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Kramers–Kronig analysis of non-normal incidence reflection

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Abstract. A method is given for using the Kramers–Kronig dispersion relations to evaluate optical and dielectric parameters of materials from reflectance data measured at 45° incidence. The method requires only a single determination of the reflectance spectrum and is valid for incident light which is either polarized or completely unpolarized. As an example, the real and imaginary parts of the complex dielectric constant, $n^2 - k^2$ and $2nk$ respectively, are evaluated from the 45° reflectance spectrum of a single crystal of magnesium oxide and compared with the values obtained from normal-incidence data.

1. Introduction

A wide variety of methods exists for the determination of the optical properties of materials. While much information on absorption processes may, for example, be derived from simple transmission measurements, in regions of the electromagnetic spectrum where photon energies are sufficient to produce fundamental absorption in the material, very thin layers of the latter may be required to permit measurement of the transmitted intensity. In particular, in the far ultra-violet region the onset of fundamental absorption in ionic crystals, such as the halides of the alkali, and alkaline earth metals, is due to electronic transitions from the filled valence bands across the forbidden energy gap to the conduction bands, and the absorption coefficients associated with such transitions are very large, being of the order of 10^5 or even 10^6 cm^{-1} . For experimental conditions where the smallest transmission that can be measured reliably is 1%, say, such intense absorption requires the specimen to be of the order of 1000 \AA or less in thickness. Two serious problems arise: firstly, in many cases preparation of, and experimentation with, such thin layers or films may be difficult, and, secondly, such films may no longer be structurally and optically characteristic of the bulk material. Hence the last fifteen years have seen a very extensive development of reflection techniques used either entirely instead of, or alternatively in conjunction with, transmission techniques. Since reflection measurements require only a single surface of the crystal the problems mentioned above in connection with thin films no longer arise.

There is, however, a very serious problem associated with reflection methods to which insufficient attention has been paid, but which nevertheless must be examined fully in all such measurements. Unless extreme care is taken, the surface examined by reflectance may not be characteristic of the bulk material—grease deposits, chemical reaction by the atmosphere or other contaminants, structural deformation, and so on, are all factors which must be considered. The importance of such precautions, particularly for measurements in the far ultra-violet region, may be readily ascertained by reference to the work of Hass and Hunter (1962) for example. The reflectance of a freshly deposited aluminium film in a vacuum of less than 10^{-6} torr was found by them to be 86% at a wavelength of 1025 \AA , but decreased to 70% within about 100 seconds of deposition, and to 54% within 8 minutes. In the following consideration of the general relations between reflectance and the other parameters it will be assumed that the former refers to an ideal surface.

2. Reflection relations

We consider the general case of monochromatic plane-polarized electromagnetic radiation incident from vacuum on to the surface of a medium of refractive index n and absorp-

tion index k . If the angle of incidence be ϕ then the Fresnel equations for the reflected amplitudes are (Fahrenfort 1961)

$$\tilde{r}_s = \frac{a - ib - \cos \phi}{a - ib + \cos \phi} \quad (1)$$

$$\frac{\tilde{r}_p}{\tilde{r}_s} = \frac{a - ib - \sin \phi \tan \phi}{a - ib + \sin \phi \tan \phi}. \quad (2)$$

In these equations r_s is the ratio of the reflected amplitude to that of the incident radiation for light polarized perpendicularly to the plane of incidence, \tilde{r}_p corresponding to the case of parallel polarized light. The symbol \sim will be used throughout this paper to denote complex quantities. The quantities a and b are directly related to n , k and ϕ such that

$$\begin{aligned} a^2 - b^2 &= n^2 - k^2 - \sin^2 \phi \\ ab &= nk. \end{aligned} \quad (3)$$

Thus if n and k are to be determined from reflection measurements, two simultaneous equations will normally have to be obtained. In practice the experimentally measured quantities are the reflected intensities R_s and R_p , which are simply $|\tilde{r}_s|^2$ and $|\tilde{r}_p|^2$ respectively. Thus the relevant equations become

$$R_s = \frac{(a - \cos \phi)^2 + b^2}{(a + \cos \phi)^2 + b^2} \quad (4)$$

$$\frac{R_p}{R_s} = \frac{(a - \sin \phi \tan \phi)^2 + b^2}{(a + \sin \phi \tan \phi)^2 + b^2}. \quad (5)$$

There is thus a number of different ways by which a and b , and hence n and k , may be obtained. For a fixed incident angle ϕ , both R_s and R_p or R_s and R_p/R_s may be measured. Alternatively, only one of the reflected intensities R_s , R_p and R_p/R_s need be measured, if the measurement is then repeated at some different incident angle. Such measurements, and minor variations on them, have been extensively reported in the literature and reference may be made to the work of Avery (1952), Simon (1951), Ditchburn (1955), Humphreys-Owen (1961) and Fahrenfort and Visser (1962).

