

## Spectral Function of Composites from Reflectivity Measurements

A. R. Day,<sup>1,\*</sup> A. R. Grant,<sup>2</sup> A. J. Sievers,<sup>2</sup> and M. F. Thorpe<sup>3</sup>

<sup>1</sup>Physics Department, Marquette University, Milwaukee, Wisconsin 53233

<sup>2</sup>Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

<sup>3</sup>Department of Physics & Astronomy, Michigan State University, East Lansing, Michigan 48824

(Received 24 August 1999)

We demonstrate a method of calculating the spectral function of a composite from measured reflectivity data. To solve this inverse problem it is necessary for the reflectivity data to be taken through a strong, high  $Q$ , resonance. By analyzing the reststrahlen region of different fill fraction KCl-diamond composites at three different temperatures, we find accurate spectral functions that are independent of temperature with the low temperature data giving the best resolution. These spectral functions are then used to successfully predict the optical response of RbCl-diamond composites.

PACS numbers: 72.80.Tm, 78.20.Bh, 78.30.Ly

The effective dielectric properties of a composite depend on both the dielectric properties of the constituent materials and on the geometry of the composite. In the Bergman-Milton [1,2] spectral formalism these two effects can be separated and the effective properties are given by an integral transform of a function, known as the spectral function, that depends only on the geometry of the composite [3,4]. The same spectral function will also determine the effective magnetic permeability, thermal conductivity, or any other property of the composite governed by Laplace's equation. In this Letter we show that an inverse method can be used to extract the spectral function from the measured reflectivity of a composite which contains at least one strong, high  $Q$ , resonance. Our results provide an important link between the spectral representation, one of the central ideas in two component composite theory, and the experimental study of composite materials. Interesting future applications should include ferroelectric/ferrimagnetic composites [5] and interstellar dust analogs [6,7].

We experimentally construct composites using a distribution of submicron sized diamond and KCl particles and measure the sample reflectance in the 40 to 200 micron wavelength region. For low temperatures these measurements provide data close enough to the branch cut in the complex plane to allow the spectral function to be accurately determined. Because the dielectric function of KCl varies rapidly with temperature, we use temperature dependent studies to demonstrate that the spectral function is indeed dependent only on the geometry of the composite. Finally, we demonstrate that the spectral function extracted from KCl-diamond data can successfully predict the experimental reflectance of RbCl-diamond composites.

For a two component material, with component dielectric constants  $\epsilon_A$  and  $\epsilon_B$ , respectively, the effective dielectric constant is given by

$$\frac{\epsilon_{\text{eff}}(s)}{\epsilon_A} = 1 - \int_0^1 \frac{h_A(x) dx}{s - x}, \quad (1)$$

where  $s = (1 - \epsilon_B/\epsilon_A)^{-1}$  and  $h_A(x)$  is the spectral function which contains all the geometric information necessary to determine the effective dielectric constant  $\epsilon_{\text{eff}}$ . The subscript  $A$  indicates that we are treating  $A$  as the host material and  $B$  as the inclusion.

Inverse problems like solving Eq. (1) to extract  $h_A(x)$  from measured values of  $\epsilon_{\text{eff}}(s)$  are often unstable and there is always some loss of information because of the broadening effect of the integral transform [8]. The numerical instability is overcome by regularization and loss of information is minimized if data are taken close to the cut where the kernel  $1/(s - x)$  is sharpest. Regularization is often based on *a priori* assumptions about the solution, but in this case we can use known properties [1-3,9-11] of the spectral function: It is positive or zero and restricted to the real interval  $x \in [0, 1]$ . The zeroth moment is equal to the volume fraction of the inclusion phase so

$$\int_0^1 h_A(x) dx = p_B, \quad (2)$$

and for any isotropic continuum material in three dimensions the first moment satisfies

