

## Optical sum rules and effective-medium theories for a polycrystalline material: Application to a model for polypyrrole

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We derive sum rules for the effective dielectric function  $\epsilon_e(\omega)$  of a polycrystalline material, under the assumption of macroscopic isotropy. If the material comprising the polycrystal is a quasi-one-dimensional or quasiplanar Drude metal, we predict that part of the oscillator strength of the polycrystal is pushed up in frequency to form an “impurity” band of confined plasmonlike excitations. Under an additional condition of “strong isotropy,” we calculate the center of gravity of this band, in terms of the zero-frequency conductivity of the polycrystal. Analogous predictions are given for the energy-loss function,  $-\text{Im}\epsilon_e^{-1}(\omega)$ . The effective-medium theory for a polycrystal composed of approximately spherical crystallites is shown to satisfy this condition of strong isotropy. A more general effective-medium theory for ellipsoidal crystallites does not satisfy strong isotropy. It does, however, obey the only sum rule which is valid for any microstructure, namely, the sum rule on the spectral density. As an application, we describe a simple effective-medium model which qualitatively accounts for the ac electromagnetic properties of polypyrrole, over a broad range of frequencies, based on the assumption of polycrystallinity. Many features of the observed optical constants are found consistent with the existence of a broad localized plasmon band arising from polycrystallinity.

### I. INTRODUCTION

Many crystals have highly anisotropic transport and optical properties. For example, the conductivities of most organic conductors are orders of magnitude larger along one preferred direction than in the other two. Another important example is the  $\text{CuO}_2$ -based high-temperature superconductors, which in their normal state conduct much better in the  $ab$  plane than in the  $c$  direction. Their superconducting properties are similarly anisotropic.

As single crystals, these materials have well-defined conductivity (or dielectric) tensors, which reflect the underlying crystal structure. But very often they are found in “polycrystalline” form—i.e., the direction of the crystal symmetry axis varies randomly point to point. Such polycrystals are sometimes desired for practical applications. In other cases, the single-crystal form may be difficult to prepare. In either case, one wishes to know how to calculate the transport and optical properties of such a polycrystal, given the single-crystal properties.

In this paper, we derive several sum rules for the a.c. electrical response of polycrystals. The derivation assumes that the quasistatic approximation holds valid even at relatively high frequencies  $\omega$ , where the differences between the principal components of the dielectric tensor are presumed small. With these assumptions, the effective polycrystal dielectric function  $\epsilon_e(\omega)$  can be obtained at high  $\omega$  from perturbation theory. (The derivation does not assume that this expansion is valid at lower  $\omega$ , since at such  $\omega$ 's there may be large differences between the principal components.) If, in addition, the correlation functions in the polycrystal satisfy a certain condition we call “strong isotropy,” then  $\epsilon_e(\omega)$  can be written down explicitly through second order in the differences between the principal components. A Kramers-Kronig analysis then leads directly to the sum rules. If

“strong isotropy” is not satisfied, then an explicit form for  $\epsilon_e$  is possible only to first order, and only the sum rules on the oscillator strength are rigorously valid.

These sum rules are useful, for example, when the single crystal has a Drude conductivity in one (or two) crystalline directions, and is an insulator in the other directions. Then the oscillator strength sum rule, when combined with that arising from strong isotropy, implies the existence of a band of confined plasmonlike optical excitations. This band has finite oscillator strength at nonzero  $\omega$ , but does not contribute to the zero-frequency Drude peak of the polycrystal. Given the static conductivity of the polycrystal, and assuming strong isotropy, the sum rules fix the center of gravity of the confined plasmon band. A similar analysis applies to the energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$  of the polycrystal, and its localized plasmon band. If the strong-isotropy sum rule is not satisfied, then no exact statement can be made about the center of gravity of the localized plasmon band, although the band is still expected to exist on physical grounds.

The commonest scheme for estimating  $\epsilon_e$  is known as the effective-medium approximation (EMA).<sup>1-4</sup> The EMA involves embedding an ellipsoidal crystallite in a self-consistently determined background medium. All such effective-medium theories, when applied to metal-insulator composites, invariably produce confined plasmon bands. As we will show, several<sup>1,2</sup> also satisfy the first-order sum rule, as required for all isotropic composites. The EMA for spherical crystallites also satisfies the second-order sum rule, which is required when strong isotropy is obeyed. The EMA for ellipsoidal crystallites is nonetheless applicable to appropriate geometries, because strong isotropy is not necessarily obeyed by all isotropic composites.

As an illustration, we apply the EMA to a model for the quasi-one-dimensional (1D) metal polypyrrole, under the assumption that it is effectively polycrystalline. Confined plasmonlike bands have been reported experimentally in

polypyrrole,<sup>5,6</sup> and similar behavior has been observed in other quasi-1D metals.<sup>7,8</sup> Our results thus suggest one possible explanation for these measurements. Obviously, there are other mechanisms which could produce such bands (e.g., excitations in grain boundaries, quantum-mechanical localization of charge carriers in a disordered material). But the polycrystalline mechanism would produce such a band under quite general geometrical conditions. Our calculations not only illustrate the influence of polycrystallinity, but also show how different crystallite shapes would alter the observed optical spectra.

We turn now to the body of this paper. In Sec. II, we derive an expansion for  $\epsilon_e$  in a polycrystal. The expansion is valid through first or second order in the differences between the principal components of the single-crystal dielectric function  $\epsilon(\omega)$ , depending on whether the strong-isotropy condition is satisfied. From this expansion we obtain the desired sum rules. Section III discusses the degree to which several common effective-medium approximations for  $\epsilon_e(\omega)$  are consistent with these sum rules. In Sec. IV, we use the sum rules to calculate the centers of gravity of the confined plasmon bands in a model quasi-1D or quasi-2D Drude metal, assuming strong isotropy. We also use an EMA to calculate the optical properties of a model for a polycrystalline sample of polypyrrole. A brief discussion follows in Sec. V.

