FAR INFRARED ABSORPTION IN ULTRAFINE AL PARTICLES DRUDE MODEL VERSUS GOR'KOV-ÉLIASHBERG THEORY

C. Granqvist, R. Buhrman, J. Wyns, A. Sievers

FAR INFRARED ABSORPTION IN ULTRAFINE AL PARTICLES DRUDE MODEL VERSUS GOR'KOV-ÉLIASHBERG THEORY (*)

C. G. GRANQVIST (**) and R. A. BUHRMAN

School of Applied and Engineering Physics
and Materials Science Center

J. WYNS and A. J. SIEVERS

Laboratory of Atomic and Solid State Physics
and Materials Science Center
Cornell University, Ithaca, New York 14853, USA

Résumé. — La transmission infrarouge (fréquences $3 < \tilde{\nu} < 150$ cm^{-1}) fut mesurée pour des particules d'aluminium de diamètre $4 < x < 40$ nm. Le coefficient d'absorption, est approximé correctement par l'expression $\alpha_{exp} \doteq C_{exp}\, \tilde{\nu}^2$. Les résultats sont comparés avec le modèle de Drude (D) et la théorie de Gor'kov et d'Eliashberg (GE). Les deux théories prédisent une variation parabolique de la fréquence avec $C_D \ll C_{exp}$ et $C_{GE} \ll C_{exp}$, démontrant qu'aucune de ces théories n'est directement applicable. Cependant une analyse de α_D en fonction de x apporte effectivement quelque support au modèle de Drude.

Abstract. — Far infrared transmission in the frequency interval $3 < \tilde{\nu} < 150$ cm^{-1} was measured for samples of Al particles with mean diameters $4 < x < 40$ nm. The absorption coefficient is well approximated by $\alpha_{exp} \doteq C_{exp}\, \tilde{\nu}^2$. The results are compared with the Drude (D) model and the Gor'kov-Eliashberg (GE) theory. Both yield parabolic frequency dependencies with $C_D \ll C_{exp}$ and $C_{GE} \ll C_{exp}$ respectively, indicating that neither theory is directly applicable. However, an analysis of α_D vs. x does give some support to the Drude model.

Two distinctly different approaches to the description of the electromagnetic properties of ultrafine particles are in current use. In the first the bulk parameters are modified simply by incorporating a size dependent mean free path in the free electron contribution to the dielectric permeability. This point of view has been very successful in explaining optical absorption in Au [1] and Ag [2] particles. The second approach, pioneered by Fröhlich [3] and by Kubo [4], regards the limited-size-induced splitting of the conduction band into individual levels with non-negligible separations. Dipole transitions between these yield an absorption which is not present in the bulk. Experimental evidence for such quantization effects has been gained in particular from NMR experiments [5, 6]. Here we report on an investigation of far infrared absorption in ultrafine Al particles. The frequencies are comparable with the expected mean intervals between adjacent size quantized energy eigenvalues. The results will be compared with the classical Drude (D) model with a size limited mean free path, as well as with the elaborate quantum mechanical theory by Gor'kov and Eliashberg (GE) [7] which explicitely regards quantized levels. The present work is an extension and reevaluation of the experiments reported on in ref. [8]. Some preliminary results from the new measurements have been given in ref. [9].

Since the far infrared wavelengths are much greater than any particle diameters studies, an *effective medium treatment* of the composite of metal particles in the surrounding medium is appropriate. Empirically, the volume fraction of metal (the *filling factor*, f) is small for our samples such that the Maxwell-Garnett (MG) theory [10] can be used to give an expression for the average dielectric permeability $\bar{\varepsilon}^{MG}$,

$$\frac{\bar{\varepsilon}^{MG} - 1}{\bar{\varepsilon}^{MG} + 2} = f \frac{\varepsilon - 1}{\varepsilon + 2}, \qquad (1)$$

which applies to identical spheres (with a dielectric function $\varepsilon \equiv \varepsilon_1 + i\varepsilon_2$) surrounded by vacuum (1). However, eq. (1) is not sufficient to describe the total absorption as magnetic polarization, resulting from eddy currents flowing in the particles, can not be neglected in general. For the diameters (x) and frequencies ($\tilde{\nu} \equiv \nu/c$) of present interest it can be

(*) Research supported by the National Science Foundation and by the Energy Research and Development Administration.

(**) Presently at Physics Dept., Chalmers University of Technology, Fack, S-402 20 Gothenburg, Sweden.

