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Optical extinction by spherical particles in an absorbing medium: Application to composite absorbing films

A.N. Lebedev[1,a], M. Gartz[2], U. Kreibig[2], and O. Stenzel[1]

[1] Technische Universität Chemnitz, Institut für Physik, 09107 Chemnitz, Germany
[2] RWTH Aachen, I. Physikalisches Institut IA, 52056 Aachen, Germany

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Abstract. The optical extinction rate of the particle embedded in an absorbing host is defined as a rate of local energy losses caused by the particle (absorption in the particle volume and scattering by the particle-matrix interface) referenced to the matrix background. The rate of scattering and absorption by the particle is calculated via integration of the appropriate Poynting vectors over the particle surface. The explicit expressions for the optical extinction and scattering rates by the spherical particle are derived. A heuristic approach to relate the local energy losses to the macroscopic extinction coefficient of the thin absorbing film with uniformly distributed embedded particles is presented. The method is applied to calculate the optical response of iron clusters embedded in a fullerite film. The calculated optical extinction coefficient of the system shows a good agreement with the overall features of experimentally obtained spectra.

PACS. 78.66.Vs Small particles – 78.20.Bh Theory, models, and numerical simulation

1 Introduction

The classical Mie theory [1] allows to calculate the linear optical response of a single homogeneous spherical particle embedded in a homogeneous non-absorbing medium. The spherical shape assumption is in many cases sufficiently near to the reality, especially in the case of nanoclusters, but can also be removed by introducing depolarization factors. An extension of the Mie theory has been presented taking into account the possible inhomogeneity of the clusters [2]. Some authors have thoroughly studied independent clusters [3], while the effects of the electromagnetic interaction between clusters in aggregates have been considered by Gerardy and Ausloos [4]. In all the above-mentioned works the matrix, in which the clusters are embedded, was supposed to be non-absorbing. Nevertheless, the effects of absorption in the matrix can significantly influence the extinction spectra of the real system cluster + matrix by changing not only the matrix properties but also the optical properties of the embedded particles. Attempts to generalize the Mie theory so that it would take into account the absorption in the matrix have been already made by various authors [5–8]. In works of Mundy et al. [5] and Chylek [6] the optical extinction of the particle was defined by analyzing the components of the net energy flow through the surface of a large integration sphere concentric with the particle embedded in an absorbing host. An attempt to generalize this method for the integration sphere of arbitrary size was made by Quinten and Rostalski [7]. In all these works, however, the extinction of the particle was a function of the size of the integration sphere whereas a physically meaningful extinction of the particle should depend only on the particle and the matrix properties. It is not clear also how the particle extinction is related to what is actually measured in experiments. An alternative approach to this problem was presented by Bohren and Gilra in [8]. They have utilized the derivation of extinction by a single particle in a non-absorbing medium given by van de Hulst [9] and extended it to the case of an absorbing matrix. This derivation considers the hypothetic experimental configuration where the extinction of the particle is defined as the difference in the energy received by a detector placed at a *large* distance from the particle with its receiving area perpendicular to the incident beam in two cases: with and without the particle interposed between light source and detector. The extinction cross-section obtained by Bohren and Gilra is a well-defined quantity that depends only on the particle and the host properties. Nevertheless, in contrast to a non-absorbing matrix where it is possible to measure optical properties on large, bulk samples, a strongly absorbing sample requires its size to be essentially limited in the direction of the light propagation. Hence, thin films with incorporated clusters are the systems we deal with. In this case a far-field approximation used in the derivation of Bohren and Gilra cannot be applied.

In our work we present a new approach to the calculation of the extinction spectra of separated spherical homogeneous particles immersed in an absorbing matrix.

[a] e-mail: a.lebedev@physik.tu-chemnitz.de

We define the extinction rate of the particle as the rate at which the energy is removed locally (*i.e.* in the particle volume) from the incident beam referenced to the matrix background. All energy rates are calculated via integration of the appropriate Poynting vectors over the surface of the particle. One of the distinctions of our method from the previous works [5–7] is that our integrating volume for the calculation of the energy losses coincides with the particle itself, whereas earlier authors used an integrating volume either of a large size or of a spherical shape, which makes it difficult to apply the theory to real systems. In contrast, our approach allows us a consideration of the host of essentially other geometry than a spherical one and of a limited size, for example thin films with embedded particles. We get a real rate at which the energy is removed *locally* from the incident beam in the volume of the particle, which provides a quantity for the extinction that depends only on the particle and the matrix properties. For thin films with embedded particles an effective extinction coefficient of the composite system is introduced and is approximated by the sum of extinction coefficients of the reference sample (pure matrix) and of the embedded clusters. The method can be directly applied to realistic cluster systems, and a comparison of the experimentally obtained optical extinction behavior of iron clusters embedded in a thin fullerite film with the calculated spectra will be given.

2 General

Let us consider a single particle, embedded in an absorbing film. The light incident on the surface of the sample will be attenuated first by reflection and scattering on the sample surface, then due to the absorption in the matrix, the absorption in the particle and the scattering from the interface particle-matrix. The rate at which the energy is removed from the incident beam defines the extinction of the system cluster + matrix. Here and further we assume the incident light beam to be already in the matrix. Thus we omit all energy losses caused by the scattering on the two surfaces of the sample and neglect an interaction of the particle with the back reflected light beams. The energy losses due to the surface scattering and reflection of the sample being significant in the case of high-reflecting thin films need a separate discussion (see, for example, [10,11]). The effects of the interaction of the secondary beams with the particle may be suppressed in the case of a strongly absorbing matrix. We assume also the incident wave in the matrix to be transversal, so we do not consider the possibility of optical excitation of longitudinal polarization waves both in the particle and in the matrix.

