MICROWAVE ABSORPTION BY SMALL METAL PARTICLES

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The dielectric response of small indium and iron crystals in complementary particle topologies is characterized by microwave absorption. A transition from non-absorptive to conducting behaviour was discovered in condensed indium–oil dispersions during thermal particle coarsening. Microwave losses in low-density networks of iron "nanocrystals" (sizes $\leqslant 10$ nm) are attributed to percolation.

1. Introduction

The electronic properties of isolated small metal particles (diameters $x \lesssim 300$ nm) are expected to be remarkably different from those of the bulk material due to both classical and quantum size effects [1,2]. In search of absorption (α) depending on either a size-limited electron scattering length or on a confined electron gas, a number of spectroscopic experiments focused primarily on the response of highly dispersed metals to electromagnetic radiation at visible and far infrared (FIR) frequencies [1–5]. Composite small particle systems consisting of a metallic component dispersed in an insulating host are characterized by particle size (x), filling factor (f), and particle arrangement. Some representative topologies (weakly coupled, percolative, and fused clusters) have recently been analyzed by Curtin and Ashcroft [6].

Theoretical studies predict absorption coefficients that are smaller by several orders of magnitude as compared to experimental absorption data of small metal particles in the FIR regime [3,7]. This puzzling discrepancy may stem either from the variety of parameters involved or from a basic defect in the present understanding. The effects of particle size

and filling factor on α should be separable by controlled variation of x, for instance by heat treatments, leaving f constant during the experiments. If the samples display only one definite topology, absorption due to percolative particle clustering can be distinguished from that due to large sized isolated crystals. The theoretical quadratic dependence of α on the frequencies (ν) of electromagnetic radiation in the FIR [1] suggests to extend the experiments to the long-wavelength limit and to check whether the above mentioned discrepancy between theoretical and experimental absorption data still holds at lower ν. This report aims to demonstrate that besides visible light and FIR spectroscopy also microwaves may help to elucidate the absorption of topologically different small particle systems with controllable parameters (particle size, filling factor, and temperature). We present microwave absorption data on two model systems based on the production of "nanocrystals" ($x \lesssim 20$ nm): indium particles dispersed in a fluid oil matrix *(isolated particle behaviour* even at high filling factors) and iron nanocrystals accumulated in high vacuum *(percolative topology)*.

2. Sample preparation and characterization

2.1. Indium nanocrystals dispersed in silicon oil.

Matrix-isolated indium nanocrystals were produced in high vacuum by direct evaporation of the metal into a silicon oil film carried around the heater. By this technique [8], the particles are continuously embedded into the fluid host upon their formation at the film surface, yielding a dispersion with an initial filling factor $f_{In} \approx 0.005$. During subsequent centrifugation at 70 000 fold gravity, f_{In} was raised to about 0.25 ± 0.05 as determined gravimetrically. At constant f_{In}, particle sizes were increased on purpose by heating the system. As dominant particle coarsening was only observed near the melting point ($T_M = 430$ K) of bulk indium, the formation of larger crystals seems to be mediated by liquid particles. Owing to the low melting temperature of indium, heat treatments could be carried out in the oil matrix. The presence of indium metal particles in the condensed dispersion before and after first heating was checked by X-ray and electron diffraction. Initial and final particle sizes were $x_{In, I} \approx 10 \dots 20$ nm and $x_{In, F} \lesssim 300$ nm, respectively, by transmission electron microscopy and small angle X-ray scattering. Much less pronounced particle growth was observed for dispersions of lower densities, which emphasizes the importance of centrifugation. Residual oxide, identified as In_2O_3 by its diffraction pattern, did not obstruct the coalescence process whereas it helped to stabilize the dispersions below T_M.

2.2. Random percolative networks of iron nanocrystals.

In contrast to the matrix isolated indium particles, an oxide-free accumulation of iron nanocrystals (mean sizes $x_{Fe} \lesssim 10$ nm) produced in-situ by condensation in a low-pressure helium atmosphere [9], collected from a cold finger and sealed in quartz tubes under high vacuum, constitutes an almost ideal model of a cluster percolation topology. As the iron nanocrystals would not undergo any particle coarsening at room temperature due to their much higher metling point, they can be well kept in metallic contact with each other and studied for percolative effects at fixed particle sizes and low filling factors ($f_{Fe} \approx 0.04$). Although the nanocrystal networks exist in high vacuum without any other insulating host material, their densities are very low owing to the large

porosity which is typical of fine-grained random structures [10].

