The coefficient d_n representing the unperturbed wave can be written in terms of the effective propagation constant K_0, while the coefficient representing the total average field $\langle\vec{E}\rangle$ can also be expressed in terms of the effective propagation constant K of the correlated medium as:

$$d_n = d_n^{\circ} \exp[i\vec{K}_0\cdot\vec{r}] \quad , \quad X_n = X_n^{\circ} \exp[i\vec{K}\cdot\vec{r}] \quad \text{and} \quad B_n = X_n^{\circ} \exp[i\vec{K}\cdot(\vec{r}-\vec{r}_j)] \quad .$$

Following the procedure described by Varadan, et. al.[13] we can use the scalar Helmholtz operator in the zeroth order approximation to simplify the above equation and reduce the volume integral to a surface integral:

$$X_n^{\circ} = \sum_{n'} M_{n'}\, X_{n'}^{\circ}\, I_{nn'} \quad , \tag{5}$$

where

$$I_{nn'} = \delta^2/(K^2-K_0{}^2) \int_{|\vec{r}|>a} \{\sigma_{nn'}(-K_0\vec{r})\, \partial\exp(i\vec{K}\cdot\vec{r})/\partial r - \exp(i\vec{K}\cdot\vec{r})\, \partial\sigma_{nn'}(-K_0\vec{r})/\partial r\}\, ds.$$

Eq. (5) represents a system of homogeneous coupled equations with unknown coefficients. Solving the associated secular equation we obtain a new dispersion relationship that takes into account pair correlations in the scattering medium. In terms of the dielectric constants this expression can be expressed as

$$\varepsilon = \bar{\varepsilon}_0 \, (1 + 2Fk^2\bar{\varepsilon}_0)/(1-Fk^2\bar{\varepsilon}_0) \quad , \qquad (6)$$

where ε is the new effective dielectric constant in the correlated medium of the film obtained from the RFSA model, $k = \omega/c$ is the propagation constant of the electromagnetic wave in vacuum, and F contains all the effects due to correlations between islands and can be expressed as

$$F= 22/50 \; f^2 \exp(-2a/L) \; (L^2+2aL) \; [(\varepsilon_r-1)/(\varepsilon_r+2)]^2 \quad ,$$

where f is the volume fraction of metal and ε_r is the ratio of the dielectric constant of the metallic islands to the external medium.

Results and Conclusions

QSE becomes an important correction to the effective dielectric constant of the metallic grains when their radius is less than 100A. In using the QSE results it is necessary to average the discrete absorption peaks with a log-normal island sizes distribution, before calculating the optical properties of cermets. The next step in improving the calculations of the optical properties is to include two point correlation between neighboring grains. In order to simplify the multiple scattering correction, the First Smoothing Approximation was used.

In performing this calculation an average dielectric constant is assumed that is conceptually compatible with the B model of a cermet. Multiple scattering corrections in the FSA approximation, with a metallic dielectric constant corrected for QSE in the cases that the islands are smaller than 100A, was shown to improve the predicted value of B theory but was unable to significantly shift the position or broaden the resonance peak of the complex index of refraction. For this reason it was considered necessary to further improve the calculation by taking into account renormalized effects in a T-matrix context. The result of this calculation shown in Eq. 6, permits the calculation of the complex effective dielectric constant of cermets taking into account correlation effects that include renormalized corrections.

We have applied this refined calculation to Ag/MgO. In making the calculations, the average radius of the islands was estimated and the mean free path and correlation length were then adjusted to obtain the best fit with experiment. When the Drude model was used in the Ag/MgO cermet (See Fig. 3) it was necessary to utilize a 3A mean free path in order to obtain the best fit with the experimental complex imaginary index of refraction. This was considered to be too short a mean free path even after taking into account that silver tends to have a large number of internal imperfections as mentioned by H. Craighead[10]. In the calculation the optimal radius for the metallic islands was 80A, a value considered to be somewhat small according to estimates made from micrographs. An improvement in this calculation was obtained when the average radius of 125A for the islands was used and the QSE corrections were made (Fig. 3). For this case, the shift in the peak was good but relatively narrow compared to the experimental results. In both cases the correlation length was equal to 6 islands, a value that is compatible with experimentally measured correlations in other cermets.

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PAPER TO APPEAR IN PHYSICAL REVIEW B

Multiple-scattering theories including correlation effects to obtain the effective dielectric constant of nonhomogeneous thin films Manuel Gómez, Luis Fonseca†, Gerardo Rodríguez††, Angel Velázquez and Luis Cruz. University of Puerto Rico, Río Piedras, Puerto Rico.

Abstract

Existing theories for the effective optical properties of a ceramic-metal granular medium (cermet), are discussed within a multiple scattering analysis and used as the starting point for taking into account correlation effects. Analysis of the nucleation and growth process in cermets, indicate that the correlation between the islands of the less abundant material are important in the study of optical properties. Multiple scattering corrections are considered by solving the field equation in the First Smoothing Approximation. The results obtained with this model are compared with other theories and against experimental data of real cermets. Quantum size effects corrections to the dielectric constant of the metallic grains in dielectric-like cermets and their effect on the results of the theory are also analyzed. Finally, renormalization effects introduced through a T-matrix formalism are discussed. Comparison between the results of the proposed model and the experimental data for different cermets shows that the developed theory has better predictive value than earlier models and good agreement is obtained with experiment even when the metal concentration is large.

†On leave from Escuela de Física, Universidad de Costa Rica.
††Present Address: Cornell University.

I. INTRODUCTION

Cermets are inhomogeneous materials consisting of immiscibles mixtures of insulators and metals. The optical properties of cermets have been extensively researched because of their potential application to the development of optically selective surfaces.[1] Considerable work has been performed to develop theoretical models which will correctly predict the optical properties of cermets when the bulk dielectric constant of the constituents is known experimentally. It has been found that the optical properties of cermets can be modified by changes in the relative concentration of the constituents and the concomitant change in microstructure.[2] Based on constituent concentration, cermets are classified into three general types: a) metallic cermets where the dominant volume fraction is metallic and as a consequence metallic properties dominate the optical properties of the material; b) dielectric cermets where the dielectric constituent is dominant, and as a result, metallic inclusions are formed in a dielectric matrix; c) intermediate cermets where an interconnected metallic network develops, in this region percolation effects are observed[3]. At opposite extremes when the volume fraction of the metallic or dielectric constituents is very high (~98%), the optical properties are determined by the major constituent. But when the concentration of the dominant constituent is less than 98% the material develops a distinct resonance which is not characteristic of either one of the constituents. The prediction of this resonance has been the goal of all theories developed for the optical properties of cermets materials.

Since for the region of interest in the electromagnetic spectrum the wavelength of the radiation is large compared to the metallic islands, an electrostatic approximation can be made. In this regime a simple relation between the internal ($\vec{E}_{in}$) and the external ($\vec{E}_{out}$) electric fields for a single spherical island can be made yielding the relationship[4]

$$\vec{E}_{in} = \frac{3}{2 + \varepsilon\,(\omega)}\,\vec{E}_{out} ,$$

which predicts a resonance when the dielectric constant $\mathrm{Re}\varepsilon(\omega) = -2$. Essentially this singularity is responsible for the resonance structure in cermets.

The technological usefulness of cermets when applied to optical devices comes from their optical response in the region between $0.8\mu m < \lambda < 2.5\mu m$. Since in the spectral region of interest the wavelength is larger than the microstructure, an effective medium dielectric constant can be used to characterize the optical response of the materials. Based on this idea several theoretical models have been proposed to obtain the effective dielectric constant of cermets in terms of the dielectric constant of the constituents, and other parameters describing the microstructure, such as island radiuses, relative concentrations of the constituents, and the shape of the islands. Two basic and widely used models are the Maxwell-Garnett (MG) and the Bruggeman (B) models.[5] The MG model is asymmetric, since it considers the cermet as composed of spheres of the less abundant constituent embedded in a matrix of the most abundant material. The effective dielectric constant is then obtained by performing a volume average over the local fields. While the B model is symmetric since it considers the two constituent materials as spheres embedded in an effective medium, a volume average is also performed to obtain a self-consistent expression for the effective dielectric constant. In both theories a resonance in the spectral response of the cermet is obtained, but neither agrees with the experimentally measured complex dielectric constant (Fig. 1). For example, comparison between the experimentally obtained imaginary part of the effective index of refraction and the MG model reveals that the theoretical resonance is too narrow and in many cases blue shifted with respect to experimental results. Several papers, like those of Granqvist[6] show that the magnitude and position of the resonance is a strong function of the inclusion's shape. Corrections to the dielectric constant of metallic grains for size effects have been extensively used to reduce the magnitude of the resonance, but they fail to produce enough red shift and broadening to explain experimental data.

The objective of this paper will be to show that corrections due to correlation between the position of the metallic islands, resulting from the formation process of the cermet, can move and broaden resonance obtained by the traditional mean field theories of Maxwell-Garnett and Bruggeman. In order to perform this correction a multiple scattering theory has been developed that starts from an effective dielectric constant that is calculated assuming no correlation between the metallic islands and labeled in this work as the zeroth order approximation. Non renormalized and renormalized theories will be discussed in which correlation effects are taken into account. The final result for the effective dielectric constant will be expressed in terms of the zeroth order effective dielectric constant $\bar{\varepsilon}_0$ (which contains no correlation effects but has been renormalized), the relative concentration of the constituents f, the dielectric constant of the less abundant constituent corrected for size effects ε_m, the radius of the inclusions a, and a correlation length L.

Existing theories including those that take into account the shape of the islands in an effort to improve the predicted value of the mean field theories will be analyzed and discussed. Also corrections for size effects on the dielectric constant of the metallic grains will be studied and it will be shown that it is necessary to take into account quantum size effects for metallic islands of good metals with radiuses less than 100A.

A. MEAN FIELD MODELS

In order to explain the characteristic resonance peak of cermets and other non-homogeneous media two basic mean field models have been proposed by J. C. Maxwell-Garnett and Bruggeman. Many derivations of these theories have been made by several authors,[7,8] and it has been shown that MG theory is a zeroth order approximation of more complex multiple scattering theories.[9,10] The authors have been able to show that Bruggeman can also be reduced to zeroth order approximation in a multiple scattering formulation of the problem. Both theories are effective medium theories within the electrostatic approximation and are obtained from volume averages. Maxwell-Garnett theory is an asymmetric model considering the cermet as composed of islands of the less abundant constituent embedded in a matrix of the most abundant material, while the Bruggeman model is a self-consistent theory and assumes that both *constituents form spheres that are surrounded by the effective medium.* The response of islands in the cermet to an external electric field produces a resonance in the complex dielectric constant. In general, Maxwell-Garnett produces resonance peaks that are too narrow and usually shifted towards the blue region of the spectrum with respect to the experimental results, while Bruggeman tends to underemphasize the structure.