The total electromagnetic field in the matrix is presented as a linear superposition of the incident and of the scattered wave, that describes the influence of the cluster

$$\mathbf{E}_\mathrm{t} = \mathbf{E}_\mathrm{i} + \mathbf{E}_\mathrm{s}\,, \tag{1}$$

$$\mathbf{H}_\mathrm{t} = \mathbf{H}_\mathrm{i} + \mathbf{H}_\mathrm{s}\,. \tag{2}$$

In contrast to the case of a non-absorbing host the incident wave is attenuated while propagating in the matrix. In the following *the incident wave* implies this non-disturbed by the presence of the particle wave attenuated only by the absorption in the pure matrix.

The net energy flow through the surface of the particle gives the rate of energy absorption in the particle W_a and is calculated as the integral of the appropriate Poynting vector over the particle surface S:

$$W_\mathrm{a} = -\frac{1}{2}\mathrm{Re}\left(\oint\limits_S [\mathbf{E}_\mathrm{t} \times \mathbf{H}_\mathrm{t}^*] \cdot \overrightarrow{\mathrm{d}s}\right), \tag{3}$$

where $\overrightarrow{\mathrm{d}s}$ is in the direction of an outward normal to the surface, Re is the real part and the asterisk denotes the complex conjugate. In the same way, the energy rate of the scattering by the particle is given by

$$W_\mathrm{s} = \frac{1}{2}\mathrm{Re}\left(\oint\limits_S [\mathbf{E}_\mathrm{s} \times \mathbf{H}_\mathrm{s}^*] \cdot \overrightarrow{\mathrm{d}s}\right). \tag{4}$$

A part of this scattered energy will be then reabsorbed in the matrix, nevertheless, we count this energy as being scattered by the particle and hence as removed from the incident beam due to the presence of the particle.

In contrast to the approach of Bohren and Gilra, where the extinction by a particle is understood as the attenuation of light received by a remote detector, we define here the extinction rate of the particle W_p embedded in an absorbing matrix as a difference in the rate of local (*i.e.* in the volume of the particle) energy losses from the incident beam (absorption + scattering) compared to the rate of energy absorption in the same volume but filled with the matrix substance:

$$W_\mathrm{p} = W_\mathrm{a} + W_\mathrm{s} - W_\mathrm{i}\,, \tag{5}$$

where the energy that would be absorbed in the particle volume, if it were filled with the matrix substance W_i, is calculated as

$$W_\mathrm{i} = -\frac{1}{2}\mathrm{Re}\left(\oint\limits_S [\mathbf{E}_\mathrm{i} \times \mathbf{H}_\mathrm{i}^*] \cdot \overrightarrow{\mathrm{d}s}\right). \tag{6}$$

Expression (5) is similar to equation (13) in [5], but here we use it to define the extinction rate of the particle subsystem only. It is obvious that the extinction rate of the particle is not characteristic for the particle only, but also for the matrix. So, the extinction rate W_p of the particle can be in some cases negative, for example for voids or dielectric particles in an absorbing host, but the total extinction rate of the system particle + matrix given by the sum of W_a and W_s is always non-negative. Substituting (3, 4) and (6) in equation (5) we get

$$W_\mathrm{p} = -\frac{1}{2}\mathrm{Re}\left(\oint\limits_S \{[\mathbf{E}_\mathrm{i} \times \mathbf{H}_\mathrm{s}^*] + [\mathbf{E}_\mathrm{s} \times \mathbf{H}_\mathrm{i}^*]\} \cdot \overrightarrow{\mathrm{d}s}\right). \tag{7}$$

If one wants to get the absorption part $W_{\rm a}$ of the particle extinction rate, it can be done by calculating $W_{\rm i}$ and $W_{\rm s}$ and using equation (5). It must be kept in mind, that in equations (3, 4) and (7) all the integrals are taken over the surface of the particle.

For the particle of spherical shape the exact analytical solution of the scattering problem can be found. To find the total field in the matrix, we proceed in a standard way [1]. The incident wave is assumed to be already in the matrix, the scattered field is also calculated only in the sample volume.

In a spherical coordinate system with the origin in the particle center incident and scattered waves and the electromagnetic fields in the particle volume can be expanded in series of spherical wave vector functions $\mathbf{m}_{qp}$ and $\mathbf{n}_{qp}$ (see Appendix A for the definition and the principal properties):

$$\mathbf{E}_{\rm i} = E_0 \sum_{q=1}^{\infty} \sum_{p=-q}^{q} a_{qp}\mathbf{m}_{qp}^{(1)} + b_{qp}\mathbf{n}_{qp}^{(1)}\,, \tag{8}$$

$$\mathbf{H}_{\rm i} = H_0 \sum_{q=1}^{\infty} \sum_{p=-q}^{q} b_{qp}\mathbf{m}_{qp}^{(1)} + a_{qp}\mathbf{n}_{qp}^{(1)}\,, \tag{9}$$

$$\mathbf{E}_{\rm s} = E_0 \sum_{q=1}^{\infty} \sum_{p=-q}^{q} c_{qp}\mathbf{m}_{qp}^{(3)} + d_{qp}\mathbf{n}_{qp}^{(3)}\,, \tag{10}$$

$$\mathbf{H}_{\rm s} = H_0 \sum_{q=1}^{\infty} \sum_{p=-q}^{q} d_{qp}\mathbf{m}_{qp}^{(3)} + c_{qp}\mathbf{n}_{qp}^{(3)}\,, \tag{11}$$

