

A NEW MODEL FOR THE INFRARED DIELECTRIC FUNCTION OF AMORPHOUS MATERIALS

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ABSTRACT

The infrared dielectric function of amorphous materials near-IR strong resonances is derived from the materials' crystalline optical constants using a simple transform. The technique assumes that there is a continuous distribution of oscillators, each with its own resonant frequency, damping, and plasma frequency. By convoluting the crystalline dielectric function with a suitable function representing the distributions, we show that the dielectric functions for amorphous quartz and olivine can be estimated with modest accuracy. The technique provides a simple means of computing the gross influence of atomic disorder on spectral characteristics of possible cosmic dust components in the vicinity of strong infrared resonances.

Subject headings: dust, extinction — infrared: general — methods: laboratory

1. INTRODUCTION

Infrared spectroscopy of solid dust particles in the laboratory has proven useful in remotely identifying the source of thermal emission features in cosmic dust. A notable instance is the silicate emission feature near $10\ \mu\text{m}$ due to the asymmetric O-Si-O vibrational resonance. The feature has been observed both in the laboratory (Salisbury et al. 1991) and in many astronomical sources from comets to galaxies (Hanner, Lynch, & Russell 1994; Gehr 1988; Knacke et al. 1993; Stein & Soifer 1983). Still, none of the astronomical spectra match laboratory spectra even closely. The latter usually show significant spectral structure that is characteristic of crystallinity, while the former are almost always smooth and featureless (Olson & Raimond 1986; Sloan & Price 1995). The lack of spectral structure in most cosmic sources is usually attributed to some degree of atomic disorder because laboratory studies have shown that amorphous materials produce smoother spectra than their stoichiometrically identical crystalline counterparts (Stephens & Russell 1979).

In attempting to model the spectra of cosmic dust, astronomers have been hampered by the lack of measured optical constants (synonyms: dielectric function, relative permittivity) for astrophysically relevant amorphous materials such as olivine and pyroxene. Although many optical constants have been measured for crystalline materials (Palik 1985), few are available for amorphous substances. The lack of amorphous dielectric functions may be due to the vague definition of "amorphous" or because dielectric functions of amorphous materials are not unique: a material can be amorphous in an infinite number of ways, and therefore its measured dielectric function may not be characteristic of samples prepared by different methods. At the same time, there has been no theoretical technique by which the dielectric function of an arbitrary disordered material could be easily estimated. Therefore, a technique is needed that will produce dielectric functions for amorphous materials.

Perfectly crystalline substances possess both long- and short-range order, while glassy materials have virtually no long-range order. Yet on the atomic level (Fig. 1, adapted from Zallen 1983), amorphous materials possess significant

short-range order, order that is quite similar to that in their crystalline counterparts (Zachariasen 1932; Zallen 1983; Elliott 1983). Their coordination numbers are usually the same, and their bond lengths, bond angles, and resonant frequencies are very close to those of their crystalline versions. These parallels are the result of similar coulombic interactions, and the similarities suggest that the dielectric functions of amorphous materials may be derivable from crystalline dielectric functions.

This paper is concerned with the following question: Given the dielectric function of a crystalline material $\epsilon(\omega)$, is it possible to compute $\hat{\epsilon}(\omega)$, the dielectric function of an arbitrarily amorphous form of the same material? The answer could provide us with the ability to simulate the effects of amorphousness on the optical properties over a wide range of disorder from purely crystalline to significantly amorphous.

2. SINGLE AND MULTIPLE OSCILLATORS

In Lorentz's classical model of damped harmonic oscillators (Jackson 1962; Bohren & Huffman 1983), the dielectric function $\epsilon = \epsilon' + i\epsilon''$ for a single oscillator of mass m , spring constant K , and damping constant b is

$$\epsilon = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma_0 \omega}, \quad (1)$$

where χ is the electric susceptibility, ω_0 is the resonant frequency $(K/m)^{1/2}$, γ_0 is the damping factor b/m , and ω_p is the lattice plasma frequency $(Ne^2/m)^{1/2}$. The derivation of equation (1) makes no assumption about the long-range order of the oscillators. The materials could be crystalline or amorphous, but since equation (1) refers to a single oscillator, it can be used to describe isotropic crystals, since they can be thought of as having only one mass and one spring constant. Single classical oscillator models are very nearly realized in many crystals (Spitzer, Kleinman, & Walsh 1959). The quantum version of dielectric function (Ziman 1972) is so similar to the classical one that at this level, we need only deal with the latter.