Several modifications have been performed in an attempt to obtain better agreement with experimental results. In particular, considerable effort has been invested in correcting the theory for effects of changes in the shape of the islands in the cermet.[11] Granqvist [6] has taken into consideration not only shape effects, but the contribution of chains, double spheres, fcc clusters, and even combinations of these shapes in order to bring mean field theories calculations closer to experimental results. In particular he calculates the logarithm of the transmission for metallic type cermet (Ag/SiO_2; 17% SiO_2) using the MG model, under the assumption that the dielectric inclusions are ellipsoids instead of spheres, and expressing the effective dielectric constant as:

$$\bar{\varepsilon}_{MG} = \varepsilon_{ma} \frac{1 + 2/3\ f\alpha}{1 - 1/3\ f\alpha} \quad ,$$

where ε_{ma} is the bulk dielectric constant of the matrix, f volume fraction of the dielectric and α is proportional to the polarizability. Under the assumption that ellipsoids are randomly oriented, the value for α is given by:

$$\alpha = \frac{1}{3} \sum_{i=1}^{3} \frac{\varepsilon_{mi} - \varepsilon_{ma}}{\varepsilon_{ma} + D_i\ (\varepsilon_{mi} - \varepsilon_{ma})} \quad ,$$

where the D_i are the triplets of the depolarization factors, ε_{mi} is the bulk dielectric constant of the less abundant constituent, and the 1/3 term is a consequence of assuming a random orientation of the ellipsoids. He then uses a log-normal distribution for the ratio of the major semi-axis a to the minor semi-axis c, a ratio that is directly connected to the D's, to calculate the effective dielectric constant of the cermets. Granqvist centered his log-normal distribution on a value of D that corresponds to the ratio $\overline{a/c} = 8.7$, with this ratio he weighted the distribution towards oblate ellipsoids. Following this procedure he obtained better agreement with experiment than when all the inclusions are assumed to be spheres.

Figure 2 illustrates the dependence of the imaginary part of the dielectric constant ε_2 on the depolarization factor D when it is varied from $.2 < D < 1.0$. From the figure it can be seen that ε_2 is strongly dependent on the depolarization factor. Several distributions were used by us to perform the average with the depolarization factors assuming values between .2 and .8, values that were considered to be consistent with observed micrographs.

By taking a log-normal distribution with a D value centered at an average D value that corresponds to a ratio $\overline{a/c} = 1$ (spheres), it was shown upon calculating the logarithm of the transmission that the result corresponds to the one obtained if only spheres would have been used for the metallic inclusions. In fact, we were able to show that averaging over a distribution of shapes was not sensitive to the type of distribution or the average value of the a/c ratio used, unless a highly asymmetric or a strongly weighted towards oblateness distribution was utilized. We concluded that the average polarizability equals the values obtained for spherical grains as long as distributions consistent with observed micrographs are used. For this reason, it was decided that all multiple scattering calculations would be performed only for spherical islands, since on the average, due to the random distribution in shape and orientation, the system behaves like a cermet made up of spherical islands.

II. SIZE CORRECTION TO THE DIELECTRIC CONSTANT OF THE METALLIC INCLUSIONS

A. QUANTUM SIZE EFFECTS (QSE)

In order to calculate the effective dielectric constant of cermets it is necessary, in general, to correct the bulk dielectric constant of the minority constituent for size effects. Normally the insulator has a dielectric constant that is essentially frequency independent in the spectral range of interest, while the metallic constituent has a strong frequency dependence in the same region. When the metal is the minority constituent, its bulk dielectric constant must be corrected for size effects when the bulk mean-free path becomes comparable to the size of the grains. Traditionally Drude's model together with experimentally obtained interband contributions is used to calculate the dielectric constant of the metal. In this procedure, the mean free path of the electrons in the metallic island is corrected for boundary scattering at the interface between the island and the external medium. Many researchers[12] have observed that in order to obtain a reasonably good fit between theory and experiment, it is necessary to use mean free paths that are considerably smaller than the ones attributed only to the size of the island. These corrections can be explained as the combination of boundary scattering at the metallic grains surface and scattering inside the island due to internal imperfections and faults. Apparently, the contributions from these faults and imperfections is the dominant factor in determining the mean-free path in most materials. This is not surprising since in many cases the formation process is based on the coalescence of small islands to form larger ones, a process that should produce substantial amounts of imperfections in the metallic grains. The Drude theory with these corrections is satisfactory for metallic grains of good metal with radiuses of more than 100A. However, when the size of the metallic particles become comparable to the electron wavelength, quantum corrections become mandatory if a realistic dielectric constant is going to be obtained.

Until recently no good theoretical models existed for calculating dielectric constant of metallic particles with radius of the order of 100A or less.[13] To solve this problem several researchers have used the Quantum Box Method within the Random Phase Approximation to calculate the dielectric constant of the metallic particles.

Kawabata and Kubo[14] have corrected the dielectric constant for size effects assuming that the spectrum of the quantum levels form essentially a continuum, while Wood and Ashcroft[15] carefully reworked the Quantum Size Method, fully taking into account the spectrum resulting from the box quantization and obtained a dielectric constant for the particles that can be expressed as

$$\mathrm{Re}\,\varepsilon(x) = 1 + \frac{4^4}{\pi^4} \frac{a}{a_0} \sum_{m=1}^{m_c} m^2 (m_c^2 - m^2)$$

$$\times \sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2-(x^2+\Gamma^2)][1-(-1)^{m+m'}]}{\Theta}$$

$$\mathrm{Im}\,\varepsilon(x) = \frac{4^4}{\pi^4} \frac{a}{a_0} \frac{\Gamma}{x} \sum_{m=1}^{m_c} m^2 (m_c^2 - m^2)$$

$$\times \sum_{m'=1}^{\infty} \frac{m'^2[\Delta^2+x^2+\Gamma^2][1-(-1)^{m+m'}]}{\Theta} \qquad (1)$$

where

$\Theta = \Delta^3 \; [(\Delta^2 - x^2 + \Gamma^2)^2 + 4x^2 \; \Gamma^2]; \quad \Delta = m'^2 - m^2$

$x = 2h\omega \; ma^2/h^2\pi^2; \quad \Gamma = hm_c^2/\tau\varepsilon_f; \; m_c = \mathrm{INT}(K_f a/\pi)$

ε_f is the Fermi energy, K_f the Fermi wave number, a is the size of the grains, a_0 the Bohr radius, and INT the integer part of the argument.

Recently this formalism has been applied by the authors of this article to real cermets in the region where the metallic inclusions in the cermets are smaller than 100A[16] and better results have been obtained for the dielectric constant than when Drude's model is used.

Figure 3 compares the imaginary part of the dielectric constant taking into account quantum size effects following Wood and Ashcroft (QSE) as expressed in Eq. (1) and Kawabata and Kubo model (KK) with the one calculated using Drude's model. In the calculation of the Drude's model the size of the silver particles are taken to be 30A and no interband contributions to the dielectric constant have been included. This model was corrected for size effect using an effective relaxation time that corrects the bulk result with boundary scattering through the relationship

$$1/\tau_{eff} = 1/\tau_b + V_f/a \quad ,$$

where τ_b is the bulk relaxation time, V_f is the Fermi velocity and a is the radius of the silver grains. The multiple peaks appearing in the QSE calculations are due to the discrete energy spectrum of an electron in a box. These peaks tend to decrease in magnitude as one moves from the infrared to the visible region of the spectrum.

Extensive computer calculations were made to compare the KK, QSE, and Drude's model for good metals such as silver, gold, and nickel and it was found that in all cases when the size of the islands exceeded 100A the three models coincide in the obtained value of the dielectric constant of the metallic inclusions, provided that the KK model is corrected for a geometric factor of $\pi/6$.[17] For that reason Drude's formula, which is the simplest one, will be preferred for metallic islands of radiuses larger than this value.

B. APPLICATIONS OF THE QSE TO REAL CERMETS

We will now apply the QSE result to the calculation of the optical properties of real cermets and compare the results with those obtained using Drude's model. In this section interband contributions to the dielectric constant of the metal grains will be fully taken into account.[18] Experimentally the resonances observed in the dielectric constant of an isolated metal grain due to quantum size effect are not observed in the effective dielectric constant of a real cermet. The disappearance of these peaks is due to the fact that the metallic grains in a real cermet do not have a unique size, but instead have a distribution of sizes as can be verified by micrographs of the materials. For this reason the dielectric constant obtained from the QSE calculations for one isolated particle were averaged over a distribution that realistically represented the variations in size of actual cermets.

If an histogram of the observed radiuses of the metallic grains is made, a distribution of the form illustrated in Fig. 4 is obtained showing that the distribution is skewed towards large radiuses. The skewedness is consistent with the formation process of the inclusions, in which large particles are formed from smaller ones by coalescence. Actually, a log-normal distribution of the following form is usually used to fit the experimental results.[19]

$$f\ (R) = (1/\sqrt{2\pi})\ 1/\sigma \left(\exp \{-1/2[\ln(R/R_0)/\sigma]^2\}\right) \quad ,$$

where R_0 is the average radius of the grains and σ is a measure of the width of the distribution and is given by $\sigma = \ell n\ (\sigma_{\ell n})$. Experimentally the value $\sigma_{\ell n}$ is found to be between 1.1 and 1.5 for most cermets.[20] Averaging the dielectric constant of one metallic grain with a *log-normal distribution* function, an effective dielectric constant for the metallic grains in the cermet is obtained. This average QSE result is then used to calculate the effective medium dielectric constant using the Bruggeman mean field, and multiple scattering corrections theories.

In Fig. 5 the unaveraged and averaged quantum calculations are compared for a particle of average radius R_0 = 30 A. As seen from the figure, the effect of taking the average with the log-normal distribution is to smooth out the quantum structure of a single particle when using the QSE approximation. Since experimentally the dielectric function of a cermet is found to be a smooth function of frequency, this is the correct dielectric constant to be used for the metal in calculating the effective dielectric constant of cermets. For radiuses in excess of 100A it is found, as expected, that the Drude and the averaged quantum results coincide.

Before applying these results to real cermets it is important to discuss the relaxation time concept as used in the Drude and the QSE methods. Usually the Drude model utilizes an effective relaxation time that corrects the bulk mean free path of the electrons for collisions with the grain walls. However, the relaxation time is not well understood for particles of radiuses below 100A. According to Wood and Ashcroft, surface scattering corrections in terms of a mean free path concept is not appropriate when the presence of the surface actually determines the eigenstates of electrons within the particle's volume. The mean free path of electrons in the bulk metal for the case of silver is of the order of 100A. While for smaller metallic particles grown by sputtering processes the mean free path is reduced due to imperfections within the metallic grain that result from the fabrication process. Small metallic inclusions in cermets are known to grow by coalescence of smaller inclusions which diffuse on the substrate, and as a result, a significant number of imperfections are trapped within the metallic grain during the formation process. To take into account the effect of these imperfections we will introduce a restricted mean free path smaller than the bulk mean free path when applying the QSE calculation to obtain an effective complex dielectric constant.

We now compare with experimental data the results obtained when the QSE dielectric constant is introduced into the calculation of the effective dielectric constant of the cermet. The theoretical calculations will be compared with the measured refractive index for the Au/Al_2O_3 and Ag/MgO cermets obtained by Craighead.[21] This experimental data was selected because it is obtained from cermets with metallic grains of average radiuses less than 50A, and consequently, the QSE method should contribute significantly to the complex index of refraction.

