

Substrate effects on infrared absorption in dielectric microcrystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 10037

(<http://iopscience.iop.org/0953-8984/3/50/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 10:58

Please note that [terms and conditions apply](#).

Substrate effects on infrared absorption in dielectric microcrystals

Shōsuke Mochizuki[†] and Raphael Ruppin[‡]

[†] Department of Physics, College of Humanities and Sciences, Nihon University,
3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156, Japan

[‡] Soreq Nuclear Research Centre, Yavne 70600, Israel

Received 5 November 1990, in final form 28 May 1991

Abstract. Infrared absorption spectra of MgO and NiO microcrystals deposited on dielectric and metallic substrates have been measured. With a metallic substrate the main absorption maximum occurred at a lower frequency than with a dielectric substrate. These effects are also calculated using the model of a small sphere near a substrate. An interpretation of the experimental results in terms of the model calculations is presented.

1. Introduction

The infrared absorption spectra of ionic microcrystals are dominated by surface phonon resonances. The absorption frequencies can be calculated exactly for isolated crystallites of various shapes [1–3]. However, optical experiments on microcrystals are usually performed on specimens containing a large number of particles which are not well separated and which are deposited on a substrate. While the effects of inter-particle interaction on the absorption spectrum have been the subject of many investigations [4–9], the subject of particle–substrate interaction has not been explored in detail. A method for calculating the absorption spectrum of a spherical crystallite above a substrate has recently been presented [10]. Calculations based on this method indicate that the most prominent effect caused by the presence of the substrate is the shift of the main absorption peak to the low-frequency side. Also, the spectrum is affected by a metallic substrate much more than by a dielectric substrate. To our knowledge, these theoretical predictions have not yet been verified experimentally. We present here the results of infrared absorption measurements on, firstly, MgO microcrystals having a well defined shape and size and, secondly, irregularly shaped NiO microcrystals. In both cases we compare the spectra obtained with dielectric and metallic substrates. The experimental method and results are described in section 2. The results of theoretical calculations for spherical MgO crystallites in the presence of similar substrates are presented in section 3. The interpretation of the experimental MgO data in terms of the theoretical results is discussed in section 4.

2. Experimental details

In order to observe the substrate effect, the microcrystal layers which are deposited on the metallic and dielectric substrates have to be sufficiently thin, i.e. quasi-two-dimensional. Inside a vacuum chamber, high-purity magnesium flakes were set on a

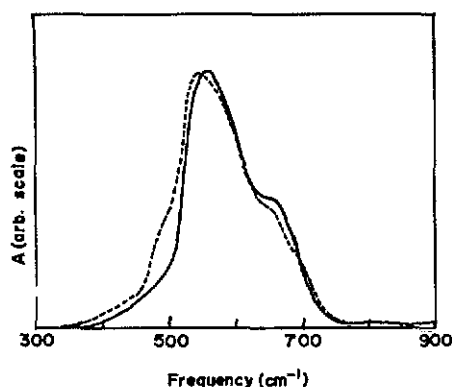


Figure 1. Measured absorption spectra of MgO microcrystals above a KRS-5 substrate (—) and above an aluminium substrate (---).

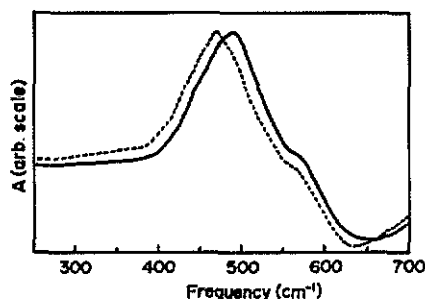


Figure 2. Measured absorption spectra of NiO microcrystals above a KRS-5 substrate (—) and above an aluminium substrate (---).

Nichrome heater. Two optically flat substrates, a KRS-5 (45.7% TlBr–54.3% TlI) disc and an aluminium evaporated mirror, and grids for electron microscopy were placed in a container separated by a shutter. The chamber was pumped out to 100 Torr and then sealed off. MgO smoke was produced by burning the magnesium flakes slowly by electric heating. After several minutes the shutter over the substrates and the grids was removed, allowing MgO microcrystals to accumulate for several hours. The MgO microcrystal layers were examined under an electron microscope. The crystallites were found to be cubes with an average dimension of 370 Å, dispersed quasi-two-dimensionally.

The reflectivity at near to normal incidence of the microcrystal-covered substrates was measured using a double-beam grating spectrophotometer. From the measured reflectivity we determined the absorption A using the method described in [11].

The infrared absorption spectra thus obtained are shown in figure 1. The full and broken curves show the absorption of the MgO microcrystals on KRS-5 and aluminium substrates, respectively. It can be seen that the main absorption maximum shifts by $\Delta = 14 \text{ cm}^{-1}$ towards low frequencies when we change from a dielectric substrate to a metallic substrate.