where E_0 is the amplitude of electric field of the incident wave (only incident light in the pure matrix, not disturbed by the presence of the particle) in the center of the coordinate system. The superscripts 1 or 3 determine which of spherical Bessel functions [12] $j_q(kr)$ or $h_q^{(1)}(kr)$ should be used in the radial part of the generating function for the spherical wave vector functions. (This choice depends on the required behavior of the light field at zero or at infinity.) $k = \frac{\omega}{c} n_{\rm m}$ for a matrix with the complex index of refraction $n_{\rm m}$. Using the properties of the spherical wave vector functions (see Eqs. (A.3) and (A.7) in Appendix A) and the Maxwell equations, the amplitude of the magnetic field becomes $H_0 = \frac{ck}{i\omega\mu} E_0$, where μ is the magnetic permeability in the matrix. We do not provide here expansions for the fields in the particle, because we will use them only to formulate the boundary conditions on the particle surface. Expressions (8-11) are formally identical to those for a non-absorbing matrix. In contrast to the empirically introduced radial dependence of the expansion coefficients in [7], the attenuation of waves caused by absorption in the matrix is *completely* described by using the spherical Bessel functions of a complex variable in the expressions for the partial waves $\mathbf{m}_q$ and $\mathbf{n}_q$. Coefficients c_{qp} and d_{qp} are to be found satisfying the boundary conditions on the surface of the particle and can be calculated [1] (see also [13], p. 99) as

$$c_{qp} = \Gamma_q a_{qp}\,, \tag{12}$$

$$d_{qp} = \Delta_q b_{qp}\,, \tag{13}$$

where Γ_q and Δ_q are the magnetic and electrical susceptibilities of the q-th order. For a spherical particle of radius R made of a substance with the refractive index $n_{\rm p}$, embedded in a matrix with the refractive index $n_{\rm m}$, they are defined as

$$\Delta_q = -\frac{\psi_q(\rho)\psi_q'(m\rho) - m\psi_q(m\rho)\psi_q'(\rho)}{\xi_q(\rho)\psi_q'(m\rho) - m\psi_q(m\rho)\xi_q'(\rho)}\,, \tag{14}$$

$$\Gamma_q = -\frac{m\psi_q(\rho)\psi_q'(m\rho) - \psi_q(m\rho)\psi_q'(\rho)}{m\xi_q(\rho)\psi_q'(m\rho) - \psi_q(m\rho)\xi_q'(\rho)}\,, \tag{15}$$

where $\psi_q(\rho) = \rho j_q(\rho)$ and $\xi_q(\rho) = \rho h_q^{(1)}(\rho)$ are Riccati-Bessel functions [12], the prime stands for a derivative with respect to the argument, $m = n_{\rm p}/n_{\rm m}$ is the complex relative index of refraction in the particle, and $\rho = kR$ is the complex size parameter in the matrix. It is assumed that the magnetic permeabilities of the particle and of the medium are equal to the permeability of vacuum. Having used the orthogonality of the spherical harmonics on a surface of spherical particle [14] we get

$$\oint_S \left[\mathbf{m}_{qp}^{(1)} \times \mathbf{n}_{lm}^{(1)*}\right] \cdot \overrightarrow{\mathrm{d}s} = \frac{\psi_q(\rho)\psi_q'^*(\rho)}{|\rho|^2}\delta_{ql}\delta_{pm}\,, \tag{16}$$

$$\oint_S \left[\mathbf{m}_{qp}^{(3)} \times \mathbf{n}_{lm}^{(1)*}\right] \cdot \overrightarrow{\mathrm{d}s} = \frac{\xi_q(\rho)\psi_q'^*(\rho)}{|\rho|^2}\delta_{ql}\delta_{pm}\,, \tag{17}$$

$$\oint_S \left[\mathbf{m}_{qp}^{(1)} \times \mathbf{m}_{lm}^{(1)*}\right] \cdot \overrightarrow{\mathrm{d}s} = \oint_S \left[\mathbf{n}_{qp}^{(1)} \times \mathbf{n}_{lm}^{(1)*}\right] \cdot \overrightarrow{\mathrm{d}s} = 0\,, \tag{18}$$

where $\overrightarrow{\mathrm{d}s} = R\sin\theta \mathrm{d}\theta\mathrm{d}\varphi\frac{\mathbf{r}}{r}$, δ_{ql} is a delta-function. It is easy to get similar expressions for the other vector products ($\mathbf{m}_{qp}^{(3)} \times \mathbf{n}_{lm}^{(3)}$ and so on).

Now substituting expansions (8-11, 12, 13) in equations (4, 7) and integrating over the surface of the particle with using equations (16-18), one obtains

$$\begin{aligned} W_{\rm s} = \frac{I_0}{|k|^2} \sum_{q=1}^{\infty} \sum_{p=-q}^{q} \Big\{ & \left(|a_{qp}|^2|\Gamma_q|^2 + |b_{qp}|^2|\Delta_q|^2\right) \\ & \times \mathrm{Im}\left(-\xi_q(\rho)\xi_q'^*(\rho)\right) \\ & - \frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\left(|a_{qp}|^2|\Gamma_q|^2 - |b_{qp}|^2|\Delta_q|^2\right) \\ & \times \mathrm{Re}\left(-\xi_q(\rho)\xi_q'^*(\rho)\right)\Big\}\,, \end{aligned} \tag{19}$$

$$W_{\rm p} = \frac{I_0}{|k|^2}\sum_{q=1}^{\infty}\sum_{p=-q}^{q}\left\{\mathrm{Re}\left(|a_{qp}|^2\Gamma_q + |b_{qp}|^2\Delta_q\right)\right.$$
$$\times\mathrm{Im}\left(\xi_q(\rho)\psi_q'^*(\rho) - \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$+\mathrm{Im}(|a_{qp}|^2\Gamma_q + |b_{qp}|^2\Delta_q)$$
$$\times\mathrm{Re}\left(\xi_q(\rho)\psi_q'^*(\rho) - \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$-\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\mathrm{Re}(|a_{qp}|^2\Gamma_q - |b_{qp}|^2\Delta_q)$$
$$\times\mathrm{Re}\left(\xi_q(\rho)\psi_q'^*(\rho) + \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$+\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\mathrm{Im}(|a_{qp}|^2\Gamma_q - |b_{qp}|^2\Delta_q)$$
$$\left.\times\,\mathrm{Im}\left(\xi_q(\rho)\psi_q'^*(\rho) + \xi_q'(\rho)\psi_q^*(\rho)\right)\right\}\,, \qquad (20)$$

where I_0 is the intensity of the incident (non-disturbed by the particle) light in the center of the coordinate system.