For a mixture of N different oscillators, the dielectric function is a linear superposition of the individual dielectric

functions (Bohren & Huffman 1983):

$$\epsilon(\omega) = \epsilon_0 + \sum_j^N (\omega_{pj}^2)/(\omega_j^2 - \omega^2 - i\gamma_j\omega), \quad (2)$$

where ϵ_0 is the mean static dielectric constant averaged over the N components and usually near unity. Being a linear superposition of individual dielectric functions, equation (2) satisfies the Kramers-Kronig relations.

Measured crystalline dielectric functions are usually fitted with sums like equation (2) along with tabulations of ω_{pj} , ω_j , and γ_j (Spitzer & Kleinman 1961; Jasperse et al. 1966), and these models work with anisotropic crystals as well. In general, each axis of symmetry adds more terms to equation (2), and the number of terms can be large for complicated crystals. Amorphous materials are very complex and almost certainly variable from sample to sample, but equation (2) may suggest a method of computing their dielectric functions, especially in the vicinity of strong IR resonances.

3. CONTINUOUS DISTRIBUTION OF OSCILLATORS (CDO) APPROXIMATION

We will assume that an amorphous material can be described by a continuous distribution of oscillators (CDO). The physical basis of this approximation derives from the atomic arrangement of atoms in an amorphous material which is similar to that found in the crystalline form (Figure 1). The main difference is that discrete properties such as the interatomic separations and bond angles can no longer be considered to have fixed values, but rather must be described by statistical distributions (Zachariasen 1932; Zallen 1983; Elliott 1983). The distribution in separation, for example, will result in a range of spring constants and a corresponding range of resonant frequencies. Laboratory studies show that the widths of the distributions may be roughly 10%–15% of the central value (Elliott 1983; Polk 1971). Similar spreading takes place in damping γ_0 and lattice plasma frequency ω_p .

This concept of amorphous materials suggests that they can be described in a manner similar to their crystalline counterparts, provided that the discrete parameters such as resonant frequency, damping, etc., are replaced by statistical distributions. The widths of these distributions are measures of the degree of atomic disorder. Crystalline materials have very narrow widths, and progressively more disordered materials have broader and broader distributions.

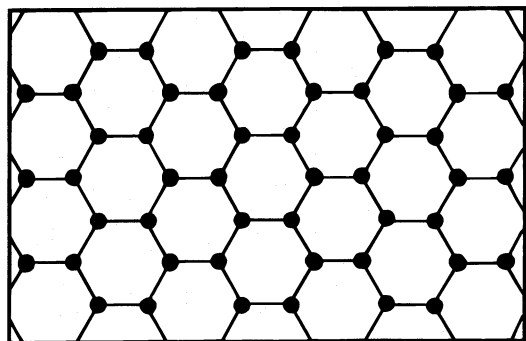


FIG. 1a

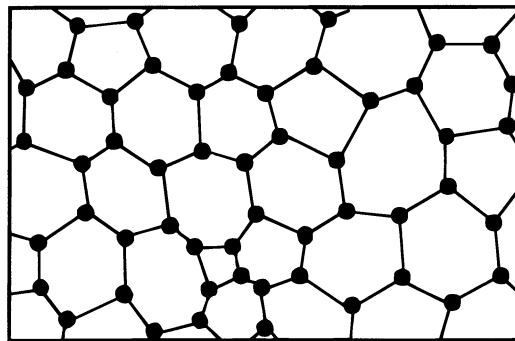


FIG. 1b

FIG. 1.—Schematic two-dimensional representations of (a) crystalline and (b) amorphous solids (adapted from Zallen 1983). (a) Crystals have identical bond lengths, bond angles, coordination numbers (3), and ring members (6). The long- and short-range orders are evident. (b) Amorphous materials have a range of bond lengths, bond angles, and ring members ($4 < n < 7$) and retain the same coordination numbers (3).

