PHYSICAL REVIEW B VOLUME 40, NUMBER 11 15 OCTOBER 1989-I

Size-governed electromagnetic absorption by metal particles

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(Received 5 June 1989)

Electromagnetic absorption by submicrometer conductors is qualitatively different from Drude absorption by bulk metals. Measurements performed between radio and far-infrared frequencies with metals having diameters of about 20 nm are now analyzed with the Landau-Lifshitz-Looyenga effective-medium formula. This procedure showed that the experimental data are consistent with a size-induced metal-insulator transition. Microwave measurements rule out a significant magnetic-dipole contribution to the absorption by mesoscopic conductors.

I. INTRODUCTION

The interaction of small metal particles with electromagnetic radiation has been of interest for several decades.[1,2] Particularly, microwave and far-infrared absorption of submicrometer conductors have been studied in order to obtain information on size-induced effects on the quasistatic electrical conductivity. The momentum relaxation time τ_m of bulk metals is $<10^{-14}$ s near room temperature. Thus the quasi-dc condition $2\pi\nu\tau_m \ll 1$, with ν the radiation frequency, is fulfilled up to frequencies in the far infrared (FIR).[3,4] Accordingly, absorption measurements were carried out to yield information of potential size effects on the conductivity of small conductors. Their transport property has to be determined for isolated particles by contact-free measurements, otherwise the contacts or the environment govern the experimental data. In the absorption measurements discussed in this Brief Report, metal particles of about 20 nm diameter were kept isolated from each other in an insulating matrix. The experiment covered the frequency range from 1 MHz (radio waves) to 3 THz (FIR).

Usually the FIR experiments were discussed and interpreted by comparing the data with those obtained from the Maxwell Garnett (MG) effective-medium formula.[1,2,5] The dielectric function of the metal $\epsilon_{\text{metal}}=\epsilon^1_{\text{metal}}-i\epsilon^2_{\text{metal}}$ was taken from the classical Drude model of electron transport in bulk material.[5]

Instead of this synthesis (reconstruction from parts) we have extracted ϵ_{metal} from the measured response $\epsilon_{\text{eff}}=\epsilon^1_{\text{eff}}-i\epsilon^2_{\text{eff}}$ using the known dielectric function ϵ_{matrix} of the pure matrix. The comparison of several effective medium formulas has demonstrated that only the Landau-Lifshitz-Looyenga (LLL) formula yields reliable ϵ^2 values for strongly dissipative particles and filling factors $f<0.3$.[6,7] The differences between values calculated with the LLL formula and others like MG, Bruggeman-Rayleigh [alias symmetric Bruggeman (BR)], and asymmetric Bruggeman (B) are essential (Fig. 1) and increase by many orders of magnitude as $\epsilon^2_{\text{metal}}/\epsilon^2_{\text{matrix}}$ increases.

Here we show that the often claimed anomalous absorption enhancement of metal particles is a consequence of the chosen effective-medium analysis. The absorption $\alpha(s)$ even decreases with particle size s in the submicron domain, as became obvious in an experiment of particle growth (coalescence) at constant filling factor.[3,4]

The interaction of magnetic dipoles with electromagnetic waves was assumed to play a dominant role in the absorption of mesoscopic metals.[5,8] Microwave spectroscopy allows us to measure both magnetic and dielectric susceptibility[9] and proves that a magnetic interaction (eddy current contribution) is negligible.

II. ABSORPTION COEFFICIENT

In Fig. 2 we present data of the effective absorption coefficient α_{eff} of In (Refs. 3 and 4) and Al (Ref. 5) particles as a function of frequency ν. For a reasonable comparison we chose particles with the same size of about 20

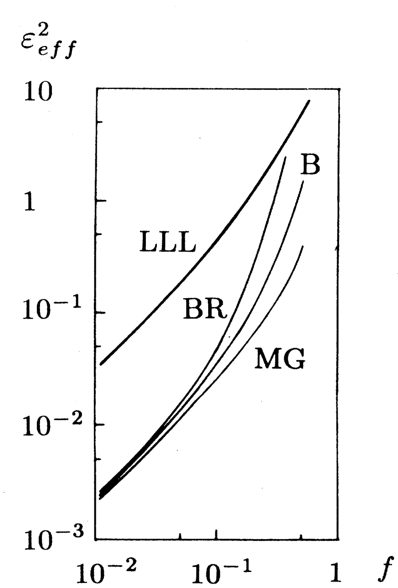

FIG. 1. Model calculations for a water ($\epsilon_{\text{water}}=60-i30$) in oil ($\epsilon_{\text{oil}}=2-i0$) system vs filling factor f of the water component. The LLL formula yields considerably larger values of the dissipative part ϵ^2_{eff} of the effective dielectric function than the MG, the B, and the BR formulas.

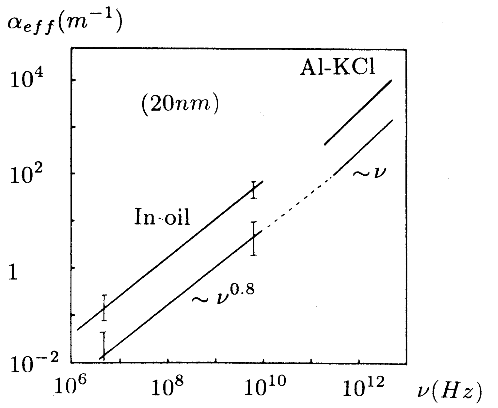

FIG. 2. log-log presentation of the effective absorption α_{eff} vs frequency ν for In (Refs. 3, 4, and 10) and Al (Ref. 5) colloids with metal particles of 20 nm diameter. The In data obtained between 1 MHz and 10 GHz and the Al FIR data give a uniform picture. The frequency dependence is roughly $\alpha\sim\nu^{0.8}$ below 10 GHz and $\alpha\sim\nu$ in the FIR. Upper curves, In-Oil ($f=0.3$) and Al-KCl (clustered particles); lower curves, In-Oil ($f=0.01$) and Al-KCl ($f=0.008$, nonclustered particles).

nm. In the whole frequency range displayed, the absorption of the different metals is conspicuously uniform. α_{eff} is roughly proportional to $\nu^{0.8}$ throughout the frequency range 1 MHz to 10 GHz. In the FIR range the slope in the log-log plot is close to unity. This result is in contradiction to the Drude power law $\epsilon_{\text{metal}}^2\sim\nu^{-1}$.