We define the extinction cross-section $C_{\rm p}$ of one particle embedded in the matrix as

$$C_{\rm p} = W_{\rm p}/I_0\,. \qquad (21)$$

Such a normalization of the extinction cross-section provides independence of its value from the particle position in the sample.

The expressions for extinction and scattering rates in the case of a non-absorbing matrix follow directly from (19, 20) by setting $\mathrm{Im}(k) = 0$, and using properties of the Riccati-Bessel functions of a real argument [12].

3 Applications

3.1 Plane linearly polarized incident wave

Up to this moment we have not fixed the type of incident wave. We shall consider now the most simple and useful case of a plane monochromatic linearly polarized wave under normal incidence on the surface of the sample (the direction of propagation coincides with the positive direction of the z-axis of the coordinate system with origin in the center of the particle)

$$\mathbf{E}_{\rm i} = \mathbf{e}_x E_0 e^{i(\mathbf{kr}-\omega t)}\,, \qquad (22)$$

where the electrical field is x-polarized, E_0 is its amplitude in the center of the coordinate system and $\mathbf{k} = (0, 0, k)$ the complex wave vector of the incident wave in the matrix.

The normal incidence makes sure that the incident wave passing through the sample is a plane homogeneous wave. As before, we assume the incident field to be already in the matrix. The expansion coefficients for such an incident wave can be found by using the orthogonality of the spherical harmonics and the expansion (10.1.47) in [12],

$$a_{qp} = i^{q+1}[\pi(2q+1)]^{\frac{1}{2}}\delta_{p,\pm1}\,;\quad b_{qp} = pa_{qp}\,. \qquad (23)$$

Substituting (23) in equations (19-20), we get

$$W_{\rm s} = I_0\frac{2\pi}{|k|^2}\sum_{q=1}^{\infty}(2q+1)\left\{\left(|\Gamma_q|^2 + |\Delta_q|^2\right)\right.$$
$$\times\mathrm{Im}\left(-\xi_q(\rho)\xi_q'^*(\rho)\right)$$
$$-\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\left(|\Gamma_q|^2 - |\Delta_q|^2\right)$$
$$\left.\times\,\mathrm{Re}\left(-\xi_q(\rho)\xi_q'^*(\rho)\right)\right\}\,, \qquad (24)$$

$$W_{\rm p} = I_0\frac{2\pi}{|k|^2}\sum_{q=1}^{\infty}(2q+1)\left\{\mathrm{Re}\left(\Gamma_q + \Delta_q\right)\right.$$
$$\times\mathrm{Im}\left(\xi_q(\rho)\psi_q'^*(\rho) - \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$+\mathrm{Im}(\Gamma_q + \Delta_q)\mathrm{Re}\left(\xi_q(\rho)\psi_q'^*(\rho) - \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$-\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\mathrm{Re}(\Gamma_q - \Delta_q)$$
$$\times\mathrm{Re}\left(\xi_q(\rho)\psi_q'^*(\rho) + \xi_q'(\rho)\psi_q^*(\rho)\right)$$
$$+\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}\mathrm{Im}(\Gamma_q - \Delta_q)$$
$$\left.\times\,\mathrm{Im}\left(\xi_q(\rho)\psi_q'^*(\rho) + \xi_q'(\rho)\psi_q^*(\rho)\right)\right\}\,. \qquad (25)$$

The expression for $W_{\rm i}$ can be obtained from equation (24) by changing the sign to the opposite, setting both susceptibilities $\Gamma_q = \Delta_q = 1$ and exchanging $\xi_q \to \psi_q$ and $\xi_q' \to \psi_q'$:

$$W_{\rm i} = I_0\frac{4\pi}{|k|^2}\sum_{q=1}^{\infty}(2q+1)\mathrm{Im}\left(\xi_q(\rho)\xi_q'^*(\rho)\right)\,. \qquad (26)$$

3.2 Film with embedded particles

The derivation of the observable extinction given by Bohren and Gilra [8] cannot be applied to consider a thin absorbing film with embedded particles because it would require the construction of the scattered fields outside the film (to calculate the net energy flow through the surface of remote detector). The expression for extinction rate obtained in the previous section gives the rate at which the energy is removed from the incident beam in the volume of the particle. This declares a concept of a local extinction, whose relation to the observed physical quantities must be explained here.

We consider here a film made from a homogeneous absorbing substance with embedded spherical particles. The particles are assumed to be uniformly distributed over the film volume. In an experiment a remote detector registers the total extinction of the sample as the difference in two cases: with and without the film interposed between detector and a light source. Here we attempt to obtain this quantity heuristically via constructing an intensity of the

transmitted light after passing the sample. We omit all energy losses due to the reflection on the film surfaces and neglect the processes of multiple scattering, *i.e.* the energy scattered by every particle is considered as removed from the incident beam. So we can define the transmitted light as the plane wave, that propagates in the forward direction and whose amplitude is attenuated both by absorption in the matrix and by removing the energy via particle absorption and scattering.