## II. FORMALISM

### A. Exact results for $\epsilon_e$ through first or second order

Our approach closely follows that of Ref. 1 for several steps. We consider a volume  $V$  of polycrystalline material in the quasistatic limit, where the local electric field  $\mathbf{E}$  can be written as the negative gradient of a scalar potential  $\Phi$ . To define  $\epsilon_e$ , we imagine the polycrystal to be enclosed by a surface  $S$ , on which the potential  $-\mathbf{E}_0 \cdot \mathbf{x}$  is specified. The space-averaged electric field within the composite is then just  $\mathbf{E}_0$ .<sup>1</sup>  $\epsilon_e$  is defined by

$$\epsilon_e = \epsilon_{av} + \langle \chi(\mathbf{x}) \rangle, \quad (1)$$

where  $\epsilon_{av} \equiv \langle \epsilon(\mathbf{x}) \rangle$ , the triangular brackets denoting an ensemble average, which we assume to be position independent. For a polycrystalline material, the ensemble average is simply an average over crystallite orientations of the (tensor) quantity enclosed in the brackets. If the crystallites are randomly oriented, so that the material at  $\mathbf{x}$  has equal probability of pointing in any direction, then it can be shown that  $\epsilon_{av} = \frac{1}{3} \sum_{i=1}^3 \epsilon_i$ , where the  $\epsilon_i$ 's are the principal values of the tensor  $\epsilon_j$ .<sup>9</sup>  $\chi$  is defined by

$$\epsilon(\mathbf{x})\mathbf{E}(\mathbf{x}) = \chi(\mathbf{x})\mathbf{E}_0, \quad (2)$$

where  $\mathbf{E}(\mathbf{x})$  is the local electric field, and satisfies

$$\chi(\mathbf{x}) = \delta\epsilon(\mathbf{x}) + \delta\epsilon(\mathbf{x}) \int_V \mathcal{F}(\mathbf{x}, \mathbf{x}') \chi(\mathbf{x}') d\mathbf{x}', \quad (3)$$

where  $\delta\epsilon(\mathbf{x}) \equiv \epsilon(\mathbf{x}) - \epsilon_{av}$ .  $\mathcal{F}$  is defined by

$$\mathcal{F}_{ij}(\mathbf{x}, \mathbf{x}') = -\frac{\partial^2}{\partial x'_i \partial x_j} G(\mathbf{x}, \mathbf{x}'), \quad (4)$$

where  $G$  obeys the differential equation

$$\nabla \cdot \epsilon_{av} \nabla G(\mathbf{x}, \mathbf{x}') = -\delta(\mathbf{x} - \mathbf{x}'). \quad (5)$$

Also,  $\mathcal{F}$  satisfies the boundary condition

$$\mathcal{F}(\mathbf{x}, \mathbf{x}') = 0, \quad (6)$$

for  $\mathbf{x}'$  on  $S$ . In the limit of a very large system, assuming that  $\epsilon_{av}$  is isotropic,  $G$  approaches the free-space solution

$$G(\mathbf{x}, \mathbf{x}') = \frac{1}{4\pi\epsilon_{av}|\mathbf{x} - \mathbf{x}'|}. \quad (7)$$

The sum rules are derived by considering  $\epsilon_e$  when  $\chi$  is small. Of course,  $\chi$  is typically not small. But at sufficiently high frequencies, where  $\epsilon(\mathbf{x})$  approaches a multiple of the unit tensor,  $\chi$  is indeed small, and only in this region does the derivation actually require a small  $\chi$ .

If  $\chi$  is small, then  $\chi(\mathbf{x}')$  on the right-hand side of Eq. (3) can be replaced by  $\delta\epsilon(\mathbf{x}')$ —a substitution which is correct through second order in  $\delta\epsilon(\mathbf{x}')$ . We then take the ensemble average of Eq. (3), using the fact that  $\langle \delta\epsilon(\mathbf{x}) \rangle = 0$ , to obtain

$$\langle \chi_{ij}(\mathbf{x}) \rangle = \sum_k \sum_l \int \langle \delta\epsilon_{ik}(\mathbf{x}) \mathcal{F}_{kl}(\mathbf{x}, \mathbf{x}') \delta\epsilon_{lj}(\mathbf{x}') \rangle d\mathbf{x}', \quad (8)$$

where the subscripts denote Cartesian components of tensor quantities.<sup>10</sup>

Now, because the ensemble-averaged composite is assumed homogeneous and isotropic, it follows that  $\langle \chi_{ij}(\mathbf{x}) \rangle$  is a multiple of the unit tensor,  $\langle \chi_{ij}(\mathbf{x}) \rangle = \langle \chi_{ii}(\mathbf{x}) \rangle \delta_{ij}$ . Substituting this result into Eq. (8), we obtain

$$\sum_{i=1}^3 \langle \chi_{ii}(\mathbf{x}) \rangle = \sum_{k=1}^3 \sum_{l=1}^3 \int_V \mathcal{F}_{kl}(\mathbf{x}, \mathbf{x}') g_{lk}(\mathbf{x}', \mathbf{x}) d\mathbf{x}', \quad (9)$$

where

$$g_{lk}(\mathbf{x}', \mathbf{x}) \equiv \sum_{i=1}^3 \langle [ \delta\epsilon(\mathbf{x}') ]_{li} [ \delta\epsilon(\mathbf{x}) ]_{ik} \rangle. \quad (10)$$

It is not possible to evaluate the right-hand side of Eq. (9) for the most general form of  $g_{lk}$  allowed by symmetry, even in a macroscopically isotropic medium. If, however,  $g_{lk}$  satisfies a “strong-isotropy” hypothesis,

$$g_{lk}(\mathbf{x}, \mathbf{x}') = g(\mathbf{x} - \mathbf{x}') \delta_{lk}, \quad (11)$$

then  $\chi_{ii}$  can be evaluated explicitly to second order in  $\delta\epsilon$ . For a polycrystalline material,  $\delta\epsilon(\mathbf{x})$  varies in space only because of the random orientation of the crystal axes. Physically, assumption (11) means that, while the directions of the crystal axes may be correlated at different points in space, that correlation depends only on the position vector connecting the two points, and is characterized by a single scalar quantity.

Substituting Eq. (11) into Eq. (9) gives

$$\sum_{i=1}^3 \langle \chi_{ii}(\mathbf{x}) \rangle = \int g(\mathbf{x} - \mathbf{x}') \sum_{k=1}^3 \mathcal{F}_{kk}(\mathbf{x}' - \mathbf{x}) d\mathbf{x}', \quad (12)$$

or, on using the definition (4) and the differential equation (5),

$$\sum_i \langle \chi_{ii}(\mathbf{x}) \rangle = -\frac{g(0)}{\epsilon_{\text{av}}}. \quad (13)$$

Here

$$\begin{aligned} g(0) &= \sum_j \langle \delta\epsilon_{ij}(\mathbf{x}) \delta\epsilon_{ji}(\mathbf{x}) \rangle = \frac{1}{3} \text{Tr}[\delta\epsilon(\mathbf{x})^2] \\ &= \frac{1}{3} \sum_i (\epsilon_i - \epsilon_{\text{av}})^2, \end{aligned} \quad (14)$$

where  $\epsilon_{\text{av}} = \frac{1}{3} \sum_i \epsilon_i$  as before. Combining all these results, we finally obtain the correct form for  $\epsilon_e$  through second order in the quantities  $\epsilon_i - \epsilon_{\text{av}}$ , under the assumption of strong isotropy:

$$\epsilon_e = \epsilon_{\text{av}} - \frac{1}{9} \frac{\sum_{i=1}^3 (\epsilon_i - \epsilon_{\text{av}})^2}{\epsilon_{\text{av}}}. \quad (15)$$

This is the same result that would be obtained for a three-component composite having equal volume fractions of three *isotropic* components  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$ . If, in particular, we have a uniaxial composite with principal dielectric constants  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_2$ , Eq. (15) becomes

$$\epsilon_e = \frac{1}{3} \epsilon_1 + \frac{2}{3} \epsilon_2 - \frac{2}{9} \frac{(\epsilon_1 - \epsilon_2)^2}{\epsilon_1 + 2\epsilon_2}. \quad (16)$$

A similar result was derived many years ago by Herring,<sup>11</sup> using quite a different approach.