Figure 6(a) compares the experimentally measured imaginary part of the complex index of refraction for Au/Al_2O_3 cermets with a 90% volume fraction of the dielectric constituent, with the Bruggeman's theory using Drude's model (BD) and Bruggeman's theory using the QSE correction (BQ). The average radius for the calculations was taken to be 20A, and the value used for the limited mean free path was also 20A. As can be observed from the figure the BD model exaggerates the magnitude of the observed resonance in the imaginary part of the index of refraction N_2. The BQ model greatly improves on the BD for N_2 by reducing the magnitude of the peak and approximating much better the actual values of N_2 in the infrared region of the spectrum. However, in this case there is no appreciable shifting of the position of the peak. Figure 6(b) shows the same experimental result for Au/Al_2O_3 cermet but now compared with Maxwell-Garnett, using for the metal the Drude dielectric constant (MGD) and the QSE (MGQ) values. As we have anticipated MG predicts a too narrow and generally blue shifted peak. In this case QSE also reduces the magnitude of the peak, and a measurable red shift of the curve and a broadening effect is observed.

III. MULTIPLE SCATTERING THEORIES

A. THE FIRST SMOOTHING APPROXIMATION (FSA)

When thin films of cermets are grown by cosputtering or coevaporation methods, nucleation processes are responsible for the formation of metallic or dielectric islands in the matrix of the corresponding more abundant constituent. Since the nucleation process is governed by diffusion effects, relative island positions must be correlated. Several authors have developed a method to measure this correlation and demonstrated its existence.[22] The Multiple Scattering Theories developed here will assume that the islands of the minority constituent are correlated and that the corresponding correlation length is sufficiently large to make important contributions to the calculation. Thus the purpose of the multiple scattering calculations will be to correct the mean field theories for the contribution of the correlation to the effective dielectric constant of the medium. It will be shown that these effects are important in obtaining a model with predictive value for the optical response of cermets.

The theory is based on the concept of a local dielectric constant that fluctuates around an average value ε_0 that is independent of position. This position-dependent dielectric constant can be written as

$$\varepsilon(\vec{r},\omega) = \varepsilon_0(\omega) + \delta\varepsilon(\vec{r},\omega) \quad ,$$

where $\delta\varepsilon(\vec{r},\omega)$ corresponds to the spatially fluctuating term. The equation governing the electric field of the electromagnetic wave can then be written in terms of this spatially-dependent dielectric constant as

$$\nabla \times \nabla \times \vec{E} - (\omega/c)^2\mu\varepsilon\vec{E} - \mu^{-1}\nabla\mu \times \nabla \times \vec{E} = 0 \quad .$$

Rewriting this equation explicitly in terms of the fluctuating part of the dielectric constant it can be expressed as

$$\nabla \times \nabla \times \vec{E} - K_0^2\vec{E} = K_0^2\,(\delta\varepsilon/\varepsilon_0)\,\vec{E} \quad ,$$

where K_0 is the average propagation in a medium with average dielectric constant ε_0. In terms of operator formalism the field equation can be defined as a non-stochastic operator

$$H \equiv \nabla \times \nabla \times - K_0^2 \quad ,$$

and a stochastic term

$$H \equiv Ko^{2} \, (\delta\varepsilon/\varepsilon_{0}) \qquad .$$

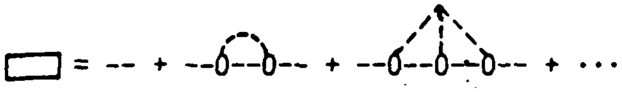
The field equation then becomes

$$\vec{E} = \vec{E}o + Go\ H_1\ \vec{E} \qquad , \qquad (2)$$

where $\vec{E}_0$ is the electric field that results from solving the non-stochastic operator. Since we are in the presence of a random medium and we will assume that an effective medium dielectric constant can be defined, an average of this equation can be performed to obtain

$$\langle\vec{E}\rangle = \vec{E}o + Go\ \langle H_1\ \vec{E}\rangle \qquad .$$

From this expression an infinite multiple scattering expansion in terms of H_1 can be performed with the condition that the fluctuating term is centered around the averaged dielectric constant and therefore, $\langle H_1\rangle = 0$. Diagrammatically this expansion can be represented as follows

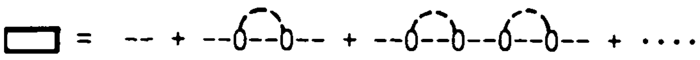


, (3)

where -- represents Green's function associated with $\vec{E}_0$, ▭ represents Green's function associated with $\langle\vec{E}\rangle$ and 0 represents H_1. The dashed line indicates correlation between local scattering points. The above equation although exact, cannot be solved. In order to be able to obtain useful values for the effective dielectric constant the First Smoothing Approximation,[23,24] which only takes into consideration pair correlation functions, will be used. This approximation yields the equation

$$\vec{E} = \vec{E}o + Go \langle H_1\ Go\ H_1 \rangle \langle \vec{E} \rangle \quad ,$$

which upon interation can be expressed diagrammatically as



This diagram contains the pair correlation functions

$$\langle \delta\ \varepsilon(\vec{r}_1)\delta\ \varepsilon(\vec{r}_2) \rangle \quad ,$$

represented by the dashed lines. Following the procedure of Karal and Keller[25] this approximation was used to obtain an effective medium dielectric constant ε_{eff}. To do this, it was necessary to assume a plane wave solution for the macroscopic field with an effective propagation constant

$$K^2 \equiv (\omega^2/c^2)\ \varepsilon_{eff}$$

Previous work by the authors[26] indicate that the pair correlation can be expressed as an exponential relationship with a correlation length L in the following form

$$\langle \delta\varepsilon(\vec{r}_1)\delta\varepsilon(\vec{r}_2) \rangle = \Delta\ e^{-r/L} \quad ,$$

$r = |\vec{r}_2 - \vec{r}_1|$ and Δ was shown to be well represented by the square of the standard deviation of the fluctuations. In the spectral range of interest the final dispersion relation becomes

$$\varepsilon_{eff} = \varepsilon_0 + \frac{\Delta}{2\varepsilon_0}\left[\frac{2}{3} + \frac{1+ia}{a^2} + \frac{2a^2}{1-i2a} - \left(\frac{1}{a} + \frac{1+a^2}{a^3}\right)\cot^{-1}\left(\frac{1-ia}{a}\right)\right] ,$$

where

$$a^2 \equiv \varepsilon_0 \omega^2 L^2/c^2 .$$

The new effective dielectric constant includes the averaged dielectric constant plus a term that is a function of the correlation length L. This calculation is conceptually based on the assumption that there is an averaged dielectric constant around which local fluctuations due to the metallic and dielectric islands occur and is known as Random Continuum model. Since this is precisely the model that is described by Bruggeman's theory, we have chosen as the averaged dielectric constant ε_0 the one obtained from that theory. This is perfectly consistent with multiple scattering theory since it can be shown that the Bruggeman model is a zeroth order approximation of multiple scattering theories. The proof consists in assuming that both the metallic and the dielectric constituents form spherical scattering sources in an average medium, and then, in the absence correlation, the average of the T-matrix <T> can be written as the volume fraction average of the single particle metal T-matrix T_1 and the dielectric particle T-matrix T_2 as: $\langle T\rangle = f\ T_1 + (1-f)T_2$ where f is the volume fraction. Then taking the long wavelength limit and assuming the self-consistent condition, $\langle T\rangle = 0$, the Bruggeman equation is immediately obtained.

The theoretical predictions of both the Bruggeman and FSA models will now be compared with experimental data for Ag/MgO; 80% MgO, and Au/Al_2O_3; 84% Al_2O_3. Figures 7(a) and 7(b) show the imaginary parts of the index of refraction of these cermets. For the calculation, as presented in the Fig. 7(a), the dielectric constant of the metallic islands was obtained from Drude's model corrected for a restricted mean free path due to size effects and due to impurities and defects. As observed, the Bruggeman model predicts higher values for the imaginary part of the index of refraction N_2, than those obtained experimentally, whereas the FSA model fits very well with experimental data in almost all the region in the case of Ag/MgO where the radius of the islands is of the order of 80A and restricted mean free path of 5A is used. In the case of Au/Al_2O_3, it was necessary to make quantum corrections in order to obtain the best fit, because the islands in this case are of the order of 30A. In this second case, the resonance in the imaginary part of N_2 is shifted towards longer wavelengths with respect to the experimental results.

B. RENORMALIZED FSA APPROXIMATION (RFSA)

The results obtained using the QSE and multiple scattering corrections in the FSA approximation to the B model shows improvements on the predicted value for the imaginary index of refraction, but these corrections, although they affect the magnitude of the resonance, do not broaden or shift the resonance peak. In general, the B and MG model do not predict correctly the position or width of the absorption peak. This suggests that a renormalized approach to the multiple scattering calculation may be the correct path to obtain the necessary corrections to the position and width of the resonance peak. A renormalized procedure can be devised[24] starting from the field Eq.(3) and then using a T-matrix calculation for single spherical scatterers. Contrary to the case of the FSA approximation, the cermet is conceived here as spherical islands of the minority constituent embedded in a matrix of the dominant constituent. Each one of these spherical islands is then taken to be a scattering source from which the overall scattering wave for the random medium can be obtained. Since this model of cermet is consistent with the MG model, the whole procedure will be constructed on a zeroth order scattering dielectric constant that is obtained from a MG theory, thus assuming a non-correlated medium in which the spherical grains serve as scattering sources. Eq. (2) can be written in diagrammatic form as

$$G = -- + --\overset{\alpha}{0}-- + --\overset{\alpha}{0}--\overset{\beta}{0}-- + --\overset{\alpha}{0}--\overset{\beta}{0}--\overset{\alpha}{0}-- + \cdots , \qquad (4)$$

where the superscripts on each point refer to a specific scatterer that produces a local fluctuation H_1 in the background medium. Defining the single scattering T-matrix as

$$T_\alpha \vec{E}_0 = H_1 {}_\alpha \vec{E}$$

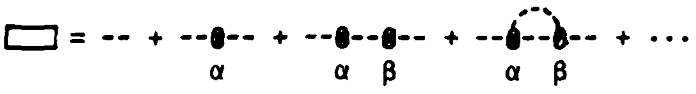
or

$$T_\alpha = \overset{\alpha}{0} + \overset{\alpha}{0}--\overset{\alpha}{0} + \overset{\alpha}{0}--\overset{\alpha}{0}--\overset{\alpha}{0} + \cdots \equiv \underset{\alpha}{\bullet} ,$$

where the symbol 0 represents the new renormalized potential for single scattering spherical sources. In terms of this new renormalized potential Eq. (4) becomes

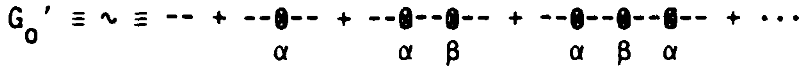
$$G = -- + --\underset{\alpha}{\bullet}-- + --\underset{\alpha}{\bullet}--\underset{\beta}{\bullet}-- + --\underset{\alpha}{\bullet}--\underset{\beta}{\bullet}--\underset{\gamma}{\bullet}-- + \cdots .$$

Naturally, in this equation the subscripts cannot be identical in two consecutive points since these terms have already been taken into account in the single particle scattering T-matrix. If the statistical average is performed on this Green's function, the following statistically averaged Green's function is obtained



,

this expression contains both correlated and uncorrelated terms. A renormalized propagator that only takes into account uncorrelated terms is then defined as



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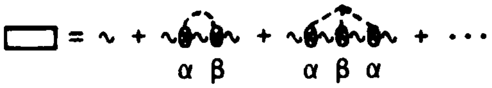
where G_0' is the renormalized uncorrelated Green's function identified with the propagation of an electromagnetic wave in an uncorrelated medium. In terms of the renormalized Green's function and scattering potentials the general correlated Green's function can be expressed as



.