Let the incident wave propagate in the z-direction. In a differential layer between z and $z + \mathrm{d}z$ the energy is removed from the incident beam (let I be the intensity of the incident beam at z) via extinction by particles and through absorption in the matrix. The absence of the matrix in the volume of particles is accounted for in the definition of the extinction rate through subtraction of the matrix background. If the number density of particles in the film is N, then the number of particles in the layer volume per unit lateral area is $N\mathrm{d}z$. Considering a differential layer makes the energy locally removed from the incident beam by particles $IC_{\mathrm{p}}N\mathrm{d}z$ per unit lateral area additive with the absorption of the pure matrix $I\alpha_0\mathrm{d}z$, where α_0 is the absorption coefficient of the pure matrix. The total intensity loss in the incident beam may be written as

$$\mathrm{d}I = -I\alpha_0\mathrm{d}z - IC_{\mathrm{p}}N\mathrm{d}z\,, \tag{27}$$

which gives after an integration over the film thickness

$$I_{\mathrm{out}} = I_{\mathrm{in}} \exp\left(-\alpha d\right)\,, \tag{28}$$

where I_{out} is the intensity of the transmitted light after passing the sample and I_{in} the intensity of the non-attenuated incident light after entering but before passing the film. d is the *total* film thickness and α the effective extinction coefficient of the system matrix + particles given by

$$\alpha = \alpha_0 + NC_{\mathrm{p}}\,. \tag{29}$$

It is intuitively clear that a consideration of a plane transmitted wave in a layer-after-layer manner requires a large number of clusters to be present in a differential layer; on the other hand, considering this layer as a differential one requires $\alpha\mathrm{d}z \ll 1$ ($\alpha D \ll 1$, where D is the particle diameter would suffice). So for strong absorbing media, where the intensity of transmitted light can be drastically attenuated already after passing through a distance less than a particle diameter, the exactness of the method presented here is questionable. Nevertheless, the qualitative description of the extinction spectral features can be obtained, as is shown in the next section.

If the diameter of clusters is small compared to the light wavelength, a quasistatic (electrostatic) approximation is widely used. To check whether it may also be applied in the case of an absorbing medium, we have calculated the extinction of iron clusters with a diameter of 2 nm embedded in a fullerite matrix using the model presented here and the expression for the particle extinction cross-section $C_{\mathrm{p}}^{\mathrm{stat}}$ in the quasistatic approximation,

$$C_{\mathrm{p}}^{\mathrm{stat}} = 4\pi R^3\,\mathrm{Re}(k)\,\mathrm{Im}\left(\frac{\epsilon_{\mathrm{p}} - \epsilon_{\mathrm{m}}}{\epsilon_{\mathrm{p}} + 2\epsilon_{\mathrm{m}}}\right)\,, \tag{30}$$

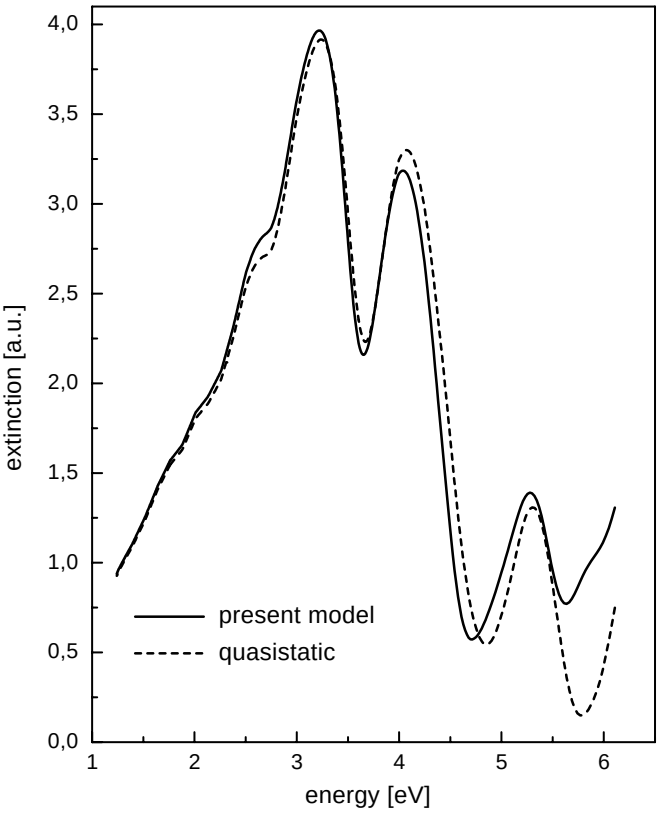

Fig. 1. Extinction coefficient (NC_{p}) of iron clusters with *a diameter of 2 nm* in a fullerite matrix calculated using the present model and the quasistatic approximation (30). The volume filling factor of iron was set to 5%.

where the *complex* dielectric functions of clusters ϵ_{p} (Fe) and of the matrix ϵ_{m} (C_{60}) are used as suggested in [15]. Equation (30) differs from the usual expression for cluster extinction in the electrostatic approximation (see Chapt. 5 in [13], for example) only in using a real part of the complex wave number k in the matrix. A comparison of the extinction (NC_{p}, the number density N corresponds to the volume filling factor of iron of about 5%) coefficient spectra calculated using (25) and (30), respectively, is presented in Figure 1. A great divergence is seen only at higher energies, which makes the use of (30) justified for at least a qualitative description of cluster extinction spectra at low frequencies (high wavelength).

Here a special computer program was written to calculate the optical extinction and scattering rates in equations (24-26). The numerical calculation of the spherical Bessel functions of a complex argument made no difficulties under the current state of computing technique and with using the algorithms described in [16] and [17].

4 Experimental

The above theory was tested by applying equation (28) to novel experiments on the system of Fe clusters embedded in a solid C_{60} film. A new laser ablation/evaporation source produced the Fe clusters (average diameter of about 20 nm, determined from TEM pictures of the films) in a continuous UHV beam. The source is driven by a high power CO_2 laser in a continuous wave mode. Details of the experimental setup are to be published soon. The sample preparation and the measurements were done at UHV conditions. Fullerite was evaporated with a rate of 0.04 nm/s from an additional furnace. A special manipulator allows the co-deposition of nanoparticles from the beam and the host material on a quartz substrate, whereas a part of the substrate is shielded from the cluster beam and is covered by the pure matrix substance only to provide a reference. The optical equipment enables the *in situ* measurement of the transmission in the UV and VIS range. The thickness d of the sample is approximately 150 nm, measured by a quartz balance. The thickness of the reference is then $d-\delta d$, where δd takes into account the thickness difference between the reference and the sample due to the Fe clusters embedded in the sample and absent in the reference. The transmission of the pure C_{60} layer (reference) can be described as

$$\frac{I_\mathrm{r}}{I_\mathrm{in}} = \exp\left[-\alpha_0(d-\delta d)\right] , \tag{31}$$

where I_r is the light intensity after passing the reference and I_in the intensity of the non-attenuated incident light. α_0 is the absorption coefficient of fullerite as mentioned before. Similarly, the transmission of the sample (Fe clusters in C_{60}) is given by

$$\frac{I_\mathrm{out}}{I_\mathrm{in}} = \exp\left[-(\alpha_0 + NC_\mathrm{p})d\right] , \tag{32}$$

where I_out is the light intensity after passing the sample.