All the above methods rely on at least two measurements, however, requiring often tedious experimentation and subsequent computation of n and k . A far more serious problem is the requirement for the incident light to be polarized, and this is difficult if not impossible to obtain in some regions of the electromagnetic spectrum. Complete plane polarization cannot readily be produced in the far ultra-violet for example, since any method based upon birefringence or dichroism will be handicapped by the intense absorption of most solid materials in this region. Some progress has been made, however, during the last year (Walker 1964, Johnson 1964, Schellman *et al.* 1964), and polarization by reflection has also been described (Cole and Oppenheimer 1962, Sasaki and Fukutani 1964). Figure 1 shows the way in which the values of R_s and R_p , and also the reflectance R for unpolarized radiation, vary with the angle of incidence. The set of curves shown applies to the typical case for $n = 2$ and $k = 1$, similar sets of curves applying to other values of n and k . It is clear that the degree of polarization of the incident light has very little importance for small angles of incidence—thus it is often desirable to make measurements at normal incidence, or at least at as near normal incidence as experimental conditions permit.

3. Reflection at normal incidence

At normal incidence the Fresnel equations reduce to

$$R_0 = R_{s,0} = R_{p,0} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (6)$$

the complex reflected amplitude being

$$\tilde{r}_0 = \tilde{r}_{s,0} = \tilde{r}_{p,0} = \frac{n - ik - 1}{n - ik + 1}. \quad (7)$$

Although the methods mentioned above for determining n and k now break down since the distinction between R_s and R_p becomes meaningless, it is still possible to proceed from a single measurement of R_0 provided the measurement is made over the whole spectrum.

The complex amplitude is expressed in terms of its argument θ , such that

$$\tilde{r}_0 = |\tilde{r}_0| e^{i\theta} = \frac{n - ik - 1}{n - ik + 1}. \quad (8)$$

Denoting $|\tilde{r}_0|$ by \sqrt{R} , and separating the real and imaginary parts of equation (8), we obtain

$$n = \frac{1 - R}{1 + R - 2 \cos \theta \sqrt{R}}. \quad (9)$$

$$k = \frac{-2 \sin \theta \sqrt{R}}{1 + R - 2 \cos \theta \sqrt{R}}. \quad (10)$$

4. Kramers-Kronig analysis

The value of θ at any particular frequency ω_c is not an independent quantity, but it is in fact directly related to the reflection spectrum by means of the integral transform

$$\theta(\omega_c) = \frac{1}{\pi} \int_0^\infty \ln \left| \frac{\omega + \omega_c}{\omega - \omega_c} \right| \frac{d \ln \{R(\omega)\}^{1/2}}{d\omega} d\omega. \quad (11)$$

This transform—one of a class called Kramers-Kronig dispersion relations after their discoverers—was first applied to reflection spectroscopy by Robinson (1952).

Thus the only experimental measurement required is that of the reflectance R at normal incidence as a function of frequency. The evaluation of $\theta(\omega_c)$ may be readily performed on modern high-speed electronic computers in a few seconds. Thus, knowing $R(\omega_c)$ and $\theta(\omega_c)$, one may calculate n and k from equations (9) and (10), and thence all the other optical and dielectric parameters of interest. This method has been used extensively during the last decade as a valuable means of studying absorption processes throughout the electromagnetic spectrum, for example the work of Spitzer *et al.* (1962) in the infra-red, and that of Jahoda (1957) and Philipp and Taft (1959) in the ultra-violet, may be mentioned.