This expression is formally equivalent to the Random Continuum final Eq. (3) that was used in the FSA approximation with the difference that now the scattering sources $\bullet_\alpha$ and the intermediate propagation Green's functions have been renormalized taking into account all uncorrelated terms. A simple correspondence can be made between the previous and the present equation through the following symbolic equivalences

- → ∿ that is $G_0 \to G_0'$

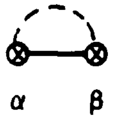
0 → ● that is $H_1 \to T$.

As previously stated, in the absence of correlation effects or equivalently in an uncorrelated medium, a zeroth dielectric constant is obtained that corresponds to the MG model.[10] Applying now the First Smoothing Approximation to this diagram, which is equivalent to neglecting all correlations higher than the two point correlation and also neglecting unlinked and nested two point correlations, this yields an equation that is formally equivalent to the FSA but renormalized and written in the following form

$$\langle\vec{E}\rangle = \vec{E}_o + G_o' \langle T\, G_o' T\rangle \langle\vec{E}\rangle \quad ,$$

diagrammatically this can be written as

$$\langle\vec{E}\rangle = \langle\vec{E}_o\rangle + \sum_{\alpha,\beta\neq\alpha}$$



$$\langle\vec{E}\rangle \quad , \qquad (5)$$

where $\langle\vec{E}_o\rangle$ is the statistically averaged field propagating in the uncorrelated medium and $\langle\vec{E}\rangle$ the effective total field. The second term in the r.h.s. of this self-consistent equation represents scattering processes where the effective total field $\langle\vec{E}\rangle$ is scattered by pairs of correlated islands α and β located respectively at $\vec{r}_i$ and $\vec{r}_j$. In order to apply this formalism an explicit mathematical representation of the diagram in the second term of the r.h.s. of Eq. (5) must be obtained. Peterson and Strom[27] developed a formalism to obtain the T-matrix for an array of n-scattering objects with well-defined spatial coordinates. Their formalism is an extension to a multiple number of scatterers of the one developed by Waterman[28] for a single scatterer. In Waterman's formalism the T-matrix for a single scatterer is obtained expanding all the local fields in terms of Spherical Harmonics, and Bessel or Hankel functions. The term describing this double scattering process in Peterson and Strom's formalism is given by:

$$\otimes\!\!-\!\!-\!\!-\!\!\otimes \;\rightarrow\; R(\vec{r}_j)\, T^{\alpha}\, \sigma(\vec{r}_i-\vec{r}_j)\, T^{\beta}\, R(\vec{r}_j-\vec{r}_i)\, R(-\vec{r}_j) \quad , \qquad (6)$$

where T^{α}, T^{β} are the single scatterer T-matrices of islands α and β, respectively, expressed with their center in the origin of the coordinate system. The formalism then translates the particle through matrices R and σ to their correct position $\vec{r}_i$ and $\vec{r}_j$. Expressions for T^{α} are described in several articles[27,28] and expressions for matrices R and σ can be found in Peterson and Strom's [27] article. Using Eq. (2) the field equation can now be expressed as:

$$\langle\vec{E}(\vec{r})\rangle = \langle\vec{E}_0(\vec{r})\rangle + 1/V^2 \sum_{\alpha,\beta\neq\alpha} \int\!\!\int g(\vec{r}_i,\vec{r}_j)\, R(\vec{r}_j)\, T^{\alpha}$$

$$\times\, \sigma(r_i-r_j)\;\; T^{\beta}\, R(r_j-r_i)\, R(-r_j)\, \langle E\rangle\, dr_i\, dr_j \quad , \qquad (7)$$

where $g\,(\vec{r}_i,\vec{r}_j)$ is the two-point correlation function and V is the volume of the film. Considering the spheres as impenetrable and the medium as isotropic, an exponential metal-metal correlation function can be defined as:

$$g(\vec{r}_i,\vec{r}_j) \;=\; \Theta(r-2a)\, \exp\,\big(-\left|\vec{r}_i - \vec{r}_j\right| / L) \quad ,$$

where Θ is the Heaviside function, L the correlation length, and the correlation function measures the excess of the metal density with respect to its average, for this reason the function goes to zero at large distances. To simplify the calculation we assume all the metallic grains to be spherical in shape and of equal radius which allows us to write $T^{\alpha}=T^{\beta}$ and make them diagonal matrices. Assuming a macroscopic volume we can change $(1/V^2)\Sigma$ by δ^2, where δ is the density of islands in the cermet. With this approximation the field equation can be written as

$$<E(r)> = <E_0(r)> + \delta^2 \int dr_j \; R(\vec{r}_j) \int_{l>2a} dl \; \exp[-\vec{l}/L] \; T$$

$$\times \; \sigma(\vec{l}) \; T \; R(-\vec{l}) \; R(-\vec{r}_j) \; <\vec{E}> \qquad ,$$

where the substitution $\vec{l} \equiv \vec{r}_i - \vec{r}_j$ has already been performed. The field $<\vec{E}>$ and $<\vec{E}_0>$ will be expanded in terms of the basis functions $\{\mathrm{Re}\vec{\psi}_n(K_0\vec{r})\}$ that are solutions to the Helmholtz equation described by Waterman.[28] The $\vec{\psi}_n$ are known as the elementary fields and K_0 is the propagation constant of the electromagnetic wave in the zeroth order effective medium. In terms of this base the fields can be expressed as:

$$<\vec{E}_0> = \sum_n d_n \; \mathrm{Re}\vec{\psi}_n(K_0\vec{r})$$

and

$$<\vec{E}(r)> = \sum_n X_n \; \mathrm{Re}\vec{\psi}_n(K_0\vec{r}) \qquad .$$

While the total effective field $<\vec{E}>$ in the second term of the r.h.s. is expanded in a base centered at one of the correlated islands:

$$<\vec{E}> = \sum_n B_n \; R_e\vec{\psi}_n[K_0(\vec{r}-\vec{r}_j)] \qquad .$$

Substituting these expansions for the fields in Eq. (7) and performing the integration over the relative coordinate between correlated islands we obtain

$$\sum_n X_n \,\mathrm{Re}\vec{\psi}_n(K_o\vec{r}) = \sum_n d_n \,\mathrm{Re}\vec{\psi}_n(K_o\vec{r}) + \delta^2 \sum_n M_n \int B_n \,\vec{\psi}_n[K_o(\vec{r}-\vec{r}_j)]\, d\vec{r}_j \quad . \tag{8}$$

Matrix elements M_n contain all the correlations effects and can be written in terms of the elements of the single scatterer T-matrix. Since the wave length of incident radiation relevant to our problem is $\lambda > .3\ \mu m$ and the radiuses of islands for typical cermets are of the order of $.01\ \mu m$, the long wave limit can be utilized, thus reducing the expansion of the electromagnetic field to the magnetic and electric dipolar terms. In this limit only the first six terms of these matrices are necessary:

$$M_1 = M_3 = M_5 = A_1 T_1^2 + A_2 T_1 T_2$$

$$M_2 = M_4 = M_6 = A_1 T_2^2 + A_2 T_1 T_2 \quad ;$$

where,

$$A_1 \cong -22\pi i/5K_o\,(L^2+2aL)\exp[-2a/L]$$

$$A_2 \cong 5/11\ A_1$$

$$T_1 \cong i\,2/15\ (K_oa)^5\,(1-\varepsilon_r)$$

$$T_2 \cong i\,2/3\,(K_oa)^3\,(\varepsilon_r-1)/(\varepsilon_r+2) \quad ,$$

ε_r is the ratio of the dielectric constants of the metallic islands and the external medium, and it represents the source of the multiple scattering processes. To perform the integral over the $\vec{r}_j$ coordinate the properties of the translation matrices σ^{29} must be used to displace the $\vec{\psi}_n$ from position $\vec{r}_j$ to the origin:

$$\vec{\psi}_n\,[K_o(\vec{r}-\vec{r}_j)] = \sum_{n'} \sigma_{n'n}(K_o\vec{r}_j)\,\mathrm{Re}\vec{\psi}_{n'}(K_o\vec{r}) \quad ,$$

then Eq. (8) reduces to

$$\sum_n X_n \, R_e\vec{\Psi}_n(K_o\vec{r}) = \sum_n d_n \, R_e\vec{\Psi}_n(K_o r)$$

$$+ \, \delta^2 \sum_{nn'} M_n \int B_n \, \sigma_{n'n}(K_o\vec{r}_j) \, Re\vec{\Psi}_{n'}(K_o\vec{r}) \, d\vec{r}_j \quad . \qquad (9)$$

All terms in Eq. (9) are now written in the same orthogonal base and, therefore, can be reduced to an equivalent set of scalar equations:

$$X_n = d_n + \delta^2 \sum_{n'} \int M_{n'} \, B_{n'} \, \sigma_{nn'} \, d\vec{r}_j \quad .$$

The limits of integration in the above expression must be restricted to values $|\vec{r}_j - \vec{r}| > a$ in order to avoid having the scattered field inside the scattering island located at $\vec{r}_j$. Since in the long wave limit the electromagnetic wave tends to average the microstructure at the scale of island sizes it can be assumed that the wave propagates in the effective medium as a plane wave. The coefficient d_n representing the unperturbed wave can be written in terms of the effective propagation constant K_o as:

$$d_n = d_n^o \exp[iK_o \cdot \vec{r}] \quad .$$

While the coefficient representing the total average field <E> can also be expressed in terms of the effective propagation constant K of the correlated medium as:

$$X_n = X_n^o \exp(i\vec{K} \cdot \vec{r})$$

and

$$B_n = X_n^{\circ} \exp[i\vec{K}\cdot(\vec{r}-\vec{r}_j)] \quad .$$

In terms of these expressions the field equation now becomes:

$$X_n^{\circ} \exp(i\vec{K}\cdot\vec{r}) = d_n^{\circ} \exp(i\vec{K}_o\cdot\vec{r})$$

$$+ \delta^2 \sum_{n'} M_{n'} X_{n'}^{\circ} \int_{|\vec{r}-\vec{r}_j| > a} \exp[i\vec{K}\cdot(\vec{r}-\vec{r}_j)]\, \sigma_{nn'}(K_o\vec{r}_j)\, d\vec{r}_j \quad .$$

Following the procedure described by Varadan et al.[10] the scalar Helmholtz operator can be used in the zeroth order approximation to simplify the above equation and reduce the volume integral to a surface integral:

$$X_n^{\circ} = \sum_{n} M_{n'} X_{n'}^{\circ} I_{nn'} \quad , \tag{10}$$

where

$$I_{nn'} = \delta^2/(K^2-K_o^2) \int_{|\vec{r}| > a} [\sigma_{nn'}(-K_o\vec{r})\, \partial\exp(iK\cdot\vec{r})/\partial r$$

$$- \exp(i\vec{K}\cdot\vec{r})\, \partial\sigma_{nn'}(-K_o\vec{r})/\partial r]ds.$$

