Size-dependent dielectric response of small metal particles

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The complex dielectric function of small metal particles is size dependent at microwave and radio frequencies. This was measured for particle diameters between 10 nm and 10 μm. In contrast to bulk electromagnetic response, the real part of the dielectric function in the small particles is positive and goes through a maximum. In addition, the temperature dependence of the loss index was found to change from positive to negative behavior near 1 μm.

I. MICROWAVE EXPERIMENTS ON MESOSCOPIC CONDUCTORS

The dielectric response of small metal particles was frequently studied during the last decade.[1-3] Investigations performed in the far infrared concentrated on the dielectric losses rather than on the real part of the complex dielectric function (DF). In this paper we report that microwave and radio frequency data reveal a size-dependent complex DF $\epsilon=\epsilon_1+i\epsilon_2$. For microwave frequencies, the real part peaks at a particle diameter s of about 1 μm. For other frequencies, such extensive size-dependent experimental data are not yet available.

The size-dependent DF ϵ of the metals is determined with the particles embedded in an insulating matrix, their volume fraction (filling factor f) being kept below the percolation threshold. [We tested the sensitivity of our microwave method to percolation effects with unsupported nanocrystal networks[4] which are stronger absorbers at small f values (≈ 0.01) than matrix-isolated particles at $f \leq 0.2$.] As a general result, the effective DF $\bar{\epsilon}$ of these heterostructures always increases solely due to doping the matrix with metal particles. The influence of particle size on the dielectric response is seen in both $\bar{\epsilon}$ and ϵ. In order to determine more quantitatively the size dependence, the DF ϵ of the metal component is extracted from the measured effective DF $\bar{\epsilon}$, taking into account the contribution ϵ_M of the pure matrix and f as indicated below.

In all experimental results obtained for different metals (Ag, Au, In, and Pt particles), the particle size s is found to play an important role for sizes up to some μm. This is shown in Fig. 1 for $\bar{\epsilon}_1$ of several metal colloids with equal filling factors but different particle sizes. Accounting for the different matrix materials in a first-order approximation, we subtracted the DF of the matrix from the effective data. According to our measurements on the same particles embedded in different matrices this is a reasonable procedure. In the submicrometer range, $\bar{\epsilon}_1$ increases with s and rolls off for larger particles. Due to the heterodispersity of the colloids available, it is difficult to pinpoint the maximum between the two measured branches. Other microwave data[5,6] for Ni and Cu particles with $s > 1$ μm are included in Fig. 1. The drop of $\bar{\epsilon}_1$ for larger particles is accompanied by a decrease of the loss index $\bar{\epsilon}_2$. Both effects can be understood as a consequence of the penetration depth δ at microwave frequencies becoming smaller than the particles ($\delta \approx 1$ μm for bulk metals at 10 GHz). Thus for $s \gg 1$ μm, the effective particle volume is limited by the skin effect and the particle reflects the incident electromagnetic radiation finally.

The most reliable procedure to determine $\epsilon_1(s)$ as a function of growing particle size is *in situ coalescence.* Such experiments were carried out with submicrometer indium particles in an oil matrix which grow by thermal coalescence when the temperature of the colloid is raised. In this way, the average particle size could be increased from about 20 nm to several hundred nm during the measurement without sedimentation. These very coalescence experiments revealed that $\bar{\epsilon}=\bar{\epsilon}_1+\bar{\epsilon}_2$ increases with parti-

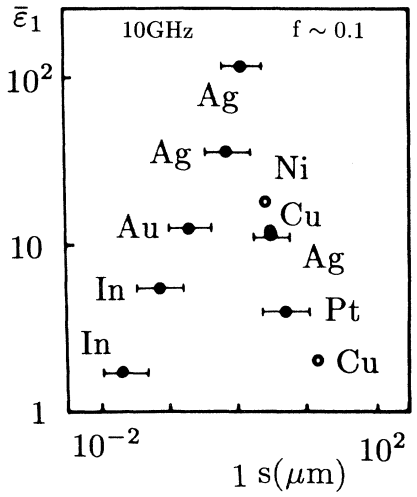

FIG. 1. Effective dielectric function $\bar{\epsilon}_1$ of various metal colloids vs particle size s measured at a microwave frequency of 10 GHz and at room temperature. The dielectric contribution ϵ_M of the different matrix materials (oil, resin, Al_2O_3, epoxy, wax) was accounted for by subtracting ϵ_M from the measured DF. The data reveal a pronounced maximum near $s \sim 1$ μm independent of the specific metal. (Empty circles are data taken from Refs. 5 and 6.)

cle size at constant filling factor.