An example of such a quasi-amorphous material might be one composed of equal numbers of Lorentz oscillators whose resonant frequencies are distributed uniformly between $\omega_0 - \Delta/2$ and $\omega_0 + \Delta/2$. Thus, ω_0 becomes a variable. We will assume that this situation can be described by equation (2). For simplicity, we will hold ω_p and γ_0 constant. In the limit of an infinite number of oscillators, the sum in equation (2) becomes an integral of the form

$$\hat{\epsilon}(\omega) = \epsilon_0 + \int \prod_{\Delta}(\omega_0 - \omega'_0)(\omega_p^2)/(\omega_0'^2 - \omega^2 - i\gamma_0\omega) d\omega'_0, \quad (3)$$

where $\hat{\epsilon}(\omega)$ is the dielectric function of the amorphous version of the materials and $\prod_{\Delta}(\omega_0 - \omega'_0)$ is the rectangular function of width Δ that represents the relative numbers of oscillators at each resonant frequency. Equation (3) is a convolution, and it is formally identical to a low-pass filter. This indicates that low-pass filtering may be useful in estimating dielectric functions of amorphous materials once their crystalline properties are known. Equation (3) is a generalization of equation (2), and therefore it also satisfies the Kramers-Kronig relation.

The crux of the CDO approximation is embodied in equation (3). The idea of low-pass filtering the crystalline dielectric function $\epsilon(\omega)$ to obtain the amorphous dielectric function $\hat{\epsilon}(\omega)$ is appealing because spectra of amorphous materials are known to have less fine structure than do crystalline ones. Viewing decrystallization as a filtration process allows a single number, the filter width Δ , to describe it. A large Δ means that there is significant degradation (amorphization), and a small Δ implies little amorphization because as $\Delta \rightarrow 0$, $\prod_{\Delta}(\omega_0 - \omega'_0) \rightarrow \delta(\omega_0 - \omega'_0)$ and equation (3) reverts to equation (1). Thus, our physical expectations are realized in both limiting cases. Note that Δ was used originally to describe the frequency band for uniform numbers of oscillators per unit frequency interval. If, for example, the resonant frequencies were distributed according to Gaussian statistics, then Δ would represent the FWHM of the Gaussian function.

For an arbitrary crystalline material whose dielectric function is $\epsilon(\omega)$, the dielectric function is

$$\hat{\epsilon}(\omega) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} F(\omega_0 - \omega'_0, \gamma_0 - \gamma'_0, \omega_p - \omega'_p) \epsilon(\omega') \times d\omega'_0 d\gamma'_0 d\omega'_p, \quad (4)$$

where $F(\omega_0 - \omega'_0, \gamma_0 - \gamma'_0, \omega_p - \omega'_p)$ is a low-pass filter that