The results (15) and (16), as pointed out above, depend on the assumption we denote “strong isotropy.” We believe that this assumption need not be satisfied in all polycrystalline materials, even macroscopically isotropic ones. It may be satisfied if the crystallites are approximately spherical. But, for reasons further discussed below, if the crystallites are nonspherical ellipsoids, then it is likely that assumption (11) for the correlation function does not hold valid. When strong isotropy is not satisfied, the second-order term may be more complicated than given above. So far, we have not succeeded in evaluating it in closed form. Thus, in this more general case, only the first-order sum rules given below are guaranteed to be exact.

### B. Sum rules for the spectral density

Just as for binary composites, the high-frequency limiting behavior of  $\epsilon_e$  [Eq. (16)], when combined with the Kramers-Kronig relations, leads to sum rules on  $\text{Im}\epsilon_e$ . As an illustration, consider a polycrystal of a quasi-1D metal, with a Drude dielectric function  $\epsilon_1 = 1 - \omega_p^2/\omega^2$  in the  $x$  direction and a constant dielectric function  $\epsilon_2 = 1$  in the  $y$  and  $z$  directions. Approximation (16) applies at sufficiently high frequencies, provided that strong isotropy is satisfied. Then the sum rules take the form<sup>12</sup>

$$\int_0^\infty \text{Im} \epsilon_e(\omega') \omega' d\omega' = \frac{\pi}{2} p \omega_p^2, \quad (17)$$

and

$$\int_0^\infty \text{Im}[\epsilon_e(\omega') - \epsilon_{\text{av}}(\omega')] \omega'^3 d\omega' = \frac{\pi}{6} p(1-p) \omega_p^4, \quad (18)$$

where  $p = \frac{1}{3}$ . In the absence of “strong isotropy” [Eq. (11)], only the first is valid.

Analogous sum rules can be obtained for the energy-loss function  $-\text{Im}[1/\epsilon_e(\omega)]$ . These take the form

$$-\int_0^\infty \text{Im}\left(\frac{1}{\epsilon_e(\omega')}\right) \omega' d\omega' = \frac{\pi}{2} p \omega_p^2, \quad (19)$$

and

$$\int_0^\infty \text{Im}\left(\frac{1}{\epsilon_e(\omega')} - \frac{1}{\epsilon_{\text{av}}(\omega')}\right) \omega'^3 d\omega' = \frac{\pi}{6} p(1-p) \omega_p^4, \quad (20)$$

where  $p = \frac{1}{3}$ . Again, only the first of these holds unless the strong-isotropy assumption is valid.

The above results also apply to a polycrystal made up of a quasi-two-dimensional (2D) metal described by a Drude dielectric function in the  $y$  and  $z$  directions, and by a frequency-independent dielectric function of unity in the  $x$  direction. The only required change in Eqs. (17)–(20) is that  $p = \frac{2}{3}$  rather than  $\frac{1}{3}$ .

### III. CONNECTION TO EFFECTIVE-MEDIUM THEORIES

In the EMA, the electric field within each crystallite is calculated as if the crystallite is embedded in a homogeneous effective medium, of dielectric function  $\epsilon_e$ , which is self-consistently determined. Typically, it is assumed that the crystallite has some convenient shape (usually ellipsoidal). If the crystallites are randomly oriented, the effective medium is isotropic and  $\epsilon_e$  is a scalar.

Two such effective-medium approximations for polycrystals have been used in the literature. Both assume ellipsoidal inclusions whose principal axes are degenerate with the crystal axes, but carry out the field averaging in different ways. Sulewski *et al.*<sup>2</sup> average the dipole fields produced by an ellipsoidal inclusion embedded in an effective medium, and choose the medium so that these fields vanish, on average. Walker and Scharnberg,<sup>3</sup> on the other hand, average the internal fields within the inclusion, and use as a self-consistency condition the requirement that the averaged internal fields should equal the field far from the inclusion. Both these approaches have been presented by Noh, Song, and Sievers.<sup>4</sup>

The dipole-averaging EMA (Ref. 2) may be written

$$\frac{1}{3} \left( \frac{\epsilon_1 - \epsilon_e}{2[(1-g_1)\epsilon_e + g_1\epsilon_1]} \right) + \frac{2}{3} \left( \frac{\epsilon_2 - \epsilon_e}{(1+g_1)\epsilon_e + (1-g_1)\epsilon_2} \right) = 0. \quad (21)$$

Here  $g_1$  is the depolarization factor of the ellipsoidal crystallite along the uniaxial direction, and  $g_2 \equiv \frac{1}{2}(1-g_1)$  is that for each of the other two directions. The field-averaging EMA (Ref. 3) takes the form

$$\frac{1}{3} \left( \frac{g_1(\epsilon_1 - \epsilon_e)}{(1-g_1)\epsilon_e + g_1\epsilon_1} \right) + \frac{2}{3} \left( \frac{(1-g_1)(\epsilon_2 - \epsilon_e)}{(1+g_1)\epsilon_e + (1-g_1)\epsilon_2} \right) = 0. \quad (22)$$

In the limit of spherical inclusions ( $g_1 = g_2 = \frac{1}{3}$ ), both reduce to a form originally written down in Ref. 1:

$$\frac{1}{3} \left( \frac{\epsilon_1 - \epsilon_e}{\epsilon_1 + 2\epsilon_e} \right) + \frac{2}{3} \left( \frac{\epsilon_2 - \epsilon_e}{\epsilon_2 + 2\epsilon_e} \right) = 0. \quad (23)$$

It is easily verified that Eq. (22) fails to satisfy (16) at first order. Equation (21) does satisfy Eq. (16) at first order, but is consistent with it at second order only for spherical particles. Since the EMA for ellipsoidal particles is intuitively so reasonable, we do not view its failure to satisfy Eq. (16) at second order as a shortcoming of the approximation. Instead, it suggests that the assumption of “strong isotropy” fails for crystallites which are ellipsoidal but not spherical. Of the two approximations (21) and (22), we believe that the first is to be preferred, on grounds that it satisfies the oscillator-strength sum rule which should hold quite generally.