Two procedures were followed in order to get information about the dissipative component (metal particles and water droplets, respectively) stored in an insulating matrix. In the first one,[1,2,5,8] the measured effective dielectric function ϵ_{eff} was compared with the calculated one, using the MG formula and Drude-like bulk values for the metal component in the heterostructure. In the second procedure,[3,4,10] ϵ_{metal} was evaluated from the measured quantities ϵ_{eff} and ϵ_{matrix}. In the Introduction we have mentioned that at small f and high loss factors, the LLL formula should be used in order to calculate the dielectric function of metal particles from the measured effective dielectric function of the heterostructure. In the long-wavelength limit $\lambda\gg s$ the electromagnetic waves cause a coherent dipole coupling also at low filling factors. This coupling results in an enhanced effective response of the heterogeneous medium. Among the various effective-medium formulas displayed in Fig. 1, the LLL formula is the only one that accounts for this coupling. Tested with water micelles in a microemulsion,[6,7] in the range $f<0.3$, only the LLL formula yields results in agreement with the literature data of water. The discrepancy between values obtained with the LLL formula and with various other effective-medium formulas is demonstrated in Fig. 1. For pure water having $\epsilon_{\text{water}}=60-i30$ and $f<0.1$, the discrepancy is larger than 1 order of magnitude. This becomes many orders of magnitude if the loss factor is metalliclike ($\epsilon^2\gg10^4$).

Originally carried out at $\nu\leq10$ GHz,[3,4,10] our investigation yielded that the absorption by small metal particles is reduced with respect to bulk absorption. This was studied in an experiment with continuous growing of particle sizes at constant filling factor in the matrix. In view of the uniform behavior of α_{eff} for frequencies up to 3 THz, as shown in Fig. 2, the reduced absorption by small metal particles seems to be a general result. It was found recently that a size-induced metal-insulator transition (SIMIT) takes place[3,4] in various metal particles. The quasi-dc conductivity σ obeys an s^3 dependence which is equivalent to size-dependent absorption. The absorption data cannot be fitted by the Drude model nor by a magnetic dipole interaction.[5,8] It is interesting to mention that the quantum-size model by Gor'kov and Eliashberg[11] predicts the $\sigma\sim s^3$ dependence in a distinct range of particle sizes.[3,4]

III. DIELECTRIC VERSUS MAGNETIC DIPOLE INTERACTION

Microwave experiments with the H_{10} mode in a rectangular waveguide allow us to measure both the magnetic and the dielectric complex susceptibility tensor. As sketched in Fig. 3, the electric field E in the waveguide has its maximum in the center and vanishes at the walls. The magnetic field B, however, is constant across the waveguide. Thus, measuring the complex electromagnetic response in the center and at one wall, the electric and magnetic interaction can be separated.[9] Our measurements with several metal colloids yield a negligible magnetic dissipation ($\mu^2\ll0.1$).

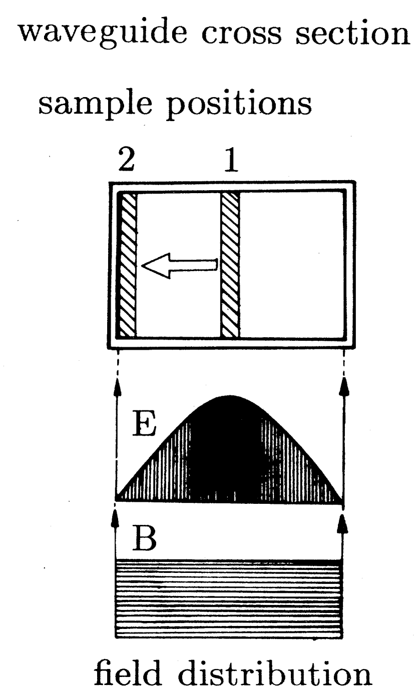

FIG. 3. Waveguide H_{10} mode. The distribution of electric field E and magnetic field B are presented in the lower part. Shifting the sample from the center to the wall allows the determination of both electric and magnetic susceptibility.

IV. CONCLUSION

Isolated mesoscopic (i.e., submicrometer) metals experience a size-induced metal-insulator transition in the quasistatic regime. With decreasing particle size the absorption coefficient, and thus, the quasi-dc conductivity, decrease. The experimental data of 20 nm In and Al particles between 1 MHz and 3 THz roughly follow the power laws $\alpha \sim \omega$. This behavior cannot be explained by classical electron transport but agrees qualitatively with the quantum-size model. As a general result, between radio and FIR frequencies the LLL effective medium analysis of all data reveals a low absorption by nanometer-sized crystals. Magnetic dipole interaction is negligible compared with the dielectric one as evidenced by microwave measurements.

ACKNOWLEDGMENTS

We gratefully acknowledge helpful discussions with G. Galeczki and B. Binggeli for the experimental data in the radio frequency range. The investigation is funded by the Deutsche Forschungsgemeinschaft (Bonn, Germany).

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