In order to separate the contributions ϵ of the metal component from the measured response $\bar{\epsilon}$, the effective medium was analyzed with the Landau-Lifshitz-Looyenga formula.[3,7,8] This procedure roughly yields the power laws $\epsilon_1(s)\sim s^2$ and $\epsilon_2(s)\sim s^3$ for the metal particles in the submicrometer regime. The power laws are not an artifact of the analysis. This is seen from the comparison of the effective data $\bar{\epsilon}_2$ versus $\bar{\epsilon}_1$ and the analyzed data ϵ_2 versus ϵ_1 in Fig. 2: Both sets $\bar{\epsilon}_2$ versus $\bar{\epsilon}_1$ and ϵ_2 versus ϵ_1 have the same slope within the experimental accuracy. The data presented in Fig. 2 were obtained by coalescence experiments carried out at frequencies between 1 MHz and 10 GHz as indicated by the different symbols.

The present results explain why, in a former radio frequency experiment on Ag particles in a glass matrix,[9] no detectable response was found. With f ranging from 10^{-4} to 10^{-2} and $x \leq 10$ nm, a change of $\bar{\epsilon}$ due to the particles would have been only about 10^{-3}, much smaller than the stated experimental accuracy of 2%.[9]

We observed another size-dependent property of metal particles. For $x < 1$ μm, the thermal coefficient $\partial\bar{\epsilon}_2/\partial T$ of the loss factor $\bar{\epsilon}_2$ is positive, whereas for $s > 1$ μm it is negative (i.e., metalliclike); this is shown in Fig. 3 for Pt particles. Having in mind that all changes are due to the particles, $\partial\bar{\epsilon}_2/\partial T$ reflects the thermal behavior $\partial\sigma/\partial T$ of their conductivity $\sigma=\epsilon_0\epsilon_2\omega$ (with ϵ_0 the free space permittivity and ω the measuring frequency). Not only does the conductivity of the submicrometer particles behave opposite to that of metals but its temperature dependence is very weak.[3]

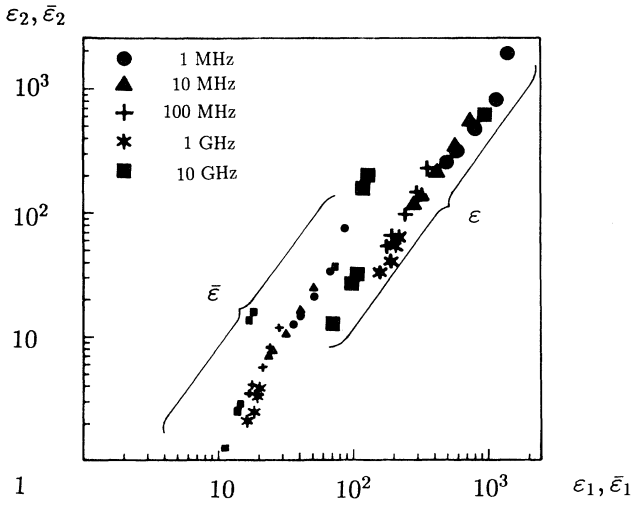

FIG. 2. Imaginary part ϵ_2 vs real part ϵ_1 of the DF of the indium component evaluated from coalescence experiments at different frequencies as indicated by the symbols. Within each set of symbols, the indium particle size grows from lower left to upper right. Both $\epsilon_1(s)$ and $\epsilon_2(s)$ are positive and increase with s. The same behavior is also seen in the measured effective data $\bar{\epsilon}_2$ vs $\bar{\epsilon}_1$ (lower data indicated by the smaller symbols).