$$\int_0^1 x h_A(x) dx = \frac{1}{3} p_B p_A. \quad (3)$$

When the  $B$  phase percolates the spectral function has a delta function at  $x = 0$  with weight that increases from zero at the percolation threshold to one when  $p_B = 1$ . It may also have another integrable singularity at the origin so we define a reduced spectral function  $g(x) = x h_A(x)$  such that

$$h_A(x) = \sigma_B \delta(x) + \frac{g(x)}{x}. \quad (4)$$

One may also choose  $B$  as the host material and  $A$  as the inclusion, in which case the spectral function becomes

$$h_B(x) = \sigma_A \delta(x) + \frac{g(1-x)}{x}, \quad (5)$$

where  $\sigma_A$  is nonzero when the  $A$  phase percolates and  $\int_0^1 h_B(x) dx = p_A$ . We choose to treat the volume fractions

$p_A$  and  $p_B$  as unknown variables that satisfy  $p_A + p_B = 1$  and impose a self-consistency constraint between the zeroth and first moments,  $\int_0^1 g(x) dx = \frac{1}{3}[\int_0^1 h_A(x) dx] \times [\int_0^1 h_B(x) dx]$ . These constraints, together with  $\sigma_A, \sigma_B \geq 0$  and  $g(x) \geq 0$  and restricted to the interval  $x \in [0, 1]$  are sufficient to regularize the inverse problem.

It is possible to obtain values of  $s$  that are close to the cut if the real part of  $\varepsilon_B/\varepsilon_A$  is negative and the imaginary part is small, which is the case if one component has a sharp dielectric resonance while the other is essentially inert in this specific frequency region. The real part of  $s(\omega)$  will pass from 0 to 1 for frequencies  $\omega$  between the transverse optical frequency,  $\omega_{TO}$ , and the longitudinal optical frequency,  $\omega_{LO}$ . This motivated our choice of a diamond-KCl composite because diamond is optically inactive in the far infrared where KCl has a strong resonance line. The method is not restricted to optically active/inert composites. For composites in which both components contain resonances,  $s(\omega)$  will still pass close to the cut in the frequency interval spanning a strong high  $Q$  resonance. An early attempt to extract the spectral function from experiment had limited success because data were not taken through a resonance [12]. More recent efforts [6,13–15] realized the importance of using data through a resonance line and obtained better results but were hampered by not having low temperature reflectivity data available.

Pure KCl was freezer milled to reduce the particle size and a powder mixture with the desired volume fraction of diamond powder was prepared by weighing. The mixture was then freezer milled again both to mix and to reduce the particle size further. Composite samples were prepared by pressing the material in an evacuated die cell to a pressure of 0.75 GPa. The samples were made approximately 7 mm thick with the back surface rounded to ensure that only reflections from the front surface were measured. The reflectivity of the sample and reference gold mirror could be examined sequentially in a variable temperature optical access cryostat. Polypropylene windows were used on the cryostat both because of its low reflectivity and also because of the negligible absorption in the reststrahlen region. Far-infrared (FIR) reflectivity measurements were made at three sample temperatures (5, 98, and 274 K) using a Bomem FTIR spectrometer with a 4.2 K Si bolometer detector.

A measured spectrum can be significantly altered by radiation entering the spectrometer from the sample chamber, two large sources being emission from the sample and background radiation reflecting from optical components in the sample chamber, such as cryostat windows. This problem was overcome by measuring both the sample and reference mirror with two FIR sources the intensity of one source much greater than the other, an Hg arc lamp, and a room temperature blackbody source, and then basically subtracting the spectrum with the weak source from that with the strong source.