We note that no absorption peak appears at the transverse optical frequency $\omega_T = 401 \text{ cm}^{-1}$. This indicates that we have succeeded in reducing the effects of clustering. In previous experimental investigations, in which MgO cube-shaped microcrystals were produced by burning magnesium ribbons in air and collecting the smoke on a substrate [12, 13], a strong absorption peak appeared at ω_T . This was attributed to the formation of chain-like clusters. Our new method of slow burning in low-pressure air eliminates this aggregation feature. We have found that, when the thickness of the microcrystal layer is increased, the absorption peak at ω_T does indeed appear, and at the same time the main absorption structure becomes insensitive to the dielectric constant of the substrate. Thus, the quasi-two-dimensional dispersion of the crystallites is essential for observing the effects of the substrate on the absorption spectrum. For specimens obeying this thickness restriction the reproducibility of the spectra is good, with $\Delta = 14 \pm 2 \text{ cm}^{-1}$. Also, electron microscopy examination of the samples indicates that the density and orientations of the deposited microcrystals do not depend on the substrate material. Thus the shift of the main absorption band is due to the different electromagnetic properties of the two substrates.

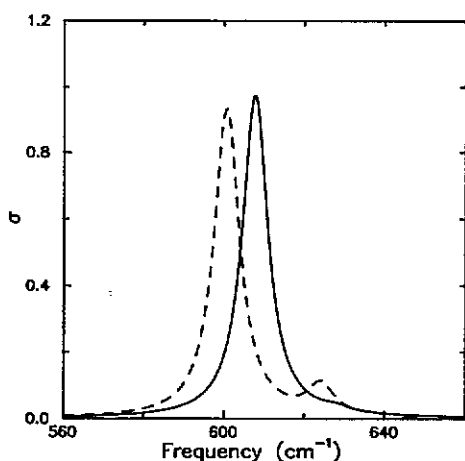


Figure 3. Calculated absorption cross section (in units of the geometric cross section) of a small MgO sphere above a KRS-5 substrate (—) and above a metallic substrate (---) for $D/R = 1.2$.

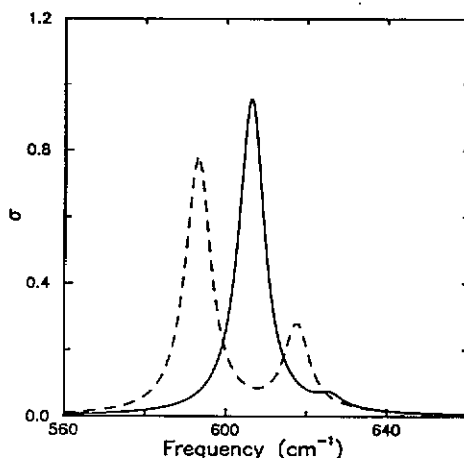


Figure 4. Same as figure 2, but for $D/R = 1.1$.

We have observed a qualitatively similar effect with NiO microcrystals deposited on KRS-5 and metal substrates (figure 2). For a metallic substrate the main absorption band was lower in frequency by about 20 cm^{-1} compared with that observed with a KRS-5 substrate. The NiO crystallites were, however, highly irregular in shape.

3. Calculations

We now restrict the discussion to the MgO case, in which the crystallites were cube shaped. In the absence of a theory for the optical properties of a cube-shaped microcrystal near a substrate, we have performed calculations for a MgO sphere near a substrate. The interpretation of the experimental results in terms of these calculations, taking the differences in geometry into account, will be presented in section 4. The absorption spectrum of a small spherical crystallite near a dielectric or metallic substrate can be calculated exactly using the technique presented in [10]. This method, which is based on developing the potentials in terms of harmonic functions in bispherical coordinates, is valid in the electrostatic limit, i.e. for microcrystals which are much smaller than the wavelength of the incident radiation. The microcrystals used in the present experiment are only 370 \AA in size and are well within this limit.

We have employed this theory to calculate the absorption cross section at normal incidence of a small MgO sphere above a KRS-5 substrate and above a metal substrate. The sphere radius was chosen so that the volume of the sphere is equal to that of a 370 \AA size cube. Of course, the measured absorption will also be proportional to the density of the microcrystals, which is not known. However, our aim here is to interpret the structure of the spectrum and we do not attempt to calculate the absolute value of the absorption. For the optical constants of MgO the experimental data due to Jasperse *et al* [14] have been employed. Examples of calculated spectra for two different microcrystal-substrate distances are shown. Figure 3 is for $D/R = 1.2$, and figure 4 is for $D/R = 1.1$,

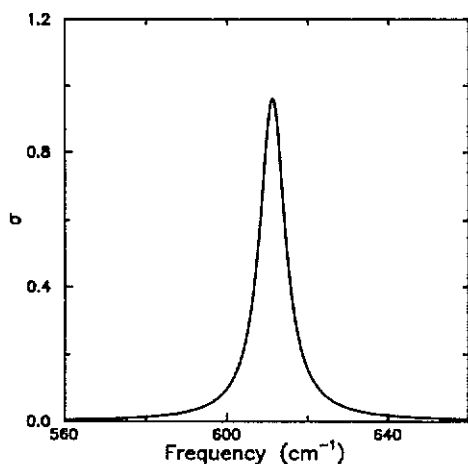


Figure 5. Calculated absorption cross section of a free small MgO sphere.