It should be noted that the evaluation of $\theta(\omega_c)$ from equation (11) strictly requires a knowledge of the reflection over all frequencies, whereas experimental observations are usually conveniently confined in the first instance to a relatively narrow region of the total spectrum, for example the near infra-red, or the far ultra-violet. For absorption processes in the infra-red region this limitation may not be too serious in fact, and n and k can be calculated with reasonable accuracy provided the whole of the dominant structure associated with the absorption system is scanned. The problem is often far more acute, however, in the far ultra-violet. Here experimental difficulties often prevent measurements being extended to sufficiently high frequencies to cover the whole of the absorption band system—indeed most solid materials are characterized by intense continuous absorption from the far ultra-violet into the x-ray region. In such cases the contribution from regions outside the frequency range scanned to the phase angle θ at ω_c cannot be assessed experimentally, and recourse to other methods is needed. Common procedure has been to use various forms of extrapolation of the reflection data to high frequencies, depending upon assumptions about the behaviour of the reflectance R at such frequencies (Stern 1963, p. 338). This problem has been discussed in a previous paper (Roessler 1965) and an alternative method suggested for dealing with it.

5. Non-normal incidence reflection data

Whilst the Kramers-Kronig technique has been applied extensively in the analysis of reflectance data at normal incidence, it does not generally appear to have been realized that the analysis is not restricted to data measured at normal incidence. Using equation (1) for the reflected amplitude \tilde{r}_s , and expressing this complex quantity in terms of its argument ψ say, we have

$$\tilde{r}_s = |\tilde{r}_s| e^{i\psi} = \frac{a - ib - \cos \phi}{a - ib + \cos \phi}. \quad (12)$$

Denoting $|\tilde{r}_s|$ by $\sqrt{R_s}$, and separating the real and imaginary parts of equation (12), as was done for equation (8) in the case of normal incidence, we have

$$a = \frac{(1 - R_s) \cos \phi}{1 + R_s - 2 \cos \psi \sqrt{R_s}} \quad (13)$$

$$b = \frac{-2 \cos \phi \sin \psi \sqrt{R_s}}{1 + R_s - 2 \cos \psi \sqrt{R_s}}. \quad (14)$$

In these equations the angle of incidence ϕ is known; hence provided R_s may be determined experimentally, only ψ remains unknown. But use of the Kramers-Kronig dispersion relation yields

$$\psi(\omega_c) = \frac{1}{\pi} \int_0^\infty \ln \left| \frac{\omega + \omega_c}{\omega - \omega_c} \right| \frac{d \ln \{R(\omega)\}^{1/2}}{d\omega} d\omega. \quad (15)$$

Determination of n and k from a and b is trivial from equation (3), and hence the procedure for computing the optical parameters is exactly similar to that for the normal incidence case, except that the reflectance R_s is measured rather than the normal incidence reflectance R .

It has thus been established that if light polarized perpendicularly to the plane of incidence of the crystal is available, a single measurement of the corresponding reflection spectrum is sufficient to enable complete determination of n and k —and any angle of incidence ϕ may be used at the convenience of the observer. Reference to figure 1 shows that R_s is a monotonically increasing function of ϕ . For the values of n and k chosen it is seen that the value of R_s at 70° incidence is nearly 60%, i.e. almost three times the normal incidence value. In the far ultra-violet, reflectances are often extremely small for many solid

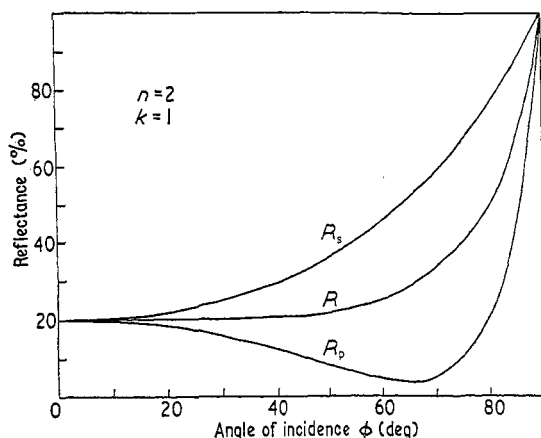


Figure 1. Dependence of reflectance of plane-polarized light upon angle of incidence. The subscripts s and p refer to the components polarized perpendicular and parallel, respectively, to the plane of incidence. The reflectance R corresponds to unpolarized light.

materials, remaining only a few per cent at photon energies exciting plasma resonances in the material. Since also the intensity of light available in the far ultra-violet is usually relatively weak, it is very desirable to measure the higher reflectances at angles of incidence other than zero. Thus two advantages of measuring reflectance at non-normal incidence are firstly that the