This yields the following equation for the effective extinction coefficient of the cluster part only:

$$NC_\mathrm{p}d = -\log\frac{I_\mathrm{out}}{I_\mathrm{r}} - \alpha_0\delta d\,. \tag{33}$$

Both transmissions were measured simultaneously and the transmission of the sample was referred to the transmission of the reference, *i.e.* the first term in the right-hand side of equation (33) is what the experiment actually gives as the output. It can be seen from equation (33) that the measured signal should be corrected to take into account the thickness difference between the reference and the sample. For the present evaluation δd was obtained from the experimentally determined filling factor (5% in the experiment) of the Fe clusters. Figure 2 shows the uncorrected and the corrected output of the experiment. The difference between both curves is also plotted in Figure 2. The comparison of the calculated ($NC_\mathrm{p}d$, the number density was calculated using the volume filling factor and the average cluster size) and measured (corrected) spectra is plotted in Figure 3. There is the cluster extinction coefficient calculated using the quasistatic approximation also placed in the same figure. As the figure shows, the divergence between the present model and the quasistatic one is rather great in this case of clusters of 20 nm in diameter, but the qualitative structure of the spectrum can still be seen.

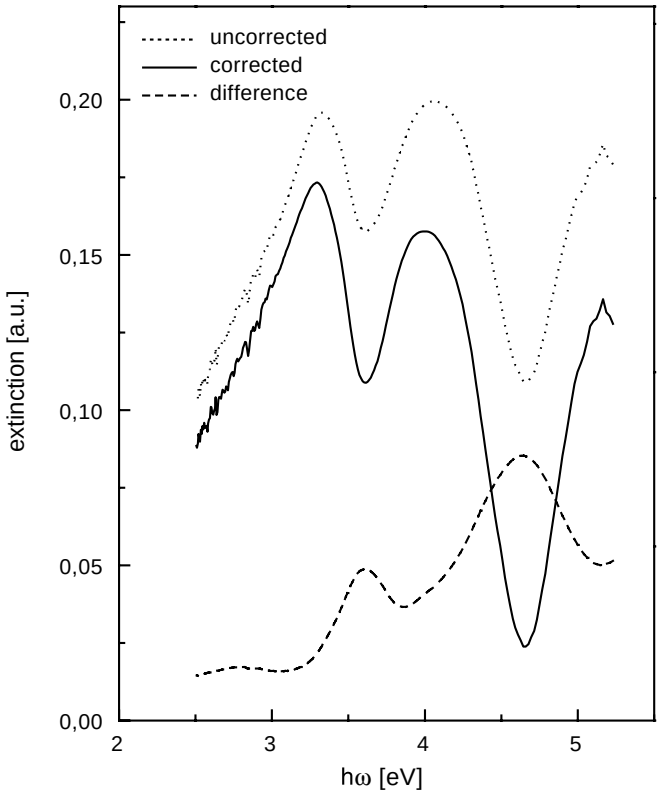

Fig. 2. Extinction spectra of iron clusters in a fullerite film: the measured signal corrected to take into account the thickness difference between the sample and the reference (solid curve) and the uncorrected measured signal (dotted curve). The dashed curve shows the difference between the corrected and uncorrected extinction spectra.

Pure fullerite layers show the strong π-interband transition peaks at 2.8 eV, 3.6 eV, 4.6 eV and 5.6 eV. This structure is mirrored in the cluster part of the calculated extinction due to the exchange of matrix material to iron clusters. As seen in Figure 2, the maxima of the C_{60} absorption structure coincide with minima in the calculated and measured (corrected) spectra. These minima are caused by the dominant third term in the right-hand side of equation (5) (*i.e.* the absorption rate in fullerite). 5% of the fullerite in fact absent in the sample volume filled with iron makes a great difference in the spectra.

It must be noted that the condition $\alpha D \ll 1$ mentioned in the previous section is actually violated between 4 eV and 5.5 eV (D is the particle diameter), nevertheless the method gives correct results in a region 4-4.6 eV. Re-