Eq. (10) represents a system of homogeneous coupled equations with unknown coefficients. Solving the associated secular equation a new dispersion relationship was obtained that took into account pair correlations in the scattering medium:

$$K^2 - K_o^2 = (-i\pi\delta^2 M_6/K_o)[2 + (K/K_o)^2] \quad .$$

In terms of the dielectric constants this expression can be expressed as:

$$\varepsilon = \bar{\varepsilon}_0 \; (1 + 2Fk^2 \varepsilon_0)/(1 - Fk^2 \varepsilon_0) \qquad , \quad (11)$$

where ε is the new effective dielectric constant in the correlated medium of the film obtained from the RFSA model, $k = \omega/c$ is the propagation constant of the electromagnetic wave in vacuum, and F contains all the effects due to correlations between islands and its explicit form is,

$$F = 22/50 \; f^2 \; \exp(-2a/L) \; (L^2 + 2aL) \; [(\varepsilon_r - 1)/(\varepsilon_r + 2)]^2 \quad .$$

IV. RESULTS AND CONCLUSIONS

The classical approach to the theory of the optical properties of cermets has traditionally used Drude's model corrected for interband transitions to obtain the complex dielectric constant of the metallic constituent with an effective relaxation time that takes into account surface scattering but fails to consider quantum effects. From the present work it is evident that this approach is valid when the radiuses of the metallic inclusions are larger than 100A when the metals used are good metals. We have shown that when the radiuses of the metallic grains are smaller than 100A, QSE becomes an important correction to the effective dielectric constant of the metallic grains when calculating the optical properties of cermets. When using the QSE results it is necessary to average the discrete absortion peaks with a log-normal distribution of island sizes. This average is necessary, since experimentally no structure is observed in obtained optical constants of cermets. In general, the ability to reproduce the experimentally observed optical properties of cermets is considerably improved when the dielectric constant of the metallic constituents for islands less than 100A is corrected for quantum size effects.

The next step to improve the calculation of the optical properties of cermets is to include two point correlation between neighboring grains. Under this condition a multiple scattering theory must be developed that will take into account interference effects between the scattering produced by neighboring metallic grains that are correlated. In order to simplify the multiple scattering correction, the First Smoothing Approximation was used, thus limiting the calculation to pair correlations through a self-consistent equation. In performing this calculation an average dielectric constant is assumed that is conceptually compatible with the B model of a cermet. Multiple scattering corrections in the FSA approximation, with a metallic dielectric constant corrected for QSE in the cases that the islands are smaller than 100A, was shown to improve the predicted value of B theory but was unable to significantly shift the position or broaden the resonance peak of the complex index of refraction. For this reason, it was considered necessary to further improve the calculation by taking into account renormalized effects in a T-matrix context. The result of this calculation shown in Eq. (11), permits the calculation of the complex effective dielectric constant of cermets taking into account correlation effects that include renormalized corrections. This equation is expressed in terms of the following basic physical parameters obtainable from experimental data: the average radius of the metallic island a; the correlation length L; volume fraction of the metallic constituents f; the bulk dielectric constant of the metallic grains ε_m and the bulk dielectric constant of the dielectric material. As the metallic concentration is reduced the correlation length tends to vanish and we recover from Eq. (11) the zeroth order approximation $\bar{\varepsilon}_0$, the effective dielectric constant of the uncorrelated medium. Since in the renormalized calculation, islands of the minority constituent are assumed to be the scattering sources embedded in a medium of the majority constituent, the proper starting zeroth order approximation dielectric constant is the MG model.

As previously stated the bulk metallic dielectric constant must be corrected for size effects for islands of 100A or less. We have applied this refined calculation to Ag/MgO and Ni/Al_2O_3 cermets where experimental data is available from Craighead's work.[21] The percentage of metallic constituent is 20% in Ag/MgO and between 39 and 46% in Ni/Al_2O_3. These concentrations are considered to be high and are normally not predicted well by mean field theories. Since as metal concentration increases correlation effects become more important, it is expected that multiple scattering effects should be more significant in these high concentration regimes. In making the calculations, the average radius of the islands was estimated and the mean free path and correlation length were then adjusted to obtain the best fit with experiment. When the Drude model was used in the Ag/MgO cermet (Fig. 8(a)) it was necessary to utilize a 3A mean free path in order to obtain the best fit with the experimental complex imaginary index of refraction. This was considered to be too short a mean free path even after taking into account that silver tends to have a large number of internal imperfections as mentioned by H. Craighead.[21] In the calculation, the optimal radius for the metallic islands was 80A, a value considered to be somewhat small according to estimates made from micrographs. An improvement in this calculation was obtained when the average radius of 125A for the islands was used and the QSE corrections were made (Fig. 8b). For this case, the shift in the peak was in good agreement but relatively narrow compared to the experimental results. In both cases the correlation length was equal to 6 islands, a value that is compatible with experimentally measured correlations in other cermets.

The main conclusion that can be obtained from this calculation is that our RFSA theory make the best correction to the MG mean field theories. It is possible to play around with the three adjustable parameters to obtain better fits, but what is significant, is that all values are compatible with experimentally known facts.

Figure 9 is a similar comparison for Ni/Al_2O_3 with metallic concentrations of 39 and 46%. Very good agreement for the position of the resonance peak and overall width was achieved with reasonable values for the mean free path of 10A, and with radiuses consistent with the micrographs.[21] The fit between theory and experiment obtained in this figure is particularly significant, since the metallic concentrations used are close to, if not within the percolation regime, a region where the mean field models totally fail to reproduce experimental results. Probably this regime is close to the limit of concentrations for which the RFSA approximation will be valid since we do not expect our calculations to be applicable in the percolation region.

The results of this and other recent paper[26] leads us to conclude that correlation effects and multiple scattering corrections make important contributions to the optical properties of cermet materials and need to be included in theories with predictive value. Equation (11) is restricted to spherical shapes in the long wave limit, but the formalism as presented here, can be extended to include other island shapes and to permit corrections for higher multipolar contributions to the field equation. These multipolar corrections may become important when the metal concentration increases to the point that island proximity is no longer compatible with the dipolar approximation. The proposed dispersion relations depend strongly on the model used for the zeroth order dielectric constant and the values used for the dielectric constant of the metallic grains. Other zeroth order models for the effective medium dielectric constant are being studied as possible starting points for the application of the dispersion relationships presented in this paper. These new calculations may permit the use of a longer and more realistic mean free path. Recently other models have been developed for $\bar{\varepsilon}_0$ that could help moderate the height and broaden the resonance with larger values for the mean free path.[30]

ACKNOWLEDGMENTS

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Figure Captions

FIG. 1. Real (N_1) and imaginary (N_2) parts of the index of refraction for Au/Al_2O_3(90% Al_2O_3) using Drude's model with an effective mean free path of 10A. Dashed line represent B calculation, solid-dashed is MG and dots are experimental data from H. Craighead.[21]

FIG. 2. Changes in the imaginary part of the dielectric constant due to the use of different depolarization factor (D) in the Maxwell Garnett equation for the dielectric constant of Ag/MgO (80% MgO).

FIG. 3. Comparison between the imaginary part of the dielectric constant as function of frequency for QSE the solid line; D the dashed line; and KK the solid-dashed line.

FIG. 4. Comparison between the experimentally obtained histogram [21] and the log-normal distribution function of metallic grains radiuses in a Ni/Al_2O_3 (20% Al_2O_3) cermet with a geometrical standard deviation σ_{ln} of 1.3 and an average grain size of 30A.

FIG. 5. Unaveraged and averaged QSE dielectric constant of Ag metallic grains for a grain distribution with average radius of 30A and a geometrical standard deviation of 1.3. Solid line is the unaveraged value and dashed line the averaged one.

FIG. 6. Imaginary part of the index of refraction for Au/Al_2O_3 (90% Al_2O_3). Interband contribution was taken from H. Ehrenreich et al.[18] Fig. 6(a) compares BD, BQ, and experimental data. [21] Fig. 6(b) compares MGD, MGQ, and experimental data. Dotted lines are used for D, solid line for QSE modek and dots for experimental data.

FIG. 7. Comparison between experimental data [21] and calculations for N_2. (a) Ag/MgO (80%MgO) cermet compared with B (dotted line) and FSA (solid line) model with L = 125A, and a restricted mean free path of 10A. (b) Au/Al_2O_3

(84%Al_2O_3) cermet compared with BD (dashed line), BQ (dotted line) and FSAQ (solid line) models with L = 80A, a = 30A, and restricted mean free path of 10A.

FIG. 8. Real N_1 and imaginary part N_2 of the refractive index is drawn for an Ag/MgO (80% MgO) cermet. Solid line is the RFSA calculation, dotted lines represent the MG model and dots are for the experimental results.[21]

(a) N_1 and N_2 using the D model with $\tau = 2.14 \times 10^{16}$s in both MG and RFSA. The radius of the islands is taken as 80A and L = 6 islands.

(b) N_1 and N_2 using QSE with a restricted mean free path of 10A for dielectric constant of the metallic grains. The island radius are taken to be 125A and L = 6 island.

FIG. 9. Real and imaginary part of the index of refraction for Ni/Al_2O_3, dotted line is MGD, solid line is RFSA and dots are experimental results.[21]

(a) 61% AL_2O_3 with $\tau = 5.6 \times 10^{16}$s, a = 60A, L = 4 islands. (b) 54% Al_2O_3 with $\tau = 3.5 \times 10^{16}$s, a = 75A and L = 4 islands.