3. Microwave response of small metal particles in different topologies.

3.1.

The microwave transmission of the condensed indium dispersions was investigated in a partially filled rectangular wave guide, a method described elsewhere [11]. The samples were sealed in rectangular teflon boats or, alternatively, in inductive posts [12]. The quantities directly recorded were the amplitude and phase shift of the microwave beam. From these values, the complex permeability $\epsilon_{eff} = \epsilon' + i\epsilon''$, and hence the sample absorption coefficient α were derived. Fig. 1 displays the temperature dependence of ϵ' (dotted line) and ϵ'' (solid line) of an indium–oil dispersion with $f_{In} = 0.20 \pm 0.03$ and initial mean particle size $x_{In, I} \approx 10$ nm. At low temperatures, ϵ' and ϵ'' are identical to the values found for the pure oil matrix. Near the melting point of indium ($T_M = 430$ K), however, ϵ' and ϵ'' change with temperature. Above T_M, both quantities irreversibly saturate into values independent of T, indicative of a transition into a state of enhanced conductivity. Obviously, this effect is related to the indium particles as the pure oil did not show any changes of ϵ' and ϵ'' in the whole temperature interval investigated. From what is known about the thermal behaviour of the indium–oil com-
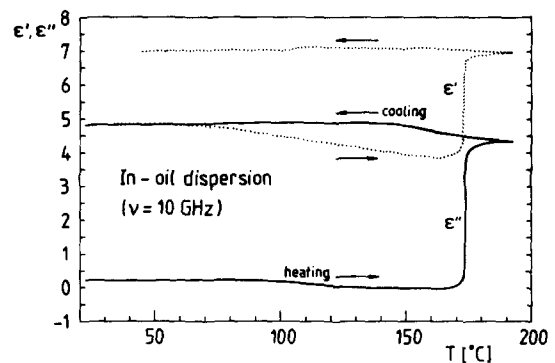

Fig. 1. Real (ϵ', dotted line) and imaginary (ϵ'', solid line) parts of the dielectric constant of an indium–oil dispersion versus temperature during the first heating cycle. The sharp increase of both ϵ' and ϵ'' above the melting temperature of the indium component indicates the transition to a state of metallic conductivity which, for this sample, is shifted towards higher temperature due to a lower filling factor ($f = 0.20 \pm 0.03$) than in fig. 2.
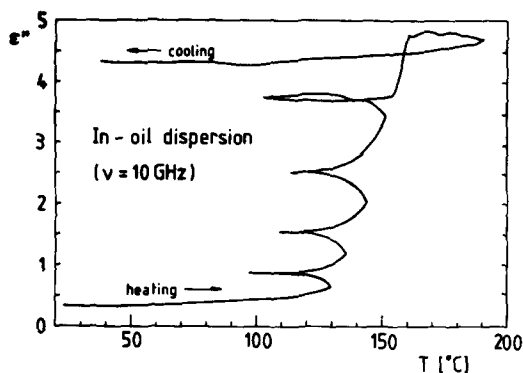
Fig. 2. Temperature dependence of ϵ'' of an indium–oil dispersion ($f = 0.25$) during a heating cycle which was repeatedly interrupted to reveal the irreversible and stepwise increase of conductivity. Note that the coalescence process is seen to set in at lower temperature and to cover a greater temperature interval than for a sample of smaller f as in fig. 1.

posites (see previous section), particle coarsening takes place while heating the samples and is most effective when the particles melt. According to the experimental results, the liquid state of the particles has no other detectable influence on ϵ' and ϵ''. When the first heating is repeatedly interrupted, the microwave transmission can be studied at various stages of coalescence (fig. 2).

According to the resolution of our microwave bridge ($\Delta\epsilon \lesssim 0.02$), the dielectric response is by at least two orders of magnitude smaller in the virgin state than in the heated ($T \geqslant T_M$) composite at the same f. In the state of higher conductivity, ϵ_{eff} (see fig. 1) yields an absorption coefficient $\alpha_{In, F} \approx 2.5$ cm^{-1}. Similar results were obtained with various samples of equally high filling factors by two microwave methods [11,12]. If left uncentrifuged ($f \approx 0.005$), the indium–oil composite did not show any transition to an enhanced conductivity, which is in agreement with the absence of particle coalescence at low densities of dispersion.