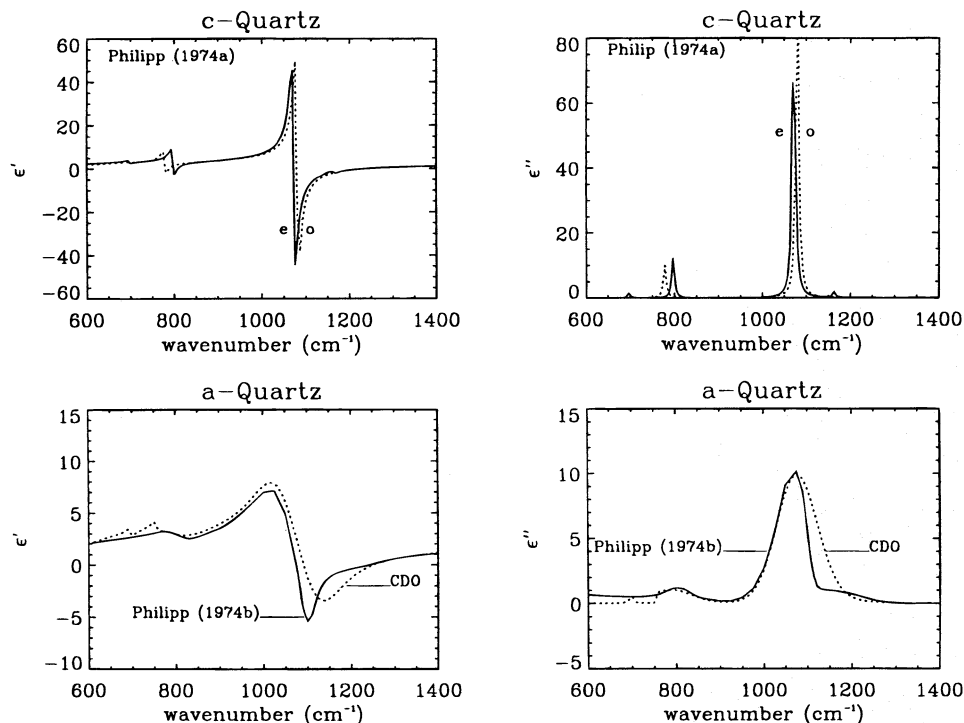


FIG. 2.—Quartz dielectric function. *Top panels*: Real and imaginary parts of $\epsilon(\omega)$ for quartz obtained by Philipp (1985a). Since quartz has two principle axes e and o , the dielectric function is shown for the electric field parallel to each. *Bottom panels*: Philipp's (1985b) measured dielectric function $\hat{\epsilon}(\omega)$ of amorphous quartz (solid line), and continuous distribution of oscillators (CDO) prediction of the dielectric function using a Gaussian filter width of 90 cm^{-1} .

is a function of ω_0 , γ_0 , and ω_p . We have included the leading term ϵ_0 in the integral because of our notion of filtration is largely one of low-pass filtering. Since ϵ_0 is a constant (DC term), will not be filtered out, and placing it inside the integral simplifies the formalism.

It may be possible to derive F from the X-ray diffraction pattern of the material. Alternatively, F might be computed from a physical model of the distribution of oscillators in a partially crystalline material, but such computations would be laborious and would usually apply to only one mixture

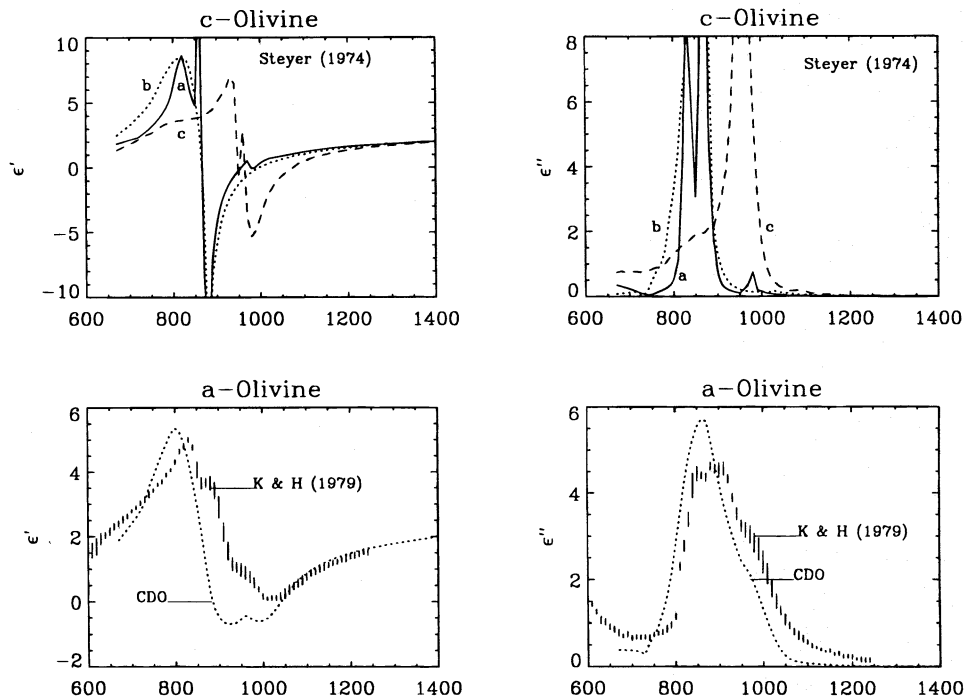


FIG. 3.—Olivine dielectric function. *Top panels*: Real and imaginary parts of $\epsilon(\omega)$ for olivine obtained by Steyer (1974). Since olivine has three principle axes a , b , c , the dielectric function is shown for the electric field parallel to each. *Bottom panels*: Krätchmer & Huffman's (1979) (K&H) measured dielectric function $\hat{\epsilon}(\omega)$ of amorphous olivine (solid line), and continuous distribution of oscillators (CDO) prediction of the dielectric function based on Steyer's dielectric functions and triangular filter width of 90 cm^{-1} .

of material. To avoid such difficulties, we have adopted the notion that the most likely distribution of oscillators in $(\omega_0, \gamma, \omega_p)$ space is a continuous region centered on the perfect oscillator constants and whose dimensions are a measure of crystallinity. This allows us to apply CDO to any material whose crystalline properties are known.