(1) Ref. [1] contains an extension of the MG theory, and other effective medium theories, to self-consistent formulations incorporating size distributions, non-spherical particles, dipole-dipole interactions and effects of dielectric coatings on the particles or an absorbing medium embedding the metal granules.

seen from § 45 of ref. [11] that the magnetic permeability is given by

$$\mu \doteq 1 + i(\pi^2/10)(x\tilde{\nu})^2 \varepsilon_2 . \quad (2)$$

From eqs. (1) and (2) it can now be shown that the absorption coefficient is

$$\alpha \doteq 2\pi\tilde{\nu} f \varepsilon_2 [9/|\varepsilon|^2 + (\pi^2/10)(x\tilde{\nu})^2] . \quad (3)$$

This expression thus contains the additive contributions from the dielectric and magnetic polarization.

The *Drude model* in the limit $\omega\tau \ll 1$ gives

$$\varepsilon_D = -(\omega_p \tau)^2 + i\omega_p^2 \tau/\omega , \quad (4)$$

where ω_p denotes the plasma frequency and the reciprocal lifetime is size limited according to

$$\tau^{-1} = \tau_b^{-1} + 2v_F/x \quad (5)$$

for diffuse scattering in a spherical granule. Here τ_b is the lifetime for the bulk metal and v_F is the Fermi velocity. From eq. (3) we now obtain in the interesting limit $\tau \ll \tau_b$

$$\alpha_D = f\, 54\pi^3 (a_B/\lambda_c) k_F^{-2} x^{-1} \tilde{\nu}^2 + f(\pi/15)(\lambda_c/a_B) k_F^2 x^3 \tilde{\nu}^2 \quad (6)$$

where k_F is the Fermi momentum, a_B is the Bohr radius and λ_c is the electron Compton wavelength. Hence there is a $\tilde{\nu}^2$ dependence both for the dielectric and magnetic contributions to α_D. Eq. (6) also shows that when x is increased an initial proportionality of α_D to x^{-1} is followed by an x^3 dependence. For Al the minimum in α_D occurs at $x \doteq 5$ nm.

The *Gor'kov-Eliashberg theory* [7] considers absorption due to non-degenerate energy eigenvalues. Their average separation is the inverted single spin density of states at the Fermi level, i.e.

$$\Delta = 12\pi\hbar^2/(m^* k_F x^3) , \quad (7)$$

where $m^* \equiv \Lambda m$ is the thermal effective mass of the electrons. The distribution of statistically independent eigenvalues can be worked out from general theories of random matrices [12]; three different statistical ensembles (orthogonal, symplectic and unitary) may be applicable depending on the symmetries of the set of Hamiltonian matrices. For our purposes the most important result of the GE theory is their derivation of the electronic susceptibility [13], which can be written as

$$\chi_{GE} = \Lambda k_F x^2/(20\pi^2 a_B) + 139\Lambda A(\eta)/(1\,200\pi^2 a_B k_F)$$

for boundary scattering of the electrons. The factor $A(\eta)$, which depends on the appropriate level statistics, is given by

$$A^{ort}(\eta) \equiv A^{ort}(\zeta) = 2 - \zeta^{-1}\sin 2\zeta - 2\zeta^{-1}\mathrm{Ci}(\zeta)(\sin\zeta - \zeta\cos\zeta) + i\{2\zeta - \zeta^{-1} + \zeta^{-1}\cos 2\zeta - \zeta^{-1}\mathrm{Si}(\zeta)(\sin\zeta - \zeta\cos\zeta)\} ; \quad (8)$$

$$A^{sympl}(\eta) \equiv A^{sympl}(z) = 2 - (2z)^{-1}\sin 2z - (z^{-1}\cos z + \sin z)x[\mathrm{Si}(z) + \pi/2] + i\{z - z^{-1}\sin^2 z - (z^{-1}\sin z - \cos z)[\mathrm{Si}(z) + \pi/2]\} \quad (9)$$

for the orthogonal and symplectic ensembles, which should apply when the atomic spin orbit coupling is weak or strong respectively. In eqs. (8) and (9) the notation $z = 2\zeta = (2\pi)^2 \hbar c\tilde{\nu}/\Delta$ is used and Si (Ci) means the sine integral (cosine integral) function. The dielectric permeability $\varepsilon_{GE} = 1 + 4\pi\chi_{GE}$ inserted into eq. (1) yields expressions for α_{GE}.