3.2. The random accumulations of iron nanocrystals ($x_{Fe} \approx 10$ nm) sealed under high vacuum in quartz tubes (inductive post geometry) absorbed microwaves already at distinctly lower densities ($f_{Fe} \approx 0.04$) than did the indium dispersions. At $\nu = 10$ GHz and $T \approx 300$ K, the absorption coefficient of the percolative nanocrystalline network was $\alpha_{Fe} \approx 1$ cm^{-1}. In order to avoid uncontrolled changes of f_{Fe} due to thermal

shrinkage, the iron networks were investigated at room temperature. In supplementary experiments, (see discussion) thermal effects on other networks were contrasted to those on the dispersions.

4. Discussion and conclusion

Evidently, the microwave conductivity of our two small particle systems can be attributed to crystal growth in the indium dispersions and to percolative interparticle contact in the iron networks. The observations on both topologies mutually support each other.

The iron networks represent the limit of extreme percolative behaviour in high vacuum at low filling factors and fixed particle sizes (8 ± 2 nm). From the absence of absorption in the much denser virgin indium dispersions, it may be concluded that, owing to their sizes, isolated nanocrystals do not exhibit microwave conductivity. If this were an interfacial effect due to a dielectric influence of the oil matrix on the electronic structure of the indium nanocrystals, the conductivity of the composite would be rather increased than suppressed [13]. The finite conductivity of the networks, therefore, does not originate from losses in individual iron nanocrystals. There is no evidence for particularly strong magnetic loss in the iron crystals. Our preliminary work on similar but diamagnetic systems indicates that gold nanocrystal networks absorb microwaves as effectively as iron networks do, even if kept in air at equally low f_{Au} $\approx f_{Fe}$ under conditions of less favourable interparticle contact. The indium dispersion in turn, is the model system for isolated particle behaviour at high filling factors with variable crystal sizes via thermally induced coalescence. The oil matrix secures particle isolation and homogeneous particle density in any state of the dispersion. Consequently, the occurrence of macroscopically percolative interparticle contact can be ruled out. The virgin state is not found conducting in contrast to the low-density iron and gold networks. If, on the other hand, percolative contact between grown crystals had developed during heating the particle density would have become smaller in the remainder of the sample volume. Due to the lower occupation by the absorptive component, this part of the volume would not contribute so effectively to the total absorption any more. This has been

simulated in supplementary experiments with networks of gold nanocrystals during thermal shrinkage. As the temperature is raised, the total absorption decreases in spite of the enhanced interparticle contact in the "sintered" sample. However, in contrast to the thermal behaviour of a network at constant total volume and filling factors, the dispersions show increasing absorption upon heating. The microwave response of small indium crystals increases by at least a factor of 100 when their sizes rise from $x_{In,I} \approx 10$ nm to $x_{In,F} \approx 300$ nm. Qualitatively, this marked effect is to be expected from model calculations by Granqvist [1] for f values as in our experiments. Classical (Drude, subscript D) or quantum arguments (Gor'kov–Eliashberg, subscript GE) predict power laws $\alpha_D \sim x^3$ or $\alpha_{GE} \sim x^5$. A quantitative fit of our experimental data, however, failed with either model when extrapolated to our measuring frequency of 10 GHz. Our result $(\alpha/f)_{In,F} \approx 7.5$ cm^{-1} is about two orders of magnitude larger than expected by the ν^2 law. A macroscopic percolative cluster at low f under high vacuum conditions like our iron network seems not to have been discussed yet by other authors.

We conclude that the discrepancy between theoretical and experimental absorption data of small metal particles as established in numerous FIR investigations still persists at microwave frequencies. We have pursued this enhancement of α in an in-situ transition covering the whole absorption range of interest. On the basis of our experiments which give results on both ϵ' and ϵ'' we can exclude ill-defined sample parameters for the misfit. To the best of our knowledge, microwave measurements have not yet been applied to three dimensional systems of highly dispersed metals under conditions of variable temperature, particle size, and filling factor. Our results demonstrate that microwave experiments are capable of sensitive detection in different particle topologies, condensed dispersions and low-density networks. Absorption effects a priori are not as strong for micro-

waves as in the case for FIR. The observed effects suggest that microwaves are suitable for further systematic investigations of the dependence of ϵ' and ϵ'' on the important parameters x, ν, f, and T. We hope that the questions raised by this work will stimulate further theoretical studies on electromagnetic wave response of small metal crystals. A more extensive paper on the subject is in progress.

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