#### IV. APPLICATIONS

##### A. Quasi-1D or quasi-2D Drude metal; centroids of localized bands

As a first illustration, we apply the sum rules to a simple model of a quasi-1D metal. Throughout this subsection, we assume that both of the sum rules (17) and (18) are valid, i.e., that the polycrystal satisfies “strong isotropy.” Another example, not based on this assumption, is given in the next subsection.

Our work is motivated by recent experiments of Kohlman *et al.*<sup>5</sup> These authors studied the a.c. response of polypyrrole, a quasi-1D organic metal, in its most highly conducting state. They found (i) a Drude behavior at low frequencies, manifested by a large negative dielectric constant at microwave frequencies, and finite d.c. conductivity; and (ii) a second plasma frequency in the near infrared. The latter was attributed to conduction electrons which are confined because of a lack of long-range three-dimensional order. We will show that such behavior can also be produced in a polycrystalline metal, each crystallite of which is highly conducting only along one crystal axis.

We consider crystallites with a Drude dielectric function

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \quad (24)$$

in the  $x$  direction, and a constant dielectric function

$$\epsilon_2(\omega) = 1 \quad (25)$$

in the other two directions. We express  $\epsilon_e$  in the form

$$\epsilon_e = \epsilon_{ed} + \epsilon_{ep}, \quad (26)$$

where  $\epsilon_{ed}$  contains the Drude peak in the effective dielectric function, while  $\epsilon_{ep}$  has the additional “plasmon” peak at finite frequency, arising from the confined charge carriers in the polycrystal. We will write  $\epsilon_{ed}$  in the form

$$\epsilon_{ed} = A \left( 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \right), \quad (27)$$

with

$$A = \frac{\sigma_e(\omega=0)}{\sigma_1(\omega=0)}, \quad (28)$$

$\sigma_e(\omega=0)$  and  $\sigma_1(\omega=0)$  being, respectively, the effective zero-frequency conductivity of the polycrystal and the zero-frequency conductivity of the single crystal along the symmetry axis. With this definition, the Drude peak includes all the spectral weight of  $\epsilon_e$  at zero frequency.

We will find the center of gravity of the confined plasmon peak from the sum rules (17) and (18). First, we rewrite

$$\epsilon_{av}(\omega) \equiv 1 - p + p\epsilon_1(\omega) \equiv \epsilon_{ed}(\omega) + \delta\epsilon_{av}(\omega), \quad (29)$$

which defines the quantity  $\delta\epsilon_{av}(\omega)$ . Then the sum rules (17) and (18) can be written as

$$\int_0^\infty \text{Im} \epsilon_{ep}(\omega') \omega' d\omega' = \frac{\pi}{2} (p-A) \omega_p^2 \equiv I_{ep} \quad (30)$$

and

$$\int_0^\infty \text{Im} [\epsilon_{ep}(\omega') - \delta\epsilon_{av}(\omega')] \omega'^3 d\omega' = \frac{\pi}{6} p(1-p) \omega_p^4, \quad (31)$$

where  $p = \frac{1}{3}$  and  $I_{ep}$  is the integrated strength of the confined plasmon band. Its center of gravity,  $\omega_{ep}$ , is given by the ratio of the left-hand side of Eq. (31) to that of Eq. (30):

$$\omega_{ep}^2 = \frac{1}{3} \frac{p(1-p)\omega_p^2}{p-A}. \quad (32)$$

This result shows that, irrespective of the details of the geometry (but still assuming “strong isotropy”), a polycrystal of quasi-1D metal has a confined “plasmon” band which is centered at a substantial fraction of the plasma frequency  $\omega_p$ . The exact position of the center of gravity  $\omega_{ep}$  depends on the zero-frequency conductivity of the polycrystal, a quantity which does depend on its geometry.

The physics underlying this confined plasmon band is straightforward. Equation (17) gives the total oscillator strength of the polycrystal in terms of the plasma frequency for charge carriers moving along the axis of symmetry. Some of this oscillator strength is soaked up by the Drude peak of the polycrystal, which lies at zero frequency. The remaining oscillator strength, which is the localized plasmon peak, must lie at finite frequency if the strong-isotropy condition holds, in order to satisfy the sum rule (18). The precise frequency depends on the strength of the polycrystalline Drude peak. Although this argument is given for a polycrystal satisfying strong isotropy, the same general physics should prevail even if that hypothesis does not hold, e.g., in a polycrystal made up of ellipsoidal inclusions. An example encompassing this more general situation is given in the next section.

A similar argument can be given for the energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$ . For the Drude model, the single-crystal  $-\text{Im}\epsilon_1^{-1}(\omega)$  has a plasmon peak at  $\omega = \omega_p$ .  $-\text{Im}\epsilon_e^{-1}(\omega)$  still has a plasmon peak at  $\omega_p$ . In addition, it has a confined peak centered at frequency  $\tilde{\omega}_{ep}$ . By arguments parallel to those for  $\epsilon_e$ , we can get an expression for  $\tilde{\omega}_{ep}$ , using the sum rules (19) and (20). We must first introduce a parameter  $\tilde{A}$  by separating out the “bulk” part of the effective loss function

$$\epsilon_e^{-1}(\omega) \equiv \tilde{\epsilon}_{ed}^{-1}(\omega) + \tilde{\epsilon}_{ep}^{-1}(\omega) \quad (33)$$

where

$$\tilde{\epsilon}_{ed}^{-1}(\omega) = \tilde{A} \epsilon_1^{-1}(\omega). \quad (34)$$

The constant  $\tilde{A}$  describes how much of the oscillator strength in  $-\text{Im}\epsilon_e^{-1}(\omega)$  is soaked up by the pole at  $\omega = \omega_p$ . The localized plasmon band in  $-\text{Im}\epsilon_e^{-1}$  comes from the remaining oscillator strength. Manipulation of the sum rules (19) and (20) leads to the following results for the integrated strength  $\tilde{A}$  and the center of gravity of the localized plasmon band in  $-\text{Im}\epsilon_e^{-1}$  (still assuming “strong isotropy”):

$$\tilde{I}_{ep} = \frac{1}{2} \pi \omega_p^2 (p - \tilde{A}), \quad (35)$$

and

$$\tilde{\omega}_{ep}^2 = \omega_p^2 \left( \frac{p^2 + \frac{1}{3}p(1-p) - \tilde{A}}{p - \tilde{A}} \right). \quad (36)$$

As previously,  $p = \frac{1}{3}$  for a quasi-1D metal, which has a finite  $\omega_p$  along one axis only.