In the next section, we will demonstrate CDO and compare the results to previous measurements. It is important to realize that although the main thrust of the demonstration is aimed at understanding transverse optical modes, there will be influences on surface modes as well, a subject discussed briefly in § 5.

4. APPLICATION OF CDO TO QUARTZ AND OLIVINE

Quartz (SiO_2) is the simplest rock-forming silicate mineral, and the optical properties of both its crystalline (α quartz, hexagonal) and amorphous forms (fused quartz) have been well studied (Phillipp 1985a). Starting with the dielectric functions for crystalline quartz (Fig. 2, *top panels*), we applied a Gaussian filter in ω space to the ordinary and extraordinary parts of the dielectric function, averaged them, and compared the result to the dielectric function of fused quartz (Fig. 2, *bottom panels*). Only one free parameter was adjusted, the filter width Δ , and no vertical scaling or normalization was done to $\hat{\epsilon}(\omega)$. This is equivalent to filtering only in ω_0 space. The width of the filter was adjusted by eye to give an acceptable match to Phillip's (1985b) dielectric functions. The best match was found using $\Delta = 90 \text{ cm}^{-1}$ and is consistent with the idea that when Δ is of the order of or exceeds the width of ϵ'' for crystalline quartz (about $\gamma_0 \approx 40 \text{ cm}^{-1}$ in this case), the material is probably fairly amorphous. The agreement between Phillip's curves and those produced by CDO, while hardly perfect, is encouraging, especially in view of the simplicity of the technique.

A more challenging test of CDO can be performed using a more complex mineral, olivine. Olivine $[(\text{Mg}, \text{Fe})_2 \text{SiO}_4]$ is a common rock-forming mineral occurring as an orthorhombic crystal (three principal axes). It is frequently mentioned in connection with cosmic dust (Day 1974) and has been identified tentatively in the spectra of comets (Campins & Ryan 1989; Hanner et al. 1994) and circumstellar material (Knacke et al. 1993). Steyer (1974) measured olivine's three components of $\epsilon(\omega)$ corresponding to the principal axes of the crystal (Fig. 3, *top panels*). A sample from the same piece of olivine was bombarded with 1.5 MeV neon atoms to produce a "disordered" form of the mineral by Krätschmer & Huffman (1979). Its dielectric function $\hat{\epsilon}(\omega)$ was then measured (Fig. 3, *bottom panels*). We filtered Steyer's three dielectric functions using a triangular filter and adopted a width of 90 cm^{-1} as the best fit (by eye), then we averaged them. As before, only a single free parameter (Δ) was used, and no vertical scaling or normalization was done. The computed dielectric function $\hat{\epsilon}(\omega)$ is compared to Krätschmer & Huffman's (K & H) in Figure 3 (*bottom panels*). Again, reasonable agreement is obtained.

5. DISCUSSION

There has heretofore been no simple and generally available technique for predicting the IR dielectric function of amorphous material. The ability of CDO to predict the dielectric functions is promising, but there are a number of limitations which should be clearly understood. As current-

ly embodied, CDO is intended for use near strong resonances in the IR. Optical and UV resonances involve electronic modes and band structure, and CDO may be too limited for effective use.

In the examples above, only one free parameter (Δ) was used, although the functional form of the filter could be considered a second parameter. Given the large number of possible amorphous forms of any material, it is likely that the distribution of oscillators in the amorphous sample is not perfectly Gaussian (or triangular), as we assumed. Local variations in the damping constant and plasma frequency, which we did not include, probably contributed also to the relatively loose fit. By allowing the damping constant and plasma frequency to vary to improve the fit would probably serve no useful purpose because, in general, we have no well-developed and understood data set of amorphous dielectric functions to try to match. Therefore, the fact that the predicted and measured dielectric functions do not match one another perfectly is to be expected. We do not claim that we have selected the optimum distributions. There may be better distributions, including those that are not symmetric or centered on the crystalline values.