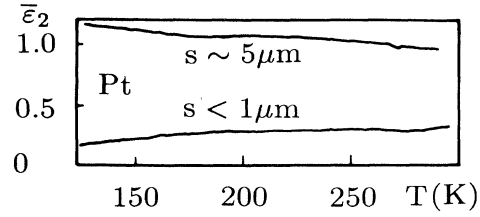

FIG. 3. Temperature dependence of the effective loss factor $\bar{\epsilon}_2$ of colloids with submicrometer Pt particles in resin (lower curve) and with the same particles after coarsening to a mean size of 5 μm by a separate heat treatment in an Al_2O_3 matrix (upper curve). The filling factor of the Pt particles was $f\sim 0.01$ in resin and $f\sim 0.1$ in Al_2O_3. The temperature dependence of the conductivity is reversed for the coarsened particles.

II. DISCUSSION

For the time being, we assume that the observed size-dependent DF is in consequence of electron localization in the metal particles. The localized electrons show dipolar response. In the following, we briefly discuss theoretical models proposed recently. The ratio of electron coherence length ξ to the confinement size decides on the observability of quantum size effects.[10–13] According to Thouless,[14,15] ξ is estimated from the elastic and inelastic mean free paths L and L_i, respectively,

$$\xi\sim\sqrt{LL_i}\ . \tag{1}$$

L_i may either be governed by electron-phonon or by electron-electron interactions, depending on carrier density and temperature. In bulk metals, ξ may lie between 10^{-8} and 10^{-7} m at room temperature.[3] Accordingly, quantum size dimensions give rise to electron wave interference, and standing waves may play an important role at least up to this size. The nonmetalliclike positive thermal coefficient of ϵ_2 is in favor of a quantum size effect. In addition, the temperature dependence of the complex dielectric response of submicrometer particles is unusually weak in the range 1–400 K. The experimental results, however, are surprising, since neither classical size nor quantum size effects are expected for the μm size range.

Formerly, the DF of metal particles was disussed in terms of a Lorentzian polarization resonance[16,17]

$$\epsilon=\epsilon_L+\frac{\omega_P^2}{\omega_0^2-\omega^2-i\omega/\tau(s)} \tag{2}$$

with ϵ_L the positive lattice contribution to the DF and ω_P the plasma frequency. In this model, damping is introduced via a size-dependent momentum relaxation frequency $1/\tau(s)=1/\tau(\text{bulk})+\omega_0$ of the Fuchs-Sondheimer type with $\omega_0\approx v_F/s$ and v_F the Fermi velocity. In our experiments, the measuring frequencies ω lie far below the plasma resonance ($\omega/\omega_P\leq 10^{-5}$). Therefore, this collective excitation is not relevant to the present investigations.

For $\omega_0\rightarrow 0$, Eq. (2) represents the Drude DF of a bulk

metal. The oscillator has become a relaxator now. The relaxator model also yields a power law $\epsilon_2 \sim s^3$. The relaxation process, however, is not appropriate for the problem in question, in contrast to recent calculations by Frahm, Mühlschlegel, and Nemeth,[18] since in the investigated size range $\tau(\text{bulk}) \ll s/v_F$ holds.[3]

Speculations about magnetic response[17] have been ruled out by our experiments. The microwave technique allows us to distinguish between electric and magnetic interactions as discussed in Ref. 8.

III. SUMMARY

Mesoscopic metal particles are characterized by a pronounced size-dependent complex DF. An appropriate theory for this interesting behavior is not available at present. At microwave frequencies, the real part of the DF passes a maximum and the loss index approaches its classical value in the μm range. The power law $\epsilon_1(s) \sim s^2$ observed in the submicrometer range extrapolates to a giant value of some 10^5 for the maximum expected near 1 μm. To check this spectacular estimate, monodisperse particle ensembles are required. Besides the basic interest in this size-dependent DF, the large positive ϵ_1 of metal particles has a stimulating potential for practical applications.[16,19]

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