The above results can be immediately generalized to a quasi-2D metal, in which  $\epsilon_2$  and  $\epsilon_3$  have the Drude form, while  $\epsilon_1 = 1$ . Such a dielectric function might serve, for instance, as a very crude model of a  $\text{CuO}_2$ -based superconductor in its normal state. Equations (32) and (36) continue to hold in this case with  $p = \frac{2}{3}$ , rather than  $p = \frac{1}{3}$ .

In Fig. 1, we plot both  $\omega_{ep}$  and  $\tilde{\omega}_{ep}$  as a function of  $A$  and  $\tilde{A}$ , for both the quasi-1D and the quasi-2D cases ( $p = \frac{1}{3}$  and  $\frac{2}{3}$ ). The ranges of  $A$  and  $\tilde{A}$  shown are chosen so that the centroids of the localized bands lie between  $\omega = 0$  and  $\omega_p$ . If we were dealing with a binary composite of isotropic components, rather than a polycrystal of an anisotropic material, then the allowed values of both  $A$  and  $\tilde{A}$  would be restricted by the so-called Hashin-Shtrikman bounds.<sup>13</sup> Although we are aware of no such bounds for a polycrystal, we have plotted the centroids of the localized bands assuming that  $A$  and  $\tilde{A}$  satisfy these bounds. For both  $p = \frac{1}{3}$  and  $p = \frac{2}{3}$ ,  $\omega_{ep}$  increases towards  $\omega_p$  as  $A$  increases. If the polycrystal has very low d.c. conductivity,  $\omega_{ep} \approx 0.2\omega_p$  and  $0.12\omega_p$  for the 1D and 2D cases. The surface plasmon band in  $-\text{Im}\epsilon_e^{-1}(\omega)$  has the opposite behavior:  $\tilde{\omega}_{ep}$  decreases towards  $\omega = 0$  as  $\tilde{A}$  increases towards its maximum value. The sum rules cannot, however, give information about the *widths* of the localized bands in either  $\text{Im}\epsilon_e$  or  $-\text{Im}\epsilon_e^{-1}$ .

### B. Quasi-1D metal, Drude and Lorentzian contributions. Effective-medium theory

In this section, we give a possibly more realistic model for the optical properties of a quasi-1D metal, which includes both Drude and Lorentzian contributions to the dielectric functions, and which therefore can be compared, at least qualitatively, to experimental results.<sup>5</sup> Also, we evaluate  $\epsilon_e$  by an effective-medium approximation which gives the bandwidths as well as their centroids. Finally, we relax the requirement of strong isotropy, so that we can consider ellipsoidal crystallites.

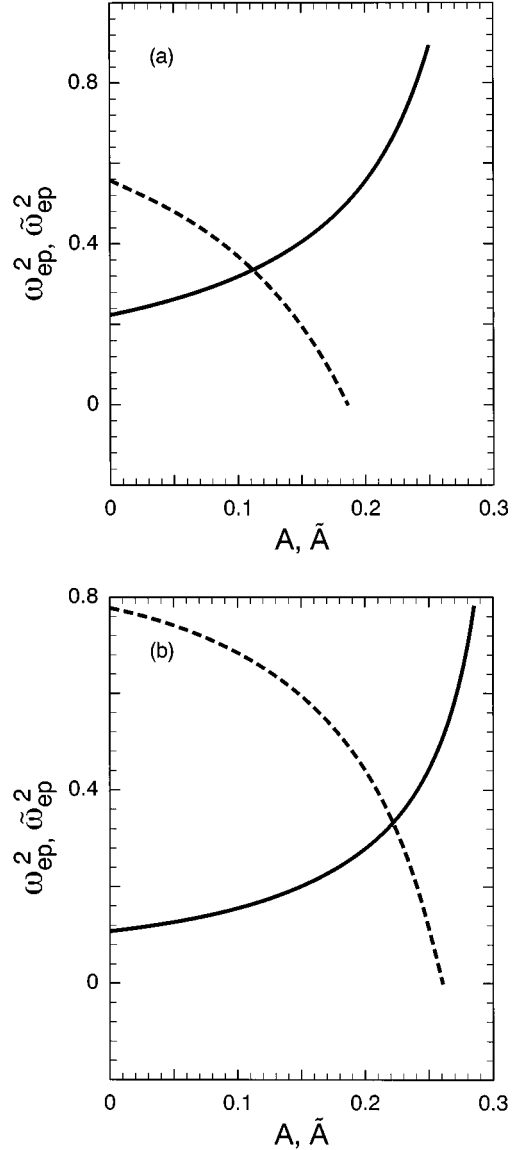


FIG. 1. (a) Calculated centroids  $\omega_{ep}$  and  $\tilde{\omega}_{ep}$  of the localized surface plasmon band in  $\text{Im}\epsilon_e(\omega)$  (solid curve) and  $-\text{Im}\epsilon_e^{-1}(\omega)$  (dashed curve) for a polycrystalline quasi-1D Drude metal ( $p = 1/3$ ) with plasma frequency  $\omega_p$ .  $A$  represents the integrated strength of the zero-frequency Drude peak in  $\text{Im}\epsilon_e(\omega)$ , divided by that of the single crystal in the high-conductivity direction.  $\tilde{A}$  is the corresponding quantity for the energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$ . (b) Same as (a) but for a quasi-2D Drude metal ( $p = 2/3$ ).

To treat a single crystal of polypyrrole, we assume that the component of the dielectric function parallel to the chain, which we write as  $\epsilon_1(\omega)$ , has the form

$$\epsilon_1(\omega) = \epsilon_{\infty,1} - \frac{\omega_{p1}^2}{\omega(\omega + i/\tau_1)} + \frac{\omega_1^2}{\omega_0^2 - \omega^2 - i\omega\gamma}. \quad (37)$$

The first term represents the high-frequency dielectric constant along the chain. The second term on the right-hand side represents the Drude contribution of free electrons, while the third is a Lorentzian term arising from an assumed localized mode. This mode could, for example, be a localized vibra-