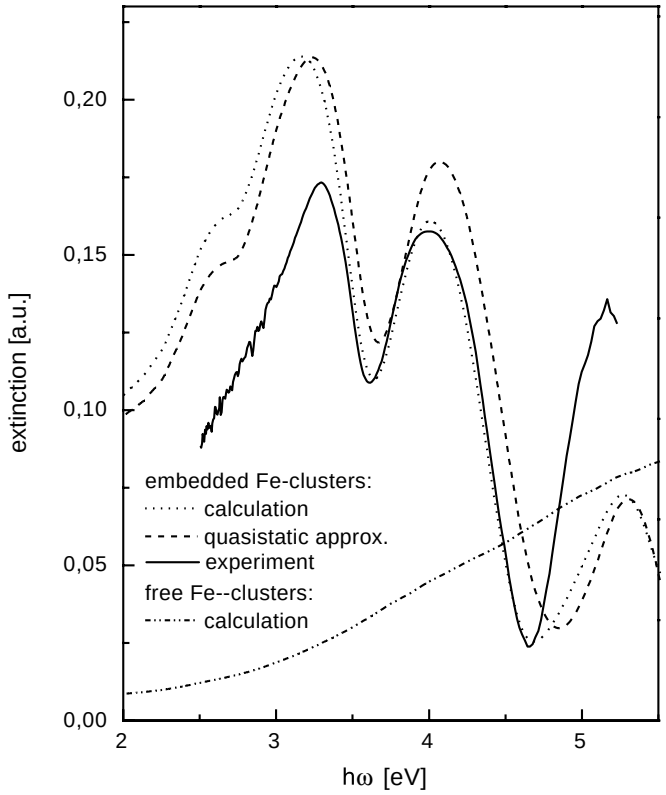

Fig. 3. Comparison of the calculated extinction spectrum ($NC_{\rm p}d$) of iron clusters in a fullerite matrix with the measured (corrected) spectrum. The dashed curve shows the extinction spectrum of Fe clusters in C_{60} calculated in the quasistatic approximation (30). Also the extinction spectrum of free iron clusters is plotted ($-\cdots-$). A dramatic difference between the extinctions of free and embedded Fe clusters is seen.

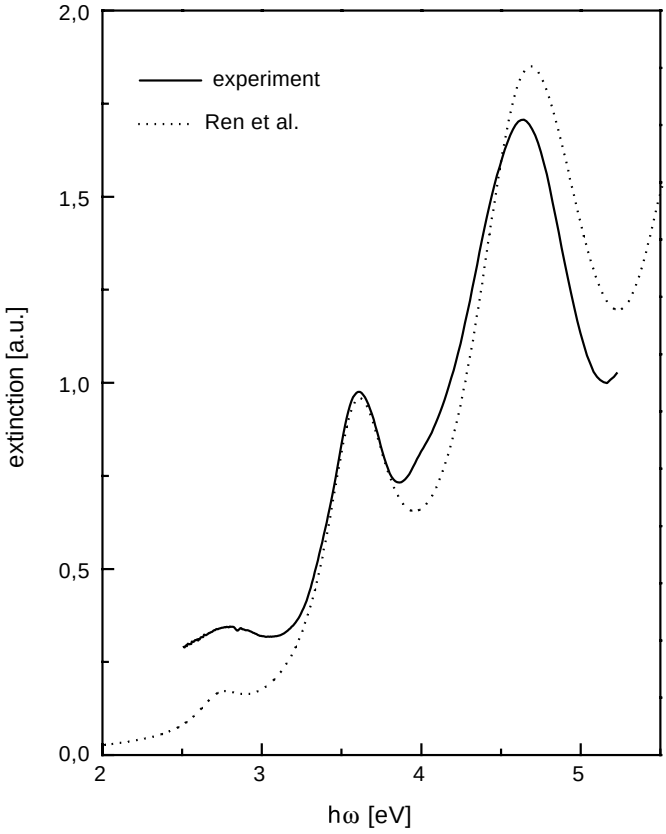

Fig. 4. Comparison between absorption coefficient spectra of a pure fullerite matrix: measured in the experiment and used in the calculation (based on the data from [18]).

maining deviations between the experiment and the calculation are supposed to have several reasons. First, the optical constants [18] used in the calculations were measured from solid C_{60} prepared in a slightly different way than samples prepared here. Figure 4 shows the measured absorption coefficient spectrum of the reference compared to the absorption of fullerite based on these optical constants from [18]. Second, from other systems (Ag clusters embedded in fullerite [19]) a charge transfer from metal cluster to the host was observed recently which causes changes in the optical spectra beyond the Mie theory. This effect is not a topic of the present paper; it has been discussed before [19] and will be discussed for the present sample elsewhere.

Finally, it should be emphasized that the extinction features of embedded iron particles as seen in Figure 3 are caused mainly by the frequency response of the matrix (fullerite) and not by the dielectric function of iron. This can be demonstrated by calculating the extinction of the same iron clusters in vacuum. In that case, a quite structureless spectrum is obtained as also shown in Figure 3.

5 Discussion and conclusions

We have presented a new method to calculate the optical extinction spectra of spherical particles surrounded by an absorbing medium. Concerning cluster sizes, this theory is as general as the classical Mie theory. In addition a simplified version based on quasistatic approximation was checked. The extinction rate of the particle is defined as the rate at which the energy is removed from the incident beam via particle absorption and scattering referenced to the matrix background and is calculated locally by integrating the corresponding Poynting vectors of the electromagnetic field over the surface of the particle. This allows a consideration of hosts of arbitrary shape, thin films for example. The extinction rate is a function of the particle size and of the optical properties of both the particle and the matrix materials only and characterizes the ability of the embedded particle to scatter and to absorb light from the incident beam.

The fact that our integration sphere coincides with the particle itself allows to avoid the introduction of the arbitrary parameter (the size of the integration sphere) which appears in some previous works [5–7] and clears the physical meaning of the extinction rate defined here. As we will show in our forthcoming paper [20], the method can be

successfully used to describe light extinction by particle *aggregates* in absorbing media as well.

One of our points of interest was to find a relation between the extinction rate of the particle and the observable transmission of the composite sample (film with embedded particles). In the work of Bohren and Gilra [8] the extinction of a single particle embedded in an absorbing matrix was related to what is observed by a remote detector also placed inside the matrix. The observable value in such an experiment is the difference in the energy received by the detector in two cases: with and without the particle in the matrix, and is not related to the absolute values of energy absorbed and scattered by the particle. (Actually, these values cannot be found following the method of Bohren and Gilra.) Often the sample size may be strongly limited in the direction of light propagation, so the distance between the particle and the detector cannot be chosen large enough for the application of the far-field approximations of the electromagnetic fields in the vicinity of the detector.