We studied four samples that nominally had volume fractions of 0%, 5%, 20%, and 35% of diamond. On

further analysis it was found that all samples contained a small fraction of voids but for convenience we will refer to them as the pure, 5%, 20%, and 35% samples. The pure, 5%, and 20% samples all had the same KCl to void ratio of 97.2:2.8; the 35% sample was 59.3% KCl, 31.9% diamond, and 8.8% voids. The spectral representation [Eq. (1)] for the effective dielectric function is exact only for a two phase composite so we make the approximation of treating the samples as diamond (the  $B$  phase) in an effective matrix of 97.2% KCl, 2.8% voids (the  $A$  phase). The dielectric function of the  $A$  phase is determined from a multiple oscillator fit to reflectance data of the pure pressed pellet sample which has a broad reststrahlen band associated with the optical mode phonon of the KCl, and a smaller two-phonon peak at higher frequencies. Over this frequency range the dielectric function of diamond is treated as a constant,  $\varepsilon_B = 5.5$ . Between  $\omega_{TO}$  and  $\omega_{LO}$  of KCl the real part of the ratio  $\varepsilon_A/\varepsilon_B$  is negative and thus the complex variable  $s(\omega)$ , plotted in Fig. 1, passes near the cut, which is shown as a bold solid line. The low temperature resonance lines are sharper than the room temperature lines so the low temperature track is closer to the cut than the room temperature track.

The inverse problem is set up in the following way. Given a set of measurements of the reflectance of the composite,  $R_i$ , at frequencies  $\omega_i$  and using the dielectric functions of the two components at these frequencies,  $\varepsilon_A(\omega_i)$  and  $\varepsilon_B(\omega_i)$ , we do a nonlinear least squares fit adjusting the spectral function [expressed in terms of  $\sigma_A$ ,  $\sigma_B$ , and  $g(x)$ ] to minimize the function

$$\chi^2 = \chi_R^2 + \chi_{\text{constraint}}^2, \quad (6)$$

where

$$\chi_R^2 = \sum_i \{R_i - R[\varepsilon_A(\omega_i), \varepsilon_B(\omega_i), \sigma_A, \sigma_B, g(x)]\}^2. \quad (7)$$

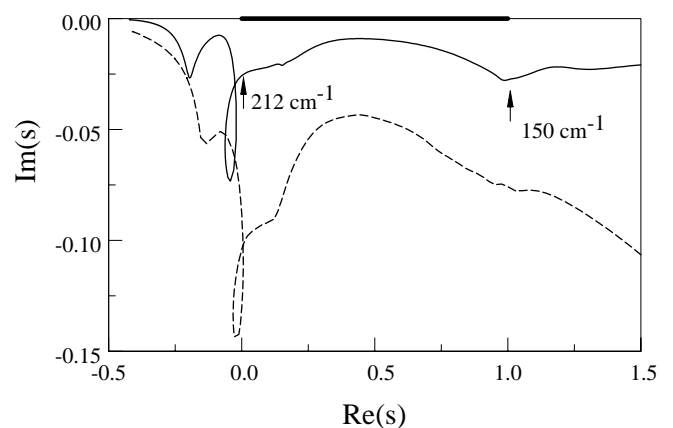


FIG. 1. The complex quantity  $s(\omega)$  shown at 5 K (solid curve), and 274 K (dashed curve). The arrows indicate the approximate frequencies of two points on the track,  $\omega_{TO}$  ( $150 \text{ cm}^{-1}$ ) and  $\omega_{LO}$  ( $212 \text{ cm}^{-1}$ ) and the bold straight line marks the cut. The loops are associated with two-phonon peaks.

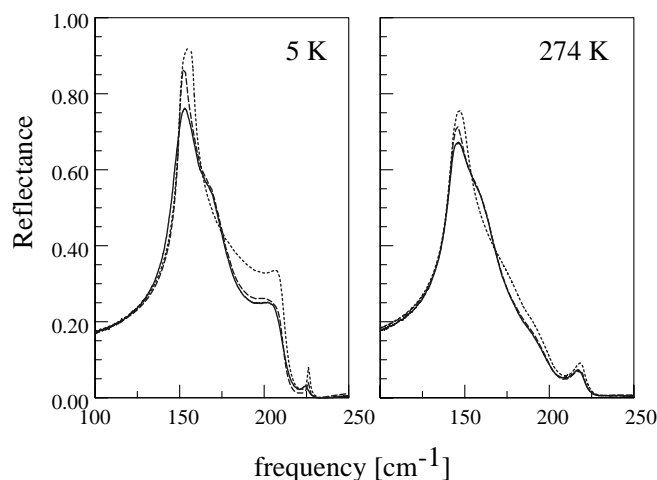


FIG. 2. The reflectance data of the 20% diamond sample at two different temperatures. The solid curves are the experimental data, the dashed curves are the best fit to the data, and the dotted curves are the effective medium theory.