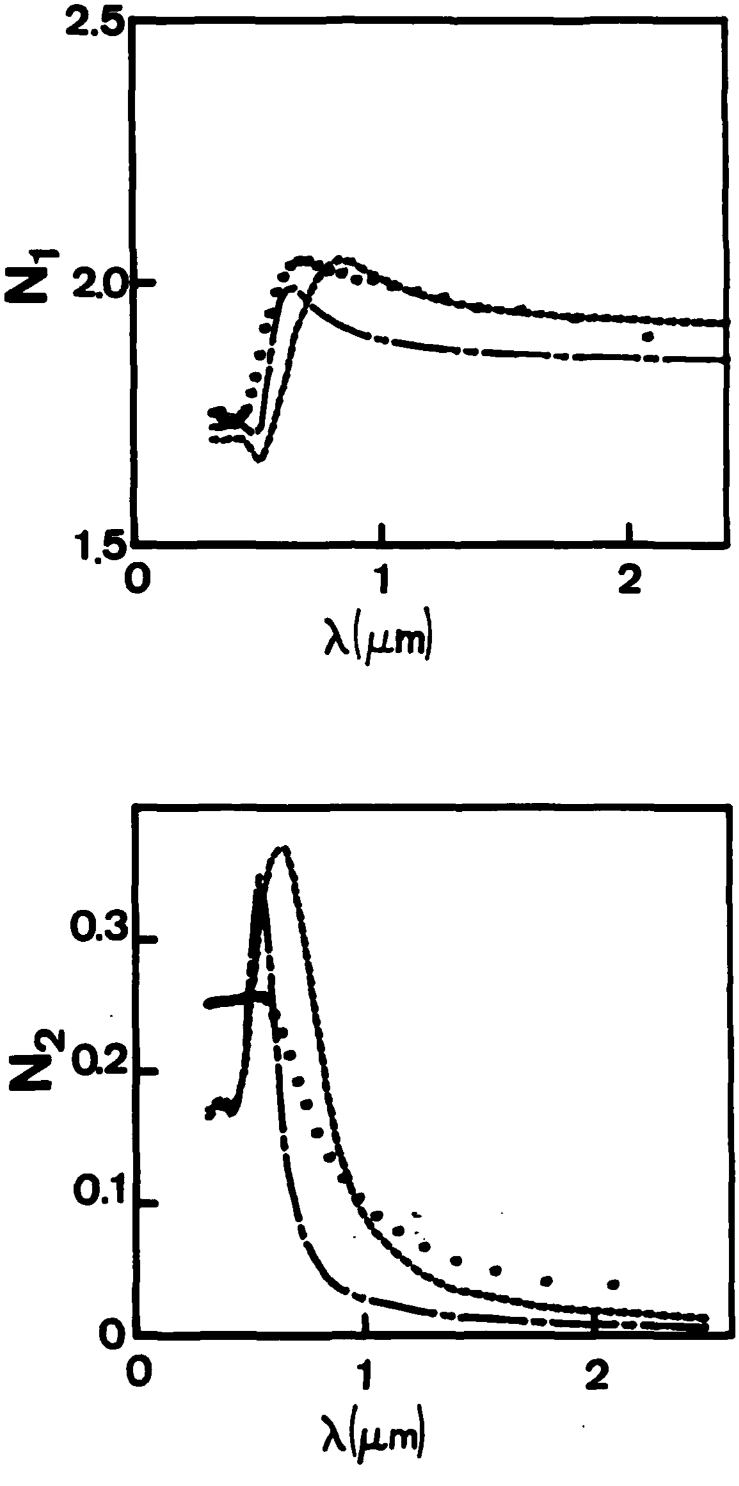


FIG 1 M. [illegible] G. F[illegible] A[illegible]

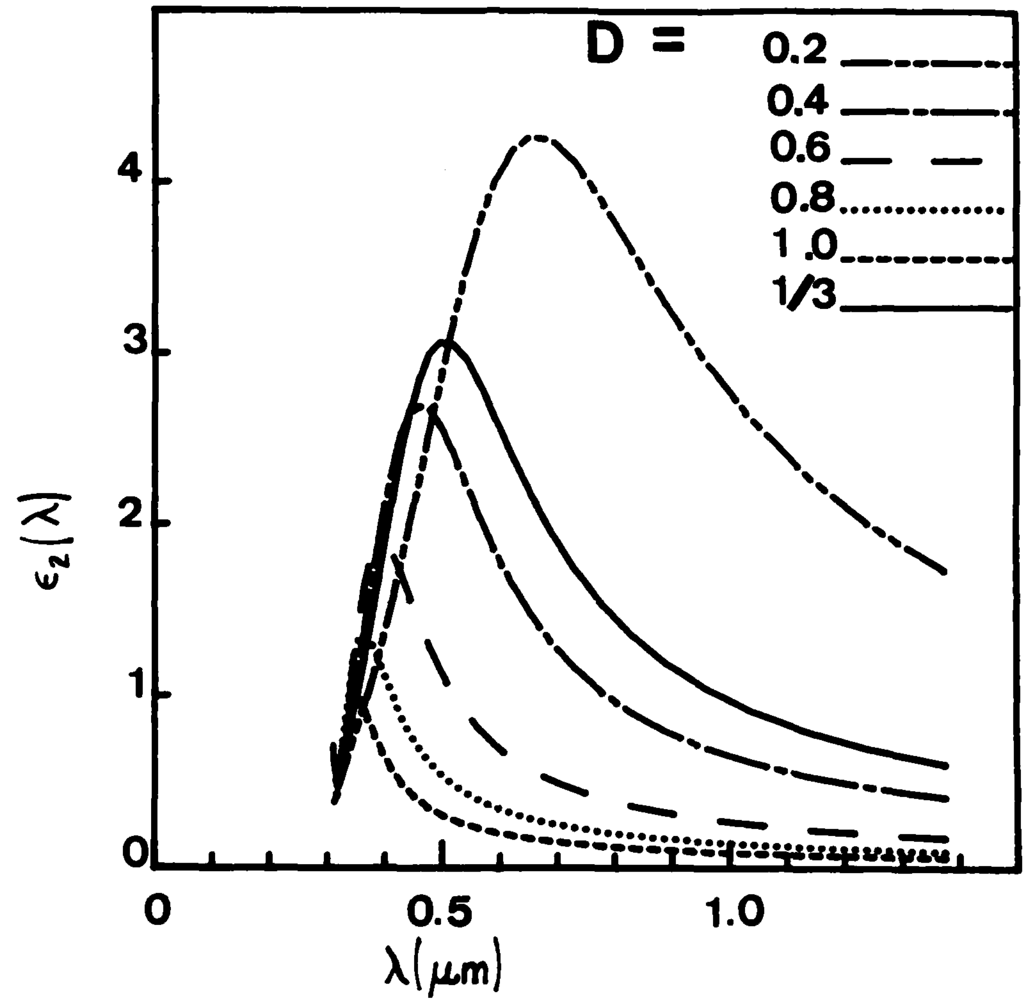


FIG. 2 M. GÓMEZ, [illegible] A [illegible]

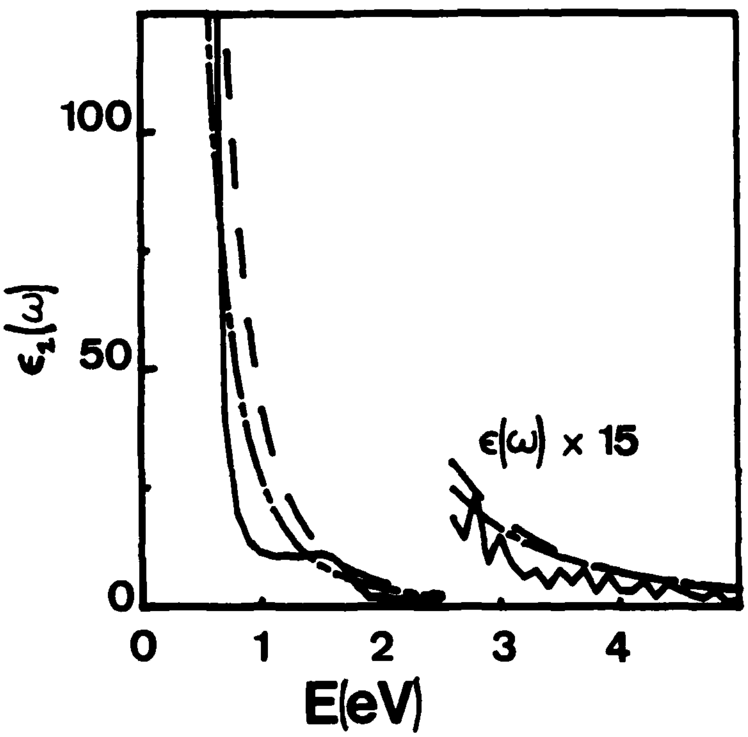


FIG 3, M GOMEZ, L. FONSECA, G. RODRIGUEZ A. VELAZQUEZ L. CR

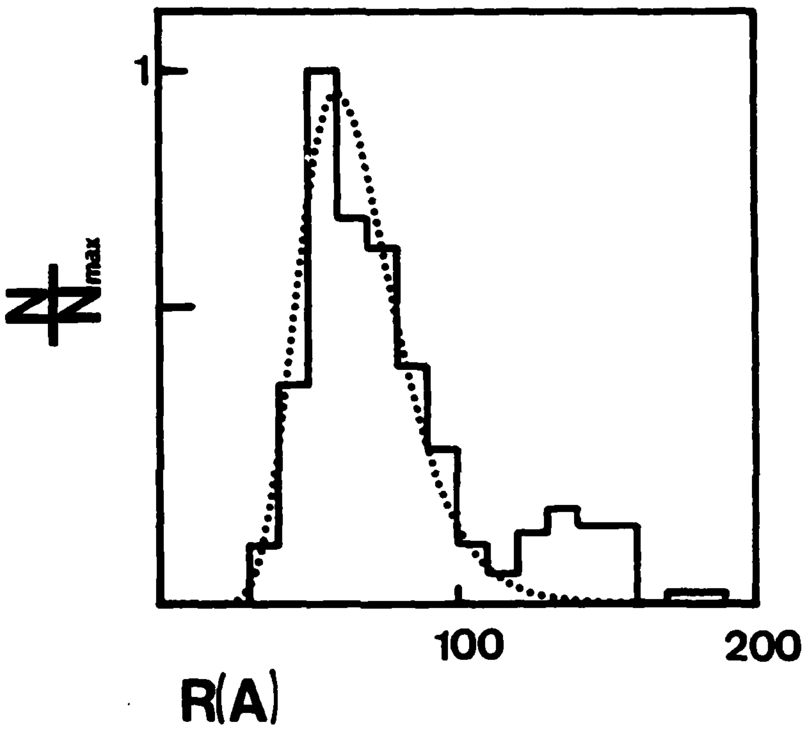
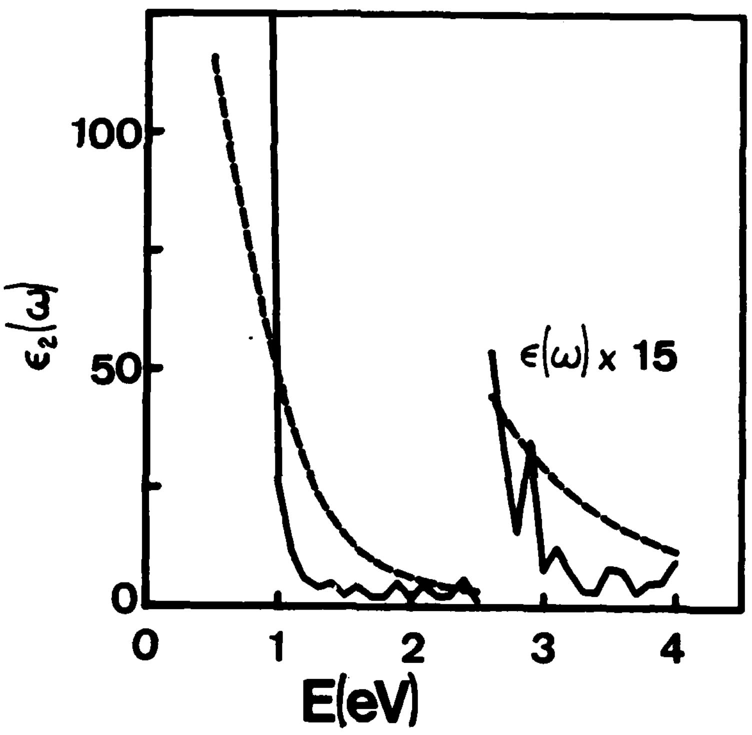


Fig 4 M. [illegible] [illegible] G. [illegible] [illegible] L. [illegible]