If the particles are uniformly distributed in the film volume, the propagation of light in such a composite medium cannot be described in terms of "remote" extinction. Instead an introduction of the extinction coefficient may be useful. This coefficient characterizes the composite medium in the same way as the absorption coefficient describes homogeneous absorbing media and is often used as the output in real transmission experiments. In contrast to Bohren and Gilra we use the energetic aspect of extinction: extinction = energy absorbed and scattered by particles. Here a heuristic concept of a local extinction is suggested. Under some conditions (Sect. 3.2) an effective extinction coefficient of the composite medium can be defined, which provides a relationship between the observable transmission of the film and the particle extinction rate. The extinction coefficient of the composite system cluster + matrix is given then as a sum of an absorption coefficient of the matrix and the extinction coefficient of the particle subsystem. The method can be directly applied to cluster systems, and the calculation of the extinction coefficient of iron clusters embedded in a fullerite matrix is presented as an example. The experimentally obtained extinction coefficient is well reproduced in the general spectral features by the calculation. The obvious deviations are supposed to be caused by effects beyond the classical electrodynamics and are not topic of the present paper.

One cannot directly relate the remote extinction cross-section defined by Bohren and Gilra with the local extinction presented in this paper. It should be noted, however, that these two different approaches may be used to describe one and the same observable value (the difference in the energy received by a detector, with and without particles in the matrix) in two different cases: if the distance between the particles and the detector also placed inside the matrix can be considered large enough, the approach of Bohren and Gilra may be preferable, in any other case our method may be applied.

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Appendix A: Spherical wave vector functions

We have used the expressions for the spherical wave vector functions as defined in [4]:

$$[q(q+1)]^{\frac{1}{2}}\,\mathbf{m}_{qp} = ipz_q(\rho)\frac{Y_{qp}(\theta,\varphi)}{\sin\theta}\mathbf{e}_\theta - z_q(\rho)\frac{\partial Y_{qp}(\theta,\varphi)}{\partial\theta}\mathbf{e}_\varphi\,, \tag{A.1}$$

$$[q(q+1)]^{\frac{1}{2}}\,\mathbf{n}_{qp} = q(q+1)\frac{z_q(\rho)}{\rho}Y_{qp}(\theta,\varphi)\mathbf{e}_r + \frac{[\rho z_q(\rho)]'}{\rho}\frac{\partial Y_{qp}(\theta,\varphi)}{\partial\theta}\mathbf{e}_\theta + ip\frac{[\rho z_q(\rho)]'}{\rho}\frac{Y_{qp}(\theta,\varphi)}{\sin\theta}\mathbf{e}_\varphi\,, \tag{A.2}$$

where z_q are the Bessel spherical functions j_q or $h_q^{(1)}$. $Y_{qp}(\theta,\varphi)$ are the normalized spherical harmonics. The spherical vector wave functions can be generated as

$$\mathbf{m}_{qp} = \boldsymbol{\nabla}\times(\mathbf{r}\zeta_{qp})\,, \tag{A.3}$$

$$\mathbf{n}_{qp} = \boldsymbol{\nabla}\times\boldsymbol{\nabla}\times(\mathbf{r}\zeta_{qp})\,, \tag{A.4}$$

where $\zeta_{qp} = z_q(\rho)Y_{qp}(\theta,\varphi)[q(q+1)]^{-\frac{1}{2}}$ is the generating function. The following properties allow to use the spherical wave vector functions as partial solutions of the wave equation:

$$\mathbf{n}_{qp} = \frac{1}{k}\boldsymbol{\nabla}\times\mathbf{m}_{qp}\,, \tag{A.5}$$

$$\mathbf{m}_{qp} = \frac{1}{k}\boldsymbol{\nabla}\times\mathbf{n}_{qp}\,, \tag{A.6}$$

$$\boldsymbol{\nabla}\cdot\mathbf{m}_{qp} = \boldsymbol{\nabla}\cdot\mathbf{n}_{qp} = 0\,. \tag{A.7}$$

It has been shown [21] that the system of the spherical wave functions is orthogonal and complete for transverse waves.

References

1. G. Mie, Ann. Phys. **25**, 377 (1908).
2. P.J. Wyatt, Phys. Rev. **127**, 1837 (1962).
3. R. Ruppin, Phys. Rev. B **11**, 2871 (1975).
4. J.M. Gerardy and M. Ausloos, Phys. Rev. B **25**, 4204 (1982).

5. W.C. Mundy, J.A. Roux and A.M. Smith, J. Opt. Soc. Am. **64**, 1593 (1974).
6. P. Chylek, J. Opt. Soc. Am. **67**, 561 (1977).
7. M. Quinten and J. Rostalski, Part. Part. Syst. Charact. **13**, 89 (1996).
8. C.F. Bohren and D.P. Gilra, J. Colloid Interface Sci. **72**, 215 (1979).
9. H.C. van de Hulst, *Light Scattering by Small Particles* (Wiley, New York, 1957) Chapt. 4.
10. R. Petrich and O. Stenzel, Opt. Mater. **3**, 65 (1994).
11. O. Stenzel, *Das Duennschichtspektrum* (Akademie, Berlin, 1996) in German.
12. M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Equations* (Dover, New York, 1972).
13. C.F. Bohren and D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).
14. E. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Chelsea, New York, 1965).
15. U. Kreibig, Appl. Phys. **10**, 225 (1976).
16. W.J. Wiscombe, Appl. Opt. **19**, 1505 (1980).
17. W.J. Lentz, Appl. Opt. **15**, 668 (1976).
18. S.L. Ren *et al.*, Appl. Phys. Lett. **59** (21), 2678 (1991).
19. U. Kreibig, M. Gartz, A. Hilger and H. Hoevel, in *Advances in Metal and Semiconductor Clusters*, 345 (1998).
20. A.N. Lebedev and O. Stenzel, "Optical extinction of an assembly of spherical particles in an absorbing medium: Application to silver clusters in absorbing organic materials", to be published in Eur. Phys. J. D.
21. J. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).