Multiple peaks in the absorption coefficient are predicted for ultrafine particles ($x \lesssim 5$ nm) if the symplectic ensemble is used, as was noticed by GE [7]. Their occurrence is of great interest because — if observed unambiguously — they would uncover a unique test of basic assumptions for the eigenvalue statistics. The frequency spacing of the maxima is a direct manifestation of the individual energy levels. From eq. (7) we have $\Delta \propto x^{-3}$ which makes it evident that a non-zero width of the size distribution for the particles will act as to smear out any fine structure in α_{GE}. For the log-normal distribution function, which is generally found [14] for particles growing *via* coalescence, the number of particles Δn per logarithmic diameter interval $\Delta(\ln x)$ is given by $\Delta n = f_{LN}(x)\Delta(\ln x)$ with

$$f_{LN}(x) = \frac{1}{(2\pi)^{\frac{1}{2}} \ln\sigma_g} \exp\left\{-\tfrac{1}{2}\left[\frac{\ln(x/\bar{x}_M)}{\ln\sigma_g}\right]^2\right\} . \quad (10)$$

Here $\bar{x}_M$ denotes the statistical median of the diameters and σ_g is the geometric standard deviation. Log-normal distributions with $\bar{x}_M = 2.5$ nm and different σ_g's are depicted in the inset of figure 1. Incorporating these size distributions in the MG effective medium theory (using a generalized version of eq. (1); cf. eq. (6) of ref. [9]) one obtains the results shown in the main part of figure 1. For a δ-function distribution ($\sigma_g = 1$) a strongly oscillatory α_{GE} is found for the symplectic ensemble, but already at $\sigma_g = 1.1$ an essentially structureless curve is encountered; furthermore the same graph is obtained for the two ensembles. Empirically [14] we do not know of any technique to prepare ultrafine particles which is capable of yielding σ_g's as small as 1.1 and hence we are forced to conclude that multiple absorptivity peaks *cannot be observed in practice.*

For $\sigma_g \gtrsim 1.1$ and $\bar{x}_M \gtrsim 2.5$ nm one is justified in setting $A^{ort}(\zeta) = A^{sympl}(z) = iz$ in eqs. (8) and (9). It can then be shown that

$$\alpha_{GE} \doteq f(139\pi^3/2)(a_B/\lambda_c) k_F^{-2} x^{-1} \tilde{\nu}^2 . \quad (11)$$

For Al this relation holds for $x \ll 50$ nm when $\tilde{\nu} = 10\ \mathrm{cm}^{-1}$ and for $x \ll 20$ nm when $\tilde{\nu} = 100\ \mathrm{cm}^{-1}$

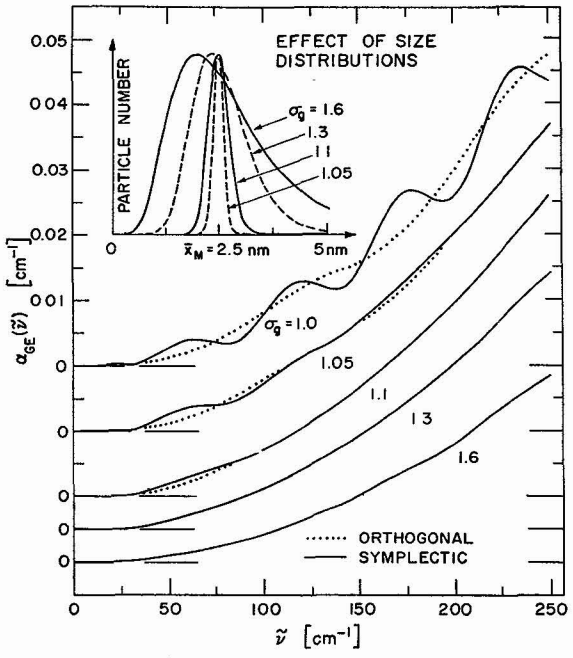

FIG. 1. — Absorptivity vs. frequency for the orthogonal and symplectic ensembles calculated for log-normal size distributions with five different σ_g's (cf. the inset). The curves are displaced vertically by 0.01 or 0.005 cm^{-1}. We used $k_F = 1.75 \times 10^8$ cm^{-1}, $\Lambda = 1.48$ and $f = 0.02$