Here

$$R[\varepsilon_A(\omega_i), \varepsilon_B(\omega_i), \sigma_A, \sigma_B, g(x)] = \left| \frac{\sqrt{\varepsilon_{\text{eff}}} - 1}{\sqrt{\varepsilon_{\text{eff}}} + 1} \right|^2 \quad (8)$$

and  $\varepsilon_{\text{eff}}$  is given by Eq. (1). The minimization routine is written to constrain  $g(x)$  to be non-negative and only nonzero in the interval  $[0, 1]$  and  $\chi^2_{\text{constraint}}$  imposes the constraints on the moments of the spectral function [10]. The reduced spectral function is represented by a histogram of 130 bins. Most of the previous attempts at this inverse problem [6,12,14,15] were based on model spectral functions with a few adjustable parameters. These can display only a limited amount of structure which is sufficient for fitting data that are far from the cut but inadequate for low temperature data where  $s(\omega)$  is very close to the real axis, as shown in Fig. 1. Our algorithm has been tested extensively on simulated reflectance data of model systems [10,11].

Figure 2 is a plot of the measured reflectance of the 20% sample at two temperatures. In the same figure we show the best fit to the reflectance obtained from the inverse method and, as a comparison, the reflectance given by a Bruggeman effective medium approximation (EMA) based on spherical inclusions. Figure 3 is a plot of the reduced spectral function extracted from the reflectance data shown in Fig. 2. At each temperature the result shown is an average from many different initial conditions that converge to approximately the same final  $\chi^2_R$ . These two figures clearly show that although the reflectance changes considerably with temperature the spectral functions obtained from the two data sets are very similar, demonstrating that the spectral function depends *only* on the geometry of the composite. The error bars on the high temperature curve are much greater than the error bars on the low temperature curve, indicating the importance of having low temperature data

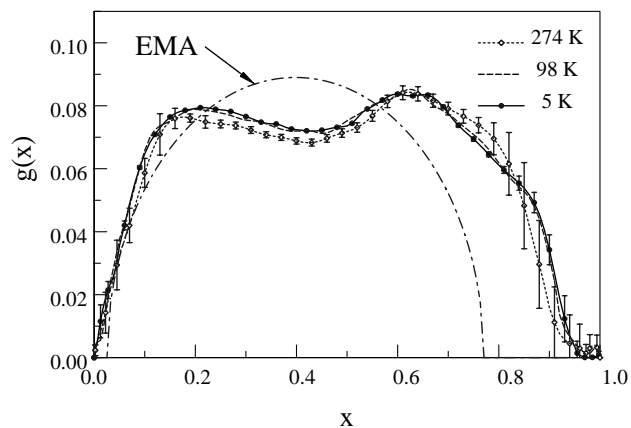


FIG. 3. The reduced spectral function  $g(x)$  for the 20% diamond sample, obtained from the reflectance data at three different temperatures. Representative error bars of 1 standard deviation are shown for the room and the low temperature data.

to get the maximum detail in the spectral function. The error bars are largest near  $x = 0$  and  $x = 1$  where the  $s(\omega)$  curve loops away from the cut and where the fitting procedure has trouble separating the delta functions from the reduced spectral function. The fit to the reflectance data (Fig. 2) is generally good but there are deviations, which may be associated with strain broadening of the KCl resonance line.