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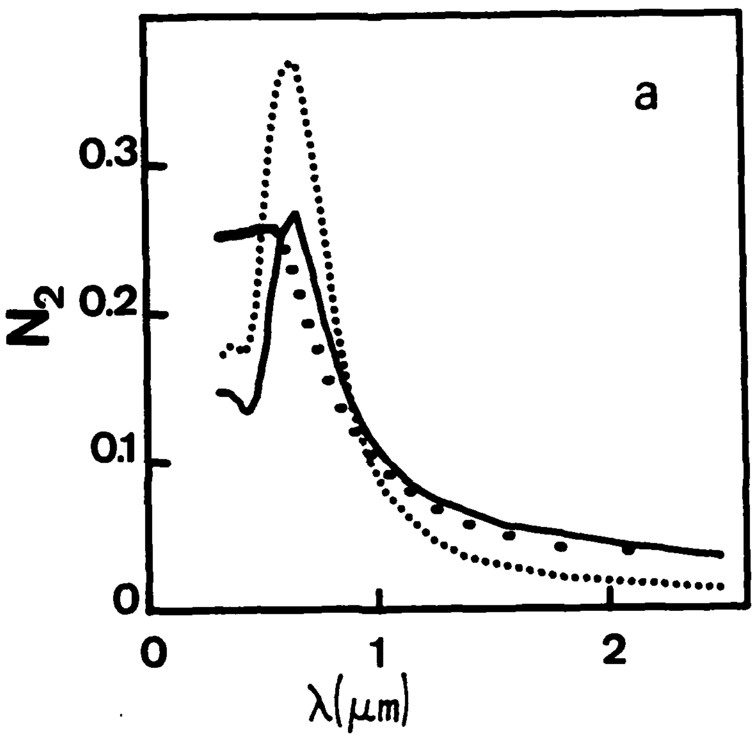

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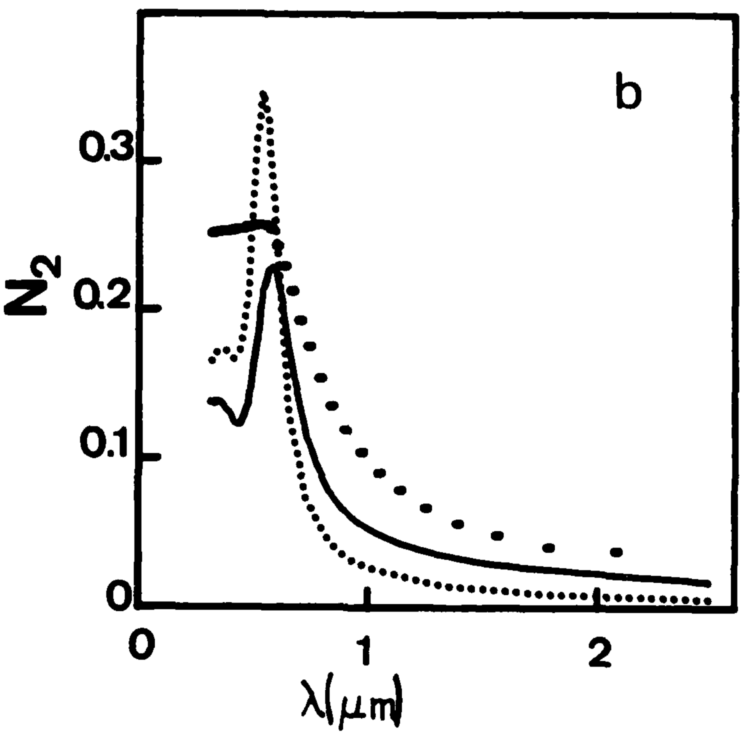

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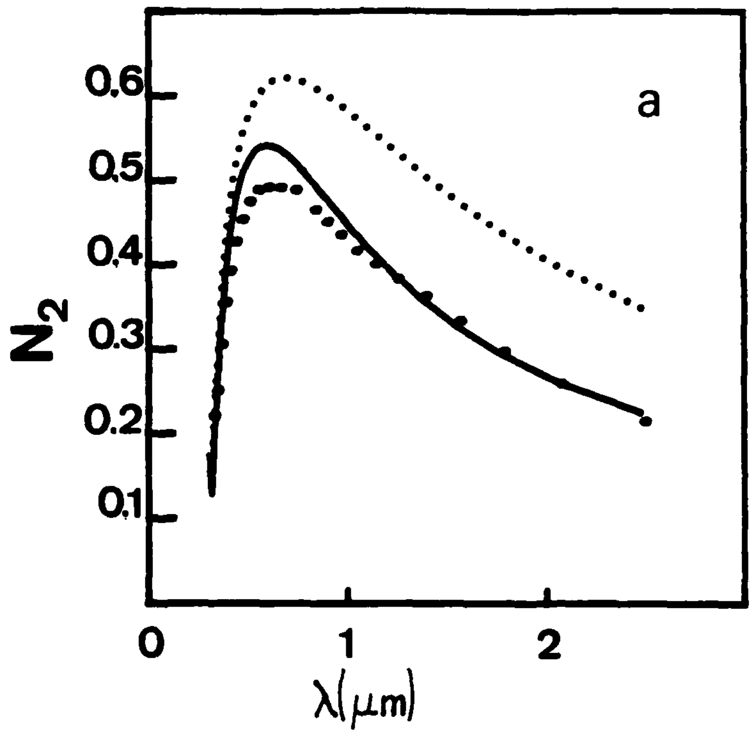
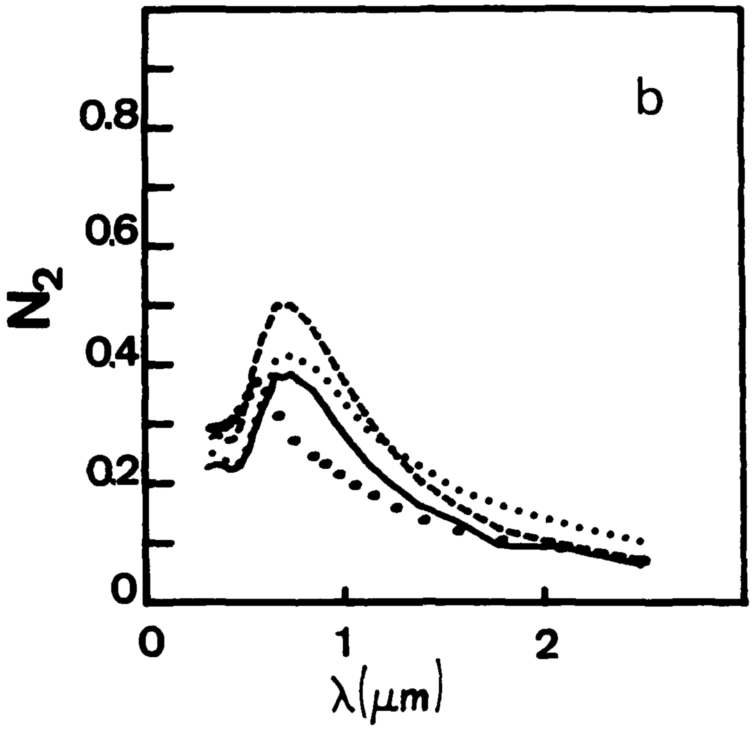


FIG. 7a M. Gomez L. Fonseca G. Rodriguez A. Velazquez L. Cruz



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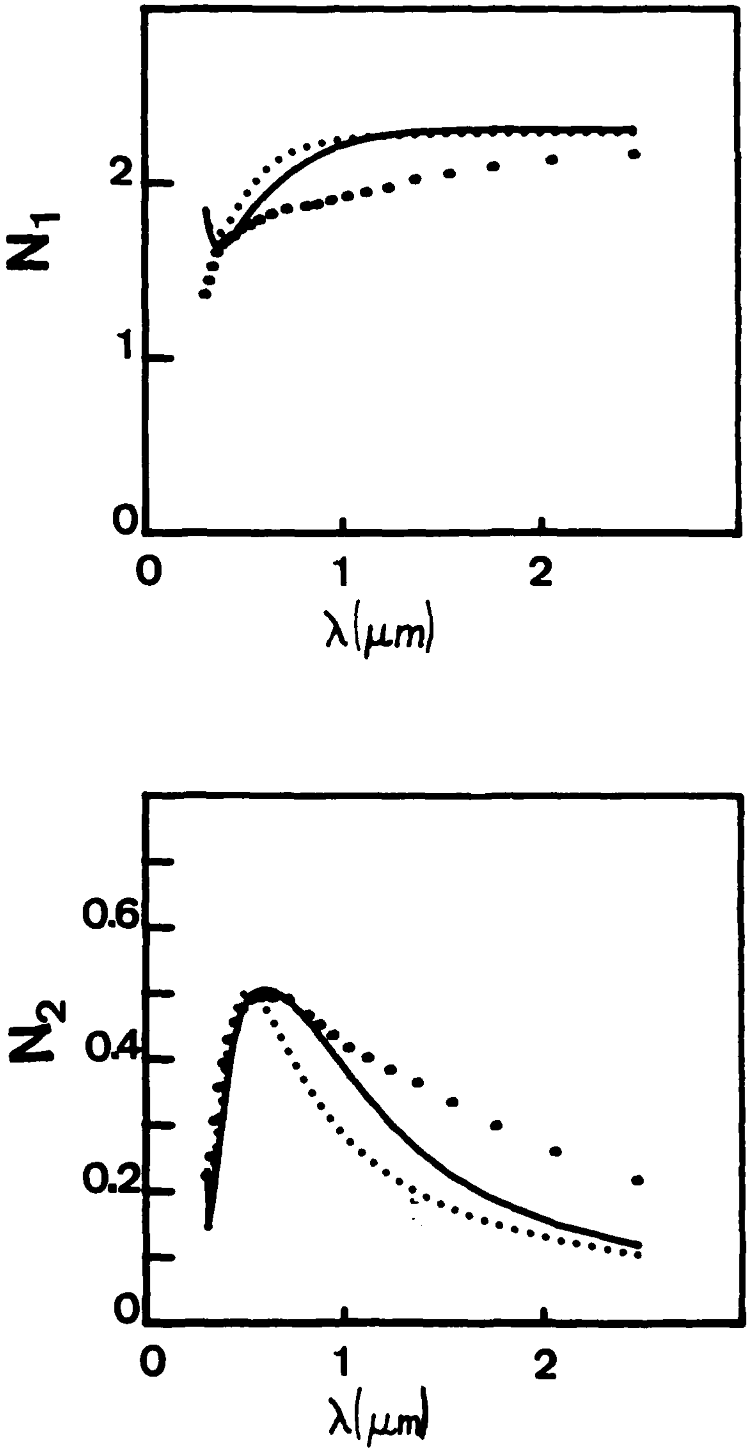

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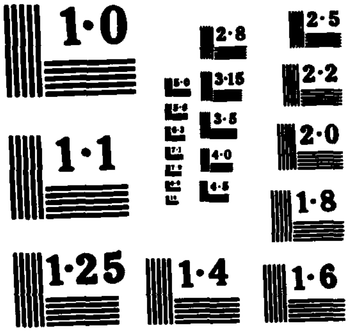