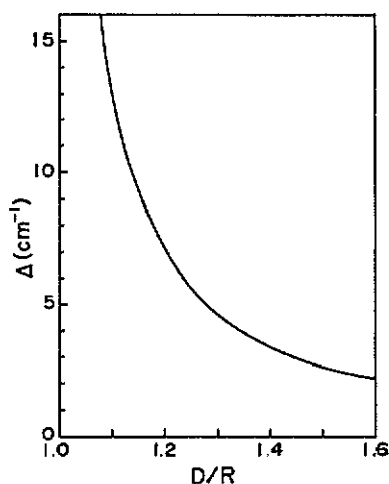


Figure 6. Calculated dependence of the shift $\omega_D - \omega_M$ on D/R .

where D is the distance from the sphere centre to the substrate and R is the sphere radius. For comparison, we show the spectrum calculated for a free sphere in figure 5. It is found that the presence of the substrate causes the main absorption peak to shift towards low frequencies. This shift increases with decreasing sphere-substrate separation, and it is larger for the metallic substrate than for the dielectric substrate. Let ω_D and ω_M denote the frequencies of the main absorption peaks for the dielectric and metallic substrate cases, respectively. Their separation $\Delta = \omega_D - \omega_M$ increases with decreasing distance from the substrate. The calculated dependence of Δ on D/R is shown in figure 6.

4. Discussion

In our MgO microcrystal specimens the distance between the cubes and the substrate is not uniform but is distributed about some average value. We cannot measure this average distance directly, but we can estimate it indirectly from the observed absorption spectra, using the following two plausible assumptions.

- (i) For a given microcrystal-substrate separation the shift of the absorption peak towards low frequencies is the same for a sphere and a cube.
- (ii) The average distance between the crystallites and the substrate is the same for the KRS-5 and the Al substrates.

From the experimental spectra (figure 1) we find that the separation Δ between the absorption maxima observed in the dielectric and the metallic substrate cases is 14 cm^{-1} . From the theoretical curve for a sphere (figure 6), we find that this value of Δ corresponds to $D/R = 1.094$. Thus, the average distance between the cube centres and the substrate is $(370/2) \times 1.094 = 202 \text{ \AA}$, and the average cube-substrate distance is 17 \AA .

The experimental data for cubes (figure 1) differ from the spectra calculated for spheres (figures 3 and 4) in peak position as well as in lineshape. These differences will now be discussed and interpreted.

4.1. Peak position

The absorption frequency ω_F of a small spherical crystallite in air is given by $\epsilon'(\omega_F) = -2$, where ϵ' is the real part of the frequency-dependent dielectric constant of the sphere material [1]. A small cube-shaped microcrystal has a number of absorption peaks, the dominant one occurring at a frequency ω_c given by $\epsilon'(\omega_c) = -3.68$ [2]. For MgO these frequencies are $\omega_F = 611 \text{ cm}^{-1}$ and $\omega_c = 566 \text{ cm}^{-1}$, respectively. For a sphere near a substrate the absorption band will occur below ω_F . For a cube near a substrate the absorption band should appear below ω_c . The experimentally observed structure (figure 1) is indeed in this frequency range.

4.2. Lineshape

The observed absorption band is much broader than that calculated for a sphere. This is because the calculated spectrum applies to a single sphere above a substrate, whereas the measured spectrum was obtained with a specimen containing a large number of microcrystals. The broadening of the absorption line due to the interaction between the particles has often been observed experimentally and also discussed theoretically [1, 4-9]. Inter-particle interaction inevitably occurs even in the quasi-two-dimensional arrangement of the crystallites achieved in our experiment. The calculations presented here suggest that the microcrystal-substrate interaction provides an additional broadening mechanism. This occurs because of the dependence of the peak position on the crystallite-substrate distance, and the fact that in the experimental specimen there exists a distribution of distances.

References

- [1] Ruppin R and Englman R 1970 *Rep. Prog. Phys.* **33** 149
- [2] Fuchs R 1975 *Phys. Rev. B* **11** 1732
- [3] Langbein D 1977 *J. Phys. A: Math. Gen.* **10** 1031
- [4] Clippe P, Evrard R and Lucas A A 1976 *Phys. Rev. B* **14** 1715
- [5] Ausloos M, Clippe P and Lucas A A 1978 *Phys. Rev. B* **18** 7176
- [6] Gerardy J M and Ausloos M 1980 *Phys. Rev. B* **22** 4950
- [7] Claro F 1982 *Phys. Rev. B* **25** 7875
- [8] Claro F 1984 *Phys. Rev. B* **30** 4989
- [9] Ruppin R 1989 *J. Phys. Soc. Japan* **58** 1446
- [10] Ruppin R 1983 *Surf. Sci.* **127** 108
- [11] Mochizuki S 1982 *Phys. Status Solidi b* **110** 219
- [12] Genzel L and Martin T P 1972 *Phys. Status Solidi b* **51** 91
- [13] Hayashi S, Nakamori N, Hirono J and Kanamori H 1977 *J. Phys. Soc. Japan* **43** 2006
- [14] Jasperse J R, Kahan A, Plendl J N and Mitra S S 1966 *Phys. Rev.* **146** 526