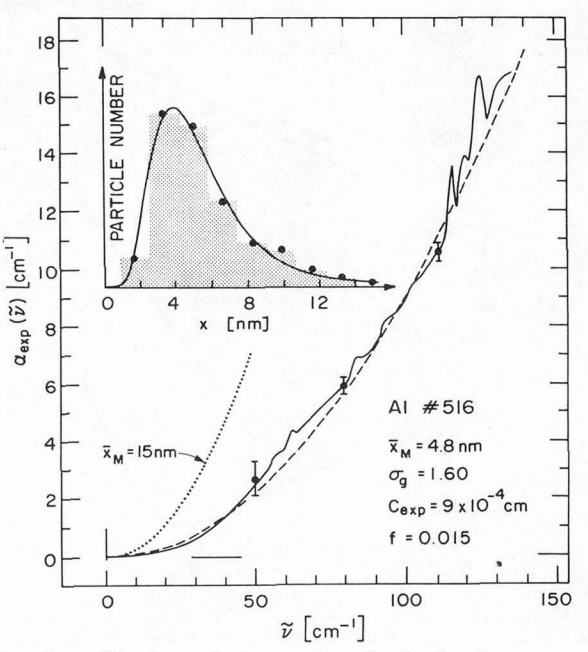

FIG. 2. — The inset depicts a size distribution for a sample prepared by evaporation in 1.5 torr of pure Ar with addition of some O_2. The solid curve in the main figure describes frequency dependent absorption coefficient of the same sample. To correct for the fact that samples of different length causes different amounts of radiation to impinge onto the detector the measured curve was displaced vertically such that $\alpha_{exp} = 0$ at $\tilde{\nu} = 0$. The error bars signify the reproducibility from one run to the next. The approximation of eq. (13) yields the dashed curve. The dotted curve shows the average variation of α_{exp} for an Al specimen with $\bar{x}_M = 15$ nm ; these data are reproduced from figure 3 of ref. [8].

At still larger diameters the magnetic polarization must be included. Comparing with eq. (6) it is seen that for $x \lesssim 5$ nm we have $\alpha_{GE} \doteq 1.3\ \alpha_D$, i.e. the two theories yield practically indistinguishable results. In the range $5 \lesssim x \lesssim 20$ nm, however, the Gor'kov-Eliashberg theory differs significantly from the Drude model due to the strong contribution from magnetic polarisation to α_D.

Ultrafine particles of Al were prepared by inert gas evaporation from a temperature stabilized oven onto a large water cooled plate. A small amount of oxygen was admitted continuously in order to give a dielectric coating on the individual particles. This novel technique to make ultrafine particles is described in ref. [14]. Size distributions were determined by electron microscopy ; an example is shown by the inserted histogram in figure 2. The closely resembling bell shaped curve, representing eq. (10) with $\bar{x}_M$ and σ_g as shown in the figure, proves the accuracy of the approximation given by the log-normal distribution function. Filling factors were obtained by weighing a known volume of the particles.

Far infrared transmission measurements were performed using both lamellar grating and Michelson interferometers [15]. The sample rotator and the ^{3}He cooled germanium bolometer detector were both housed in the same ^{4}He cryostat [16]. The samples were constructed by clamping 2 mil polyethylene sheets onto a hald inch brass ring filled with the powder. At low frequencies, where the samples were essentially transparent, we observed Fabry-Perot fringes appropriate for two parallel surfaces separated by the brass spacer thickness. In the frequency region where the sample absorbed, the fringes were not seen and we determined the absorption coefficient from a simple ratio measurement between powder samples of two different thicknesses l_1 and l_2. In this case α_{exp} is given by

$$\alpha_{exp} = (l_1 - l_2)^{-1} \ln (I_1/I_2) \qquad (12)$$

where I signifies the intensity transmitted through the sample. The main part of figure 2 depicts measured frequency dependent absorption coefficient. The whole curve is found to be well approximated by a parabola,

$$\alpha_{exp} = C_{exp}\, \tilde{\nu}^2 , \qquad (13)$$

where C_{exp} is frequency independent. The earlier reported [8] peak structure for one sample with larger Al particles could *not* be established either in the sample of figure 2 or in other ones of similar mean diameters.