Figure 4 is a plot of the reduced spectral function  $g(x)$  obtained from the low temperature data for the three different samples with the curves scaled so each has unit weight. The weights of the delta functions,  $\sigma_A$  and  $\sigma_B$ , are also obtained from the fitting procedure. We find that  $\sigma_A$  decreases from 0.86 to 0.58 to 0.32, and  $\sigma_B$  increases from 0.0 to 0.01 to 0.13, as the volume fraction of diamond increases [16]. In Fig. 4 note how the spectral function broadens as the volume fraction of the inclusion phase increases and that all three curves have a gap near  $x = 1$  because they are well above the percolation threshold of the A phase, as is indicated by the nonzero values of  $\sigma_A$ .

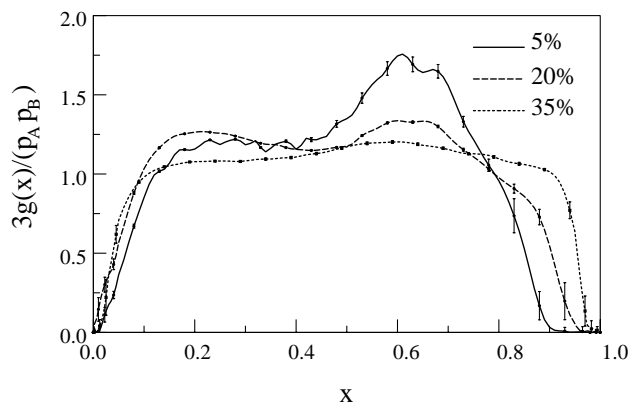


FIG. 4. The reduced spectral functions  $g(x)$ , scaled by  $p_A p_B / 3$ , as obtained from the low temperature data for the three different diamond concentrations. Representative error bars of 1 standard deviation are shown.

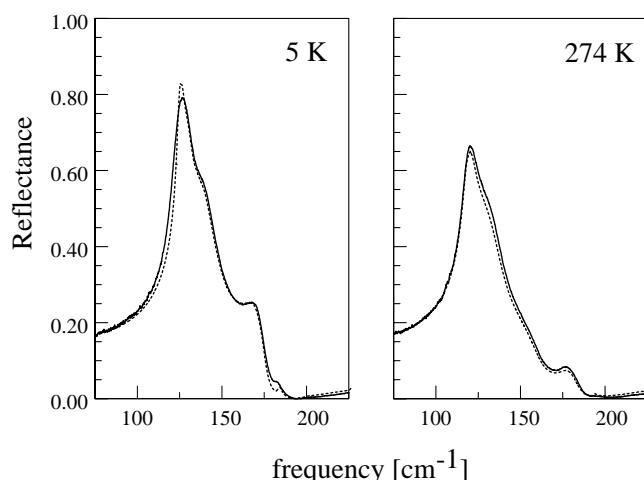


FIG. 5. The measured reflectance data (solid curves) for the 20% diamond in RbCl sample at two different temperatures, and the predicted reflectance (dotted curves) calculated from the spectral function of the 20% diamond in KCl sample, the dielectric function of diamond, and the dielectric function obtained from the pure RbCl pressed pellet.

For the 20% sample the small value of  $\sigma_B$  and the fact that  $g(x)$  extends all the way to  $x = 0$  suggests that the diamond phase is just above the percolation threshold but this result is within the noise. The 5% sample has a small gap at  $x = 0$  because it is well below the percolation threshold of the diamond phase; the 35% sample also has a small gap at  $x = 0$  because it is well above the percolation threshold.

The fitting procedure gives the volume fraction of the A phase for the three samples as  $p_A = 0.92, 0.75,$  and  $0.59$ . The measured volume fractions of KCl plus voids are  $0.951, 0.806,$  and  $0.681$ , respectively. We attribute the differences to the approximation of treating the KCl and voids as a single phase and the imperfect fit to the reflectance data. Our approach works well for the 5% and 20% samples but not so well for the 35% sample which has a much larger volume fraction of voids.