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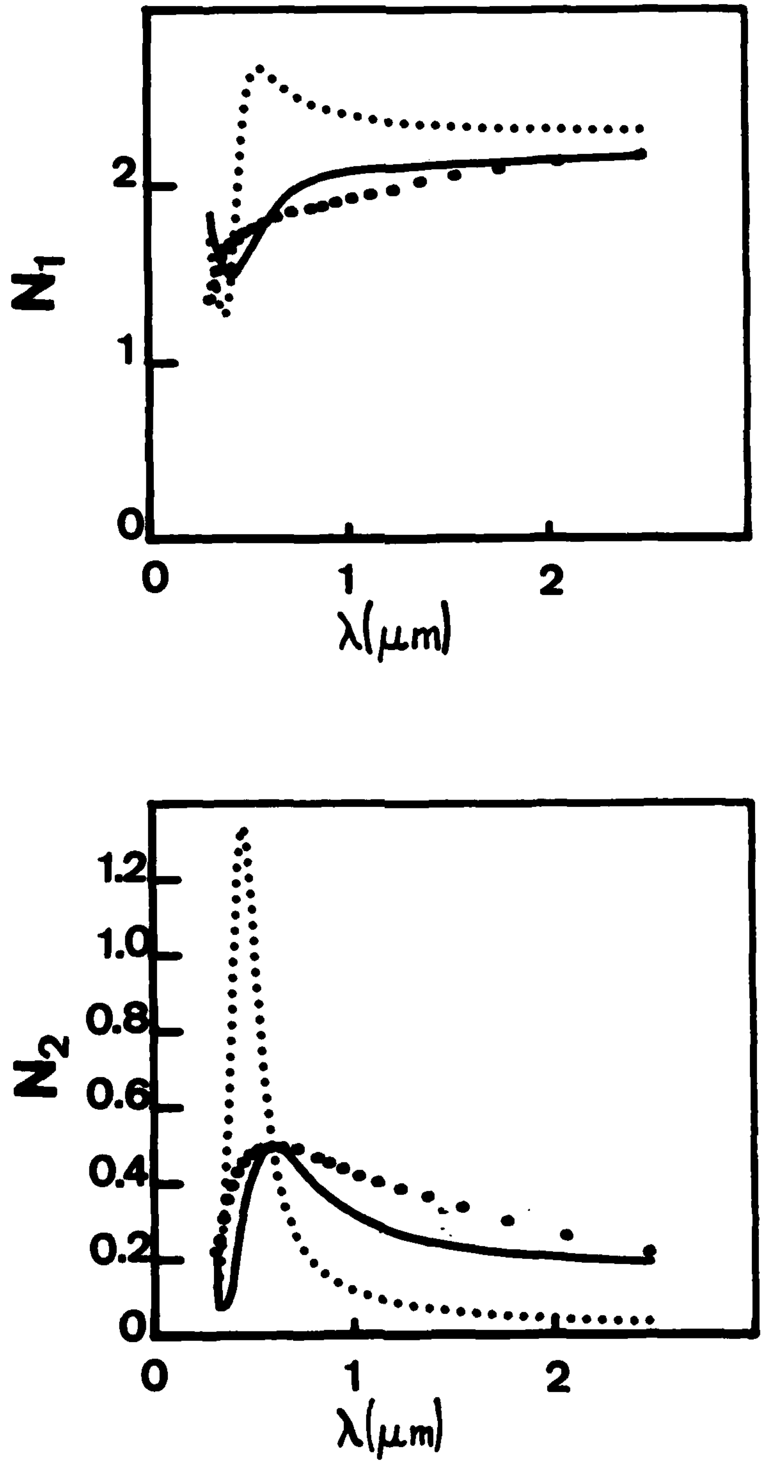

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FIG 3b M. G[illegible] L. F[illegible]SECA [illegible]

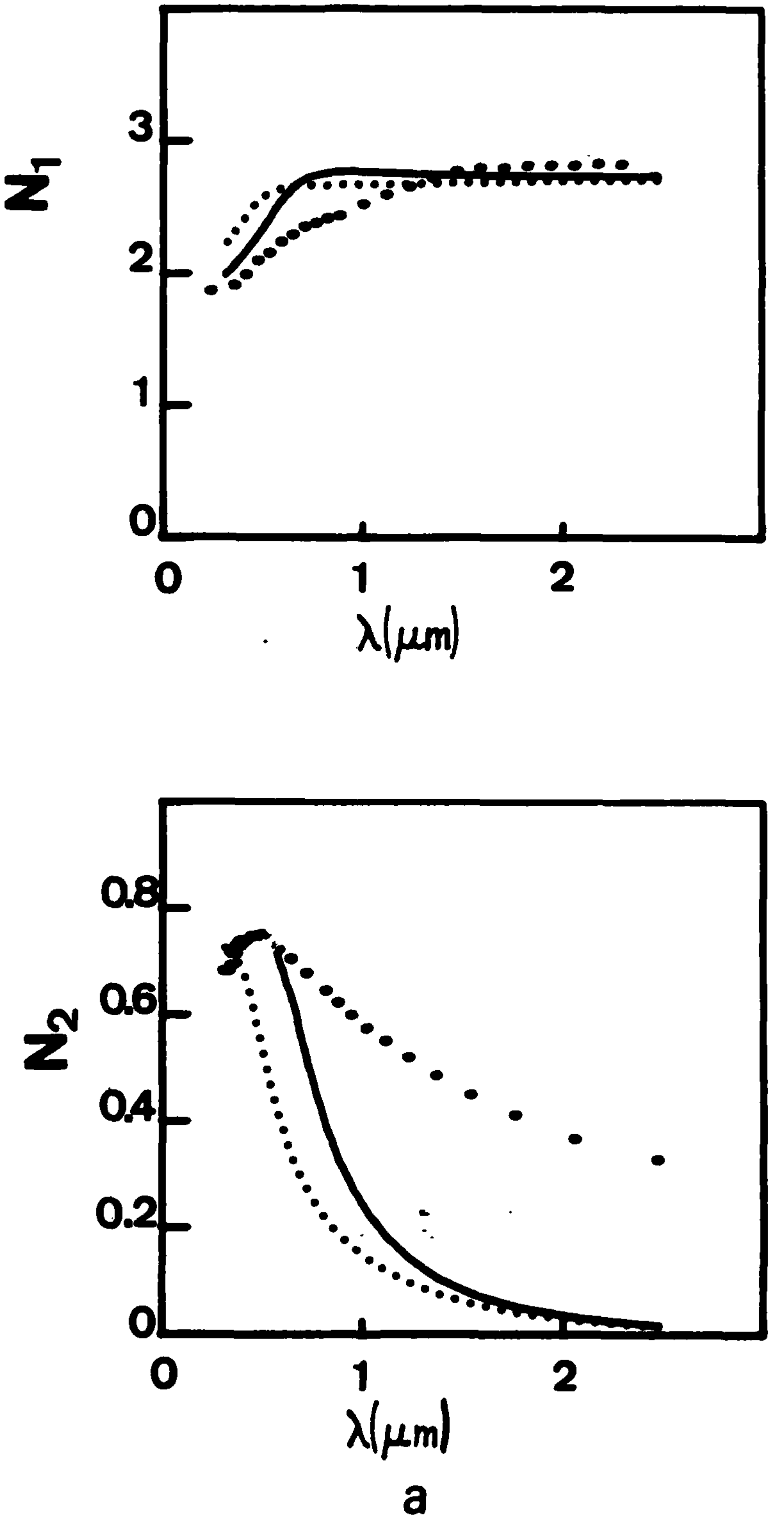
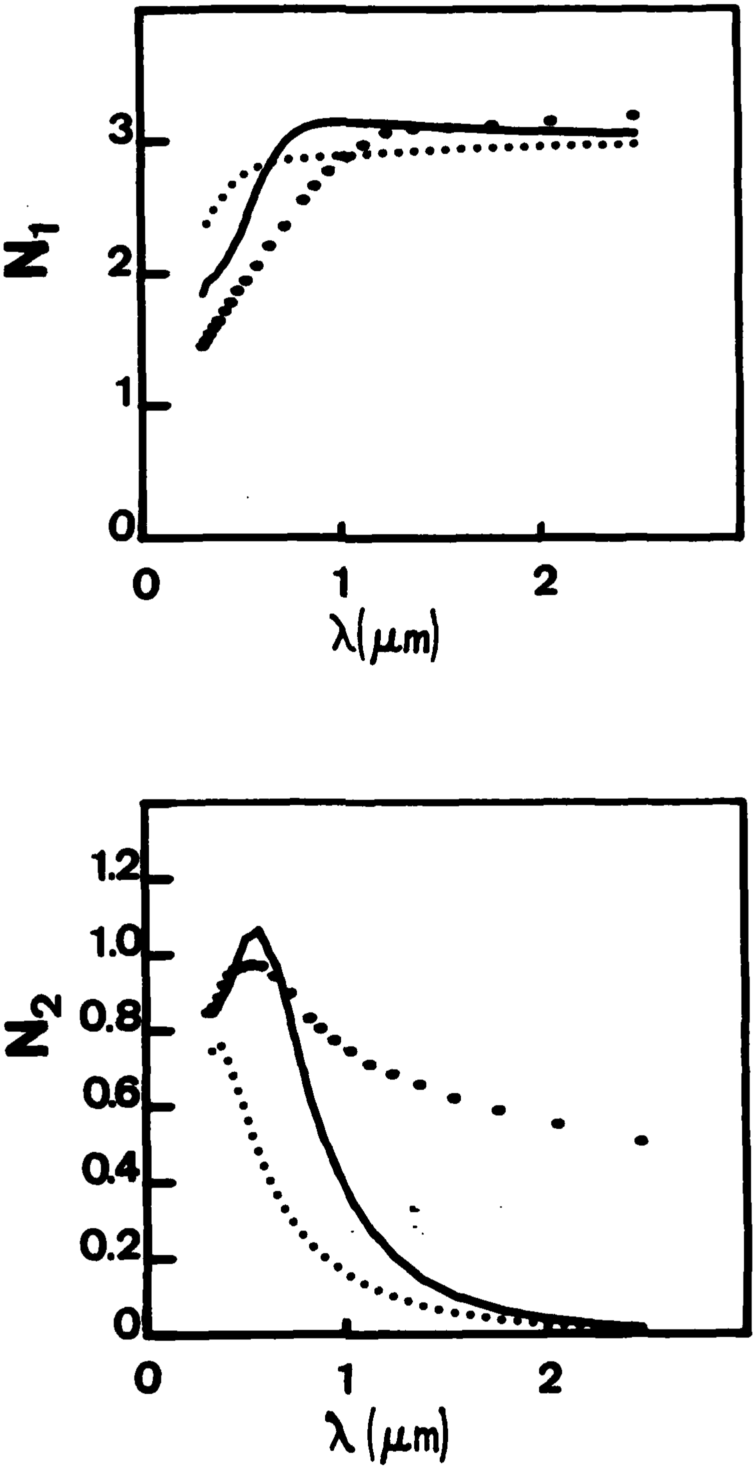


FIG 1a M. GOMEZ L. FONSECA G. RODRIGUEZ A. VELAZQUEZ L. CRUZ



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