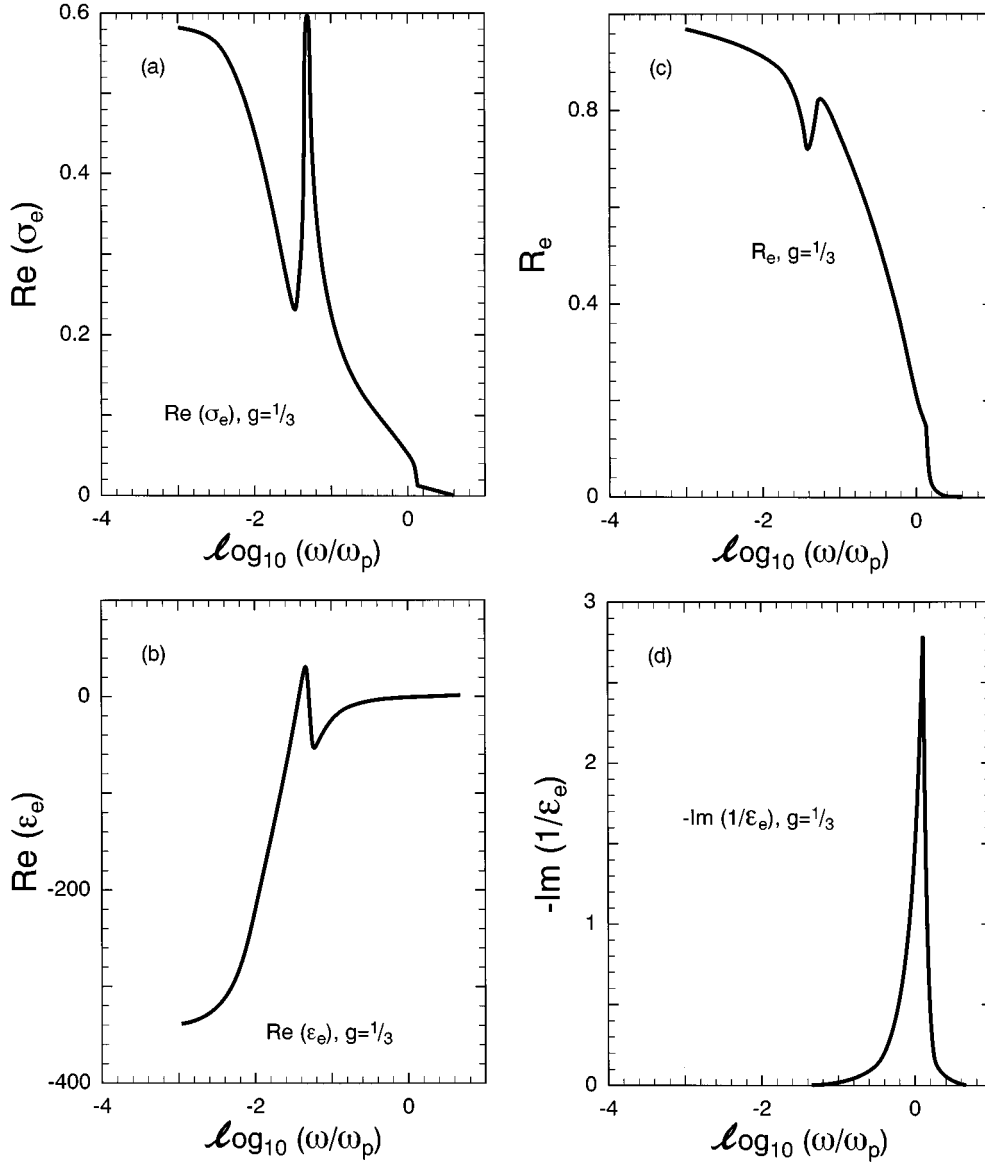


FIG. 2. (a) Real part of conductivity,  $\text{Re}\sigma_e(\omega)$ ; (b) real part of the dielectric function,  $\text{Re}\epsilon_e(\omega)$ ; (c) reflectivity  $R_e(\omega)$ ; and (d) energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$ , for a polycrystalline sample of “polypyrrole,” as calculated in the effective-medium approximation assuming spherical crystallites ( $g_1 = 1/3$ ). Horizontal line is  $\log_{10}(\omega/\omega_p)$ , where  $\omega$  is the frequency and  $\omega_p$  the plasma frequency. Parameters and model described in the text.

tional excitation which couples to an applied electric field parallel to the chain. The component  $\epsilon_2$  perpendicular to the chain is assumed to be expressible as a constant plus a term arising from a weak interchain conductivity:

$$\epsilon_2 = \epsilon_{\infty,2} - \frac{\omega_{p2}^2}{\omega(\omega + i/\tau_2)}. \quad (38)$$

For simplicity, we assume that  $\omega_{p2} = \omega_{p1}$ , but that  $\tau_1 \gg \tau_2$ . These assumptions seem plausible if the same number of charge carriers are involved in both perpendicular and parallel transport, but if perpendicular transport involves a much larger scattering rate.

We briefly justify treating the experimental samples as polycrystalline. Typical samples of polypyrrole are observed photomicrographically to be a collection of crystalline grains, separated by regions of amorphous material. The most important feature of the observed structure is the random spatial orientation of the polymer chain axis. In a large

enough sample, this axis points with equal probability in any direction, and the directions are uncorrelated for two points sufficiently well separated in space. The linear dimension of the “grains” is roughly the orientational correlation length. If this is larger than the single-crystal scattering length, then each grain could be viewed as a homogeneous material with its own transport coefficients. It therefore seems reasonable to model this material as a collection of randomly oriented, compact grains.

We first calculate the optical properties of the polycrystal in the EMA for spherical grains [Eq. (23)]. In Fig. 2 we plot  $\text{Re}\epsilon_e(\omega)$ ,  $\text{Re}\sigma_e(\omega) \equiv \text{Im}[n_e(\omega)/(4\pi)]$ , and the energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$ , as calculated from Eq. (23). Also shown is the calculated reflectivity  $R_e(\omega) \equiv |[n_e(\omega) - 1]/[n_e(\omega) + 1]|^2$ , where  $n_e(\omega) = \sqrt{\epsilon_e(\omega)}$  is the complex index of refraction. We assume parameters  $\omega_{p1} = \omega_{p2}$ ,  $\gamma = 0.01\omega_{p1}$ ,  $\omega_{p1}\tau_1 = 100$ ,  $\omega_1 = \omega_{p1}$ ,  $\omega_0 = 0.05\omega_{p1}$ ,  $\epsilon_{\infty,1} = \epsilon_{\infty,2} = 1$ , and  $\omega_{p2}\tau_2 = 1$ . For comparison, we also show in Fig. 3 the corresponding quantities for a single crystal with electric field parallel to the polymer axis:

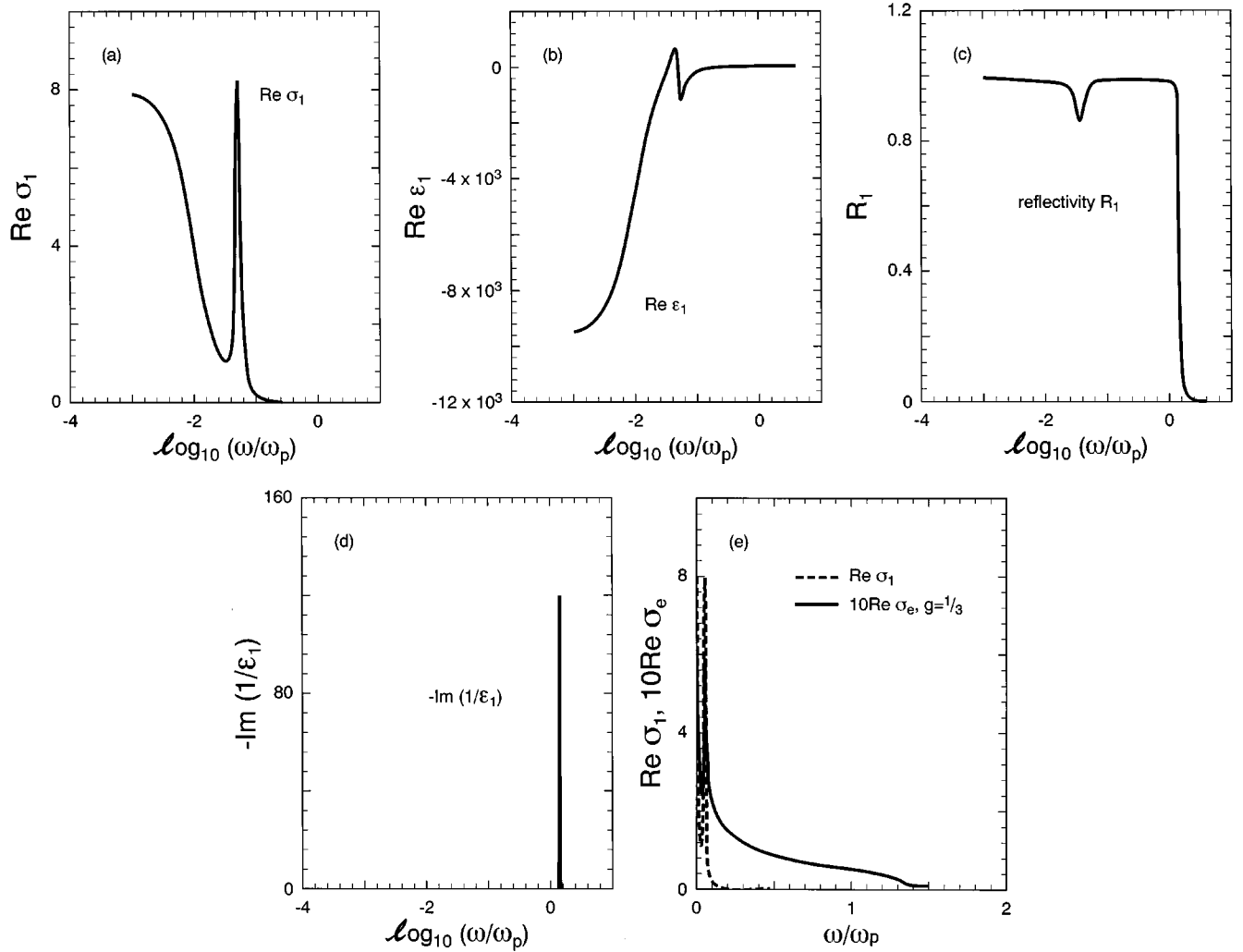


FIG. 3. Same as Fig. 2 except assuming a single crystal with electric field parallel to the high-conductivity axis.

$\text{Re}\epsilon_1(\omega)$ ,  $\text{Re}\sigma_1(\omega)$ ,  $R_1(\omega) \equiv |[n_1(\omega) - 1]/[n_1(\omega) + 1]|^2$ , and  $-\text{Im}\epsilon_1^{-1}(\omega)$ . All plots are on a logarithmic frequency scale, except for Fig. 3(e), where we plot  $\text{Re}\sigma_1(\omega)$  and  $10\text{Re}\sigma_e(\omega)$  on a linear frequency scale in order to facilitate comparison of the two conductivities.

The calculated  $\text{Re}\epsilon_e(\omega)$  exhibits three zero crossings (or “plasma frequencies”). The uppermost of these (which is difficult to see in the figure) occurs at about  $\omega = 1.07\omega_{p1}$ , slightly above the plasma frequency of the free charge carriers along the chain, while the lower two are associated with the quasiphonon mode included in  $\epsilon_1$ .  $\text{Re}\sigma_e(\omega)$  has three peaks: a Drude peak centered at zero frequency, a low-frequency peak associated with the quasiphonon mode, and a broad “composite” peak which extends from nearly zero frequency to a substantial fraction of  $\omega_{p1}$ . This last is present in neither  $\epsilon_1$  nor  $\epsilon_2$ , but results from the localized plasmon modes described earlier. It is more easily seen on the linear frequency scale of Fig. 3(e). As a confirmation of this, we observe in Figs. 3(a) and 3(e) that  $\text{Re}\sigma_1(\omega)$  has the Drude peak and the finite-frequency “phonon” peak but not the broad “composite” peak.

All these features have their counterparts in  $R_e(\omega)$  [Fig. 2(c)]. In particular, the composite peak shows up in the broad drop in reflectivity which starts nearly at zero frequency

(with a small peak due to the phonon absorption). By contrast,  $R_1(\omega)$  remains close to unity as far as the bulk plasma frequency (the uppermost zero crossing of  $\text{Re}\epsilon_1$ ). The experimental behavior of the reflectivity in polypyrrole very much resembles that of Fig. 2(c), lending credence to the possibility that the experiments are indeed detecting effects of polycrystallinity.

The energy-loss function  $-\text{Im}\epsilon_e^{-1}(\omega)$  also shows effects of polycrystallinity. Whereas  $-\text{Im}\epsilon_1^{-1}(\omega)$  is characterized (for these parameters) by a very strong, sharp peak at the plasma frequency of about  $1.07\omega_{p1}$  [Fig. 3(d)], the corresponding quantity in the polycrystal [Fig. 2(d)] has a much broader peak which shows the influence of the localized plasmon band at frequencies below  $\omega_{p1}$ . Both loss functions also show very weak secondary peaks near the Lorentzian “phonon” peak which occurs around  $0.05\omega_p$  for our parameters (not visible in our plots).