Although the spectral function does not determine the geometry uniquely, we have tested how well our result can be used to describe composite systems with statistically similar microstructures, which should have the same spectral function. Using the spectral function obtained from the KCl-diamond samples and a dielectric function determined by a multiple oscillator fit to a pressed pellet of pure RbCl (that contained 2% voids) we calculate the reflectivity of RbCl-diamond composite samples containing 5%, 20%, and 35% diamond and compare our findings to the reflectivity results measured for these three fill fractions. In Fig. 5 we show the predicted and measured reflectance for the 20% sample at two temperatures. The predicted curve agrees with the measurement to the same accuracy as the original fit to the KCl-diamond reflectance data for the 20% sample, shown in Fig. 2.

In summary, we have shown how the spectral function can be extracted from experimental reflectivity data by

using an inverse method and that the most accurate determination of the spectral function comes from the low temperature data. The successful application of the spectral function determined for one composite to predict the optical properties of a chemically different but structurally similar second composite has been demonstrated. Our results suggest that reflectivity data in the reststrahlen region of the more complex ferroelectric/ferrimagnetic composites [5] could be used to accurately predict the effective permeability and permittivity in a completely different frequency regime, a class of problems of some practical importance.

This work was supported by NSF Grants No. DMR-97-04099 and No. DMR-9979483 and by NASA Grant No. NAG5-4504. One of us (A. R. D.) thanks the Center for Fundamental Materials Research at Michigan State for sponsoring summer visits to Michigan.

\*Corresponding author.

Email address: dayroy@marquette.edu

- [1] D. J. Bergman, Phys. Rep. **43**, 378 (1978); Phys. Rev. Lett. **44**, 1285 (1980); Phys. Rev. B **23**, 3058 (1981).
- [2] G. W. Milton, Appl. Phys. Lett. **37**, 300 (1980); J. Appl. Phys. **52**, 5286 (1981); **52**, 5294 (1981).
- [3] K. Ghosh and R. Fuchs, Phys. Rev. B **44**, 7330 (1991).
- [4] K. Hinsien and B. U. Felderhof, Phys. Rev. B **46**, 12955 (1992).
- [5] J. V. Mantese, A. L. Micheli, D. F. Dungan, R. G. Geyer, J. Baker-Jarvis, and J. Grosvenor, J. Appl. Phys. **79**, 1655 (1996); G. W. Milton, D. J. Eyre, and J. V. Mantese, Phys. Rev. Lett. **79**, 3062 (1997).
- [6] R. Stognienko, Th. Henning, and V. Ossenkopf, Astron. Astrophys. **296**, 797 (1995).
- [7] N. I. Agladze, A. J. Sievers, S. A. Jones, J. M. Burlitch, and S. V. W. Beckwith, Astrophys. J. **462**, 1026 (1996).
- [8] G. Cowan, *Statistical Data Analysis* (Clarendon Press, Oxford, 1998), pp. 153–187.
- [9] K. Golden and G. Papanicolaou, Commun. Math. Phys. **90**, 473 (1983).
- [10] A. R. Day and M. F. Thorpe, J. Phys. Condens. Matter **11**, 2551 (1999).
- [11] A. R. Day, M. F. Thorpe, A. R. Grant, and A. J. Sievers, Physica (Amsterdam) **279B**, 17 (2000).
- [12] D. Stroud, G. W. Milton, and B. R. De, Phys. Rev. B **34**, 5145 (1986).
- [13] J. Sturm, P. Grosse, and W. Theiss, Z. Phys. B **83**, 361 (1991).
- [14] M. Hornfeck, W. Theiss, and R. Clasen, J. Non-Cryst. Solids **145**, 154 (1992).
- [15] W. Theiss, *Festkörperprobleme: Advances in Solid State Physics*, edited by R. Heilbrig (Vieweg, Braunschweig, 1994), Vol. 33, p. 149.
- [16] The weight of the delta function is the normalized dc conductivity of a conducting/insulating composite with the same microstructure.