The broadening of the dielectric function that occurs when it is filtered is not surprising. It is useful, however, to understand just how the increased width translates to broader spectra. There are two types of resonances that give rise to absorption, transverse optical modes and surface modes (Bohren & Huffman 1983). The former are associated with bulk properties of the material and are present, in some form, regardless of the size, shape, and thickness of the particles. Transverse optical modes occur in the vicinity of ω_T , the frequencies at which ϵ' crosses zero near the maximum in ϵ'' . Surface modes appear at Fröhlich frequencies ω_F . Fröhlich resonances can occur anywhere that $\epsilon' < 0$, a region bounded by the transverse optical frequency ω_T and the longitudinal optical frequency ω_L , where ω_L is defined as the frequency at which $\epsilon = 0$. The precise Fröhlich frequency depends on composition and shape, but not size as long as the particles are small. Therefore, absorption in a collection of small, many-shaped particles will be due to bulk properties and shape properties, and the range of absorption will be between approximately ω_T and ω_L , the zeros of ϵ' .

When ϵ is filtered, ω_T changes very little as long as $\Delta < \gamma$ because ϵ' is nearly symmetric about zero. ω_L , however, shifts to higher frequencies because near ω_L , ϵ' is not symmetric about zero. The amount by which ω_L shifts will depend on Δ , γ , ϵ_0 , and ω_p in a less obvious way. The result of amorphization, then is the frequency range of surface modes expands and shifts to higher frequencies. Frequency shifts very much like those suggested here have been reported by Stephens & Russell (1979). In their laser vaporization experiments, they found that the width of the absorption feature in amorphous olivine increased by about 25% relative to crystalline olivine, and the central frequency increased by about 10%. Similar results were reported on enstatite.

It is interesting that a CDO filter width of about 90 cm^{-1} (about 9%) provided the best fit to the measured data for both quartz and olivine. This seems consistent with earlier findings that the measured distribution widths for amorphous materials are of order of 9%. It is also consistent with experimental results of Stephens & Russell and may indicate that the equilibrium configuration for many amorp-

ous materials is well defined and can be characterized by a filter width of about 10%. Unfortunately, there are not enough data available on the dielectric functions of amorphous materials from which to generalize with any confidence. Therefore, we suggest provisionally that in a blind attempt to compute $\hat{\epsilon}$ from ϵ for a material with no measured amorphous dielectric function, 9% should be about right for the filter width.

As a final note, we recognize that the CDO fits are far from perfect. This may be due to the relative simple nature of the technique, or to the fact that the amorphous samples measured by Philipp (1985b) and Krättschmer & Huffman (1979) may not be representative of the many different varieties of the amorphous mineral. CDO's power lies in its ability to predict dielectric functions for a wide variety of astronomical materials to an accuracy that at least matches the large uncertainties in our astronomical knowledge. It predicts successfully the muting of spectra structure and the shift to higher frequencies of surface modes. It may be useful in placing limits on how amorphous a mineral could be and still fit the observed astronomical spectra. CDO is hardly the last word in modeling spectra of amorphous material, but rather the first step. We look forward to future laboratory measurements as well as to more sophisticated theories of dielectric functions for amorphous materials.

6. SUMMARY AND CONCLUSION

We have demonstrated the fundamental concepts of a technique for computing the dielectric functions of partially

amorphous materials in the vicinity of strong IR absorption features. This is done by low-pass filtering the crystalline dielectric functions using a single free parameter, Δ , the filter FWHM. In principle, the technique should be applicable to any phonon resonance in the infrared. The technique is based on the generally accepted, short-range atomic order in amorphous materials and its close resemblance to crystalline materials. The resulting dielectric functions satisfy the Kramers-Kronig dispersion relations. Comparisons of laboratory and theoretical dielectric functions for olivine and quartz show the technique to be relatively accurate and versatile. In view of the lack of data on the dielectric function of materials in various states of atomic disorder, the CDO approximation provides a useful first-order method for computing dielectric functions of a material whose crystalline properties are known.

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