Figure 4 shows the same quantities as in Fig. 2, but now calculated assuming ellipsoidal crystallites with a depolarization factor  $g_1 = 0.1$  (the principal axes of the crystallites are always assumed parallel to those of the dielectric tensor), and using the dipole-averaged EMA.<sup>2</sup> The Drude peak in  $\text{Re}\sigma_e(\omega)$  is now stronger than in the spherical case. This occurs because the randomly oriented crystallites with

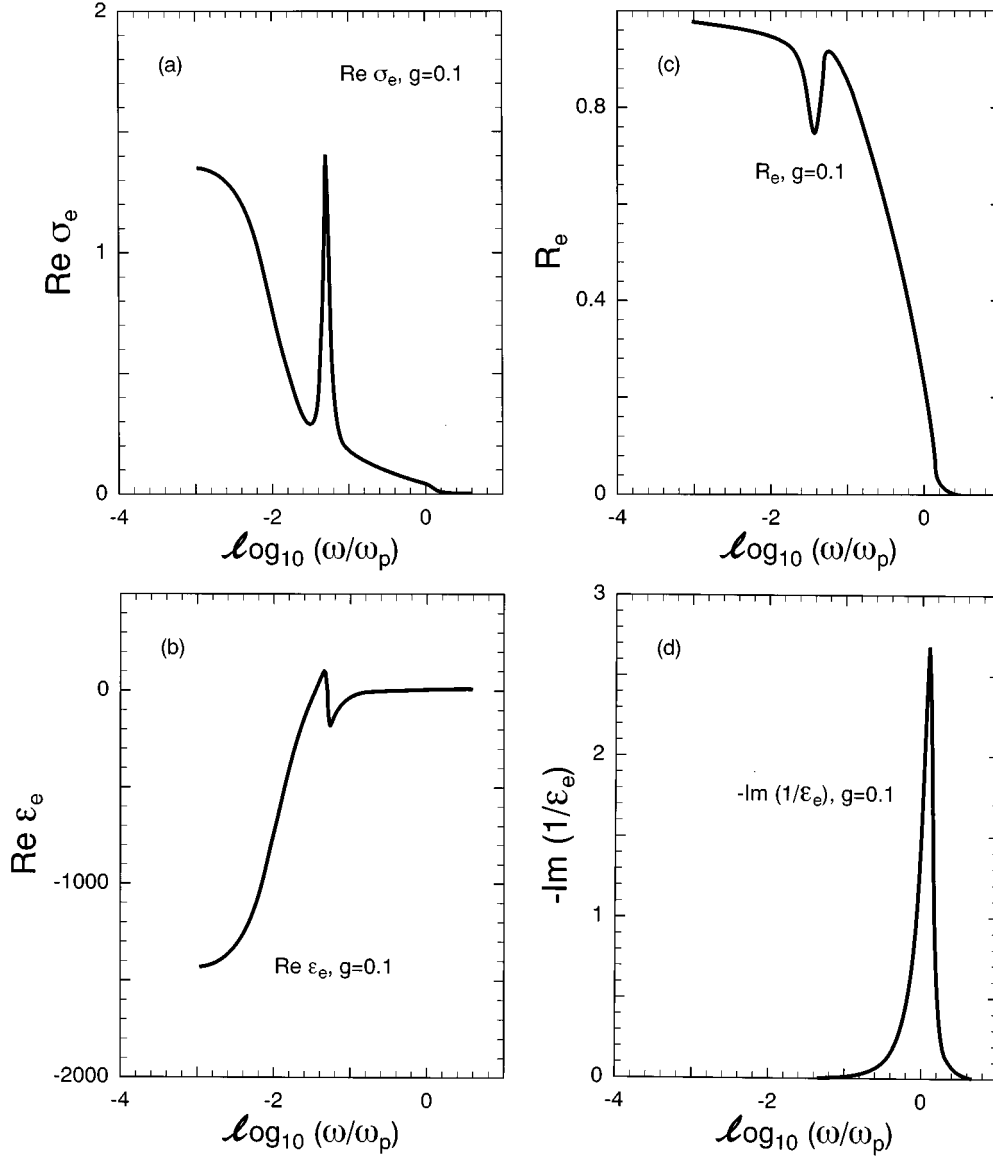


FIG. 4. Same as Fig. 2 but assuming ellipsoidal crystallites with  $g_1=0.1$ .

$g_1=0.1$  more easily carry current through the polycrystal than do spheres. For the same reason,  $\text{Re}\epsilon_e(\omega)$  is now much more strongly negative at low frequencies than is the case for spherical crystallites. This larger negative dielectric constant seems to agree better with experiment,<sup>5</sup> suggesting that the observed materials may have effectively ellipsoidal crystallites with small  $g_1$ .

## V. DISCUSSION

We have derived sum rules for  $\epsilon_e(\omega)$  and  $\epsilon_e^{-1}(\omega)$  in a polycrystal of an anisotropic material. The sum rules on the lowest moments of  $\text{Im}\epsilon_e(\omega)$  and  $-\text{Im}\epsilon_e^{-1}(\omega)$  are valid quite generally, but the next-order sum rules require that certain correlation functions obey conditions of strong isotropy, most likely to be obeyed by polycrystals made up of spherical crystallites. The sum rules, as applied to quasi-1D or quasi-2D Drude metals, imply the existence of a band of localized plasmonlike excitations in  $\text{Im}\epsilon_e(\omega)$  and

$-\text{Im}\epsilon_e^{-1}(\omega)$ . Under the special conditions of strong isotropy, the central frequencies of these localized bands are determined by the zero-frequency conductivities of the polycrystal.

To illustrate these ideas, we calculate the optical properties of a hypothetical polycrystal of quasi-1D metal. For a plausible choice of dielectric functions parallel and perpendicular to the high-conductivity axis, the optical response of the polycrystal, as calculated by an effective-medium approximation, closely resembles experiment.<sup>5</sup> In particular, one finds a large negative dielectric constant at very low frequencies, three zero crossings of the dielectric constant at finite frequencies, and a broad band of “localized plasmon” excitations arising from confined free carriers on the chain within a local region of the polycrystal. Analogous phenomena are found in the energy-loss function and reflectivity. Finally, the optical constants depend significantly on the assumed crystallite shapes, and for ellipsoidal crystallites with sufficiently small depolarization factors  $g_1$ , the magnitude of the negative static dielectric constant starts to approach ex-

periment. While other models, based perhaps on quantum-mechanical electron localization, may conceivably account for the data equally well, the type of localized plasmons discussed here should occur under quite general circumstances. Thus the present model may possibly have a wide range of applicability to quasi-1D materials.

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<sup>9</sup>In brief, the argument for this result is as follows. In an isotropic material,  $\epsilon_{av}$  is a multiple of the unit tensor; so each of the diagonal elements may be written as  $\text{Tr } \epsilon_{av}/3$ . But  $\text{Tr } \epsilon_{av} = \text{Tr}(R^{-1}\epsilon R) = \text{Tr } \epsilon = \sum_{i=1}^3 \epsilon_i$ . Here  $R$  is a rotation matrix and we have used the identity  $\text{Tr}(AB) = \text{Tr}(BA)$ . The last equality completes the proof.

<sup>10</sup>Reference 1 considers mostly volume averages rather than ensemble averages. We are assuming that for a sufficiently large system, the two types of average are equivalent.

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