The parabolic *frequency dependence* agrees with both the Drude model and the GE theory as seen from eqs. (6) and (11). However, the experimental value for the sample of figure 2, $C_{exp} = 9 \times 10^{-4}$ cm, is orders of magnitude larger than the experimentally predicted ones, $C_D \doteq C_{GE} = 4 \times 10^{-7}$ cm (defined in analogy with eq. (13)). For the *size dependence* of the absorption

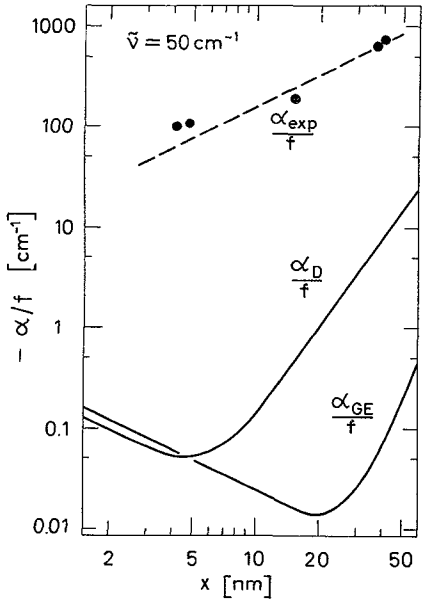

FIG. 3. — Absorption coefficient divided by filling factor versus particle diameter. The results apply to a constant frequency. Experimental results are shown as heavy dots. Data for the three largest x's were extracted form ref. [8]. The dashed line represents $\alpha_{exp}/f \propto x$. The solid curves show the predicted size dependencies for the classical and quantum mechanical theories.

coefficient we first notice from the dotted curve in figure 2 that α_{exp} is enhanced when x increases. This is directly counter to the expected variation for α_{GE}. Actually, the observed size dependence is inconsistent also with α_D as seen from figure 3, where we have plotted absorptivity versus x for constant $\tilde{\nu}$. Experimentally we find roughly an $\alpha_{exp} \propto x$ behaviour, whereas the Drude model yields $\alpha_D \propto x^3$ over most of the interesting size range. If $\tau \doteq \tau_b$ we get instead $\alpha_D \propto x^2$.

In conclusion, neither the classical nor the quantum mechanical theory seem to be able to explain the absolute magnitude or the detailed size dependence of the experimentally observed far infrared absorption coefficient. Some preference should be given to the Drude model as being the only theoretical description which combines a $\tilde{\nu}^2$ variation with the prediction that the absorptivity goes up when x is increased. In order to understand the drastic discrepancies between C_{exp} and C_D (or C_{GE}) we are presently trying to include dipole-dipole interactions in the effective medium treatment. Such interactions are known [1] to enhance significantly the optical absorption for gas evaporated particles, but it seems doubtful whether it is the sole reason for the unexpectedly large α_{exp}.

References

[1] GRANQVIST, C. G. and HUNDERI, O., *Phys. Rev.*, in press, and references therein.

[2] KREIBIG, U., *J. Phys. F. Metal Phys.* **4** (1974) 999.

[3] FRÖHLICH, H., *Physica* **4** (1937) 406.

[4] KUBO, R., *J. Phys. Soc. Japan* **17** (1962) 975.

[5] KOBAYASHI, S., TAKAHASHI, T. and SASAKI, W., *J. Phys. Soc. Japan* **36** (1974) 714.

[6] YEE, P. and KNIGHT, W. D., *Phys. Rev.* **B 11** (1975) 3261.

[7] GOR'KOV, L. P. and ELIASHBERG, G. M., *Zh. Eksp. Teor. Fiz.* **48** (1965) 1407 [English transl. *Sov. Phys.-JETP* **21** (1965) 940].

[8] TANNER, D. B., SIEVERS, A. J. and BUHRMAN, R. A., *Phys. Rev.* **B 11** (1975) 1330.

[9] GRANQVIST, C. G., BUHRMAN, R. A., WYNS, J. and SIEVERS, A. J., *Phys. rev. Lett.* **37** (1976) 625.

[10] MAXWELL-GARNETT, J. C., *Philos. Trans. R. Soc. Lond.* **203** (1904) 385 ; **205** (1906) 237.

[11] LANDAU, L. D. and LIFSHITZ, E. M., *Electrodynamics of Continuous Media* (Pergamon Press, New York) 1960.

[12] PORTER, C. E., *Statistical Theories of Spectra : Fluctuations* (Academic Press, New York) 1965.

[13] STRÄSSLER, S., RICE, M. J. and WYDER, P., *Phys. Rev.* **B 6** (1972) 2575.

[14] GRANQVIST, C. G. and BUHRMAN, R. A., *J. Appl. Phys.* **47** (1976) 2200.

[15] SIEVERS, A. J., *J. Appl. Phys.* **41** (1970) 980.

[16] TANNER, D. B., *Phys. Rev.* **B 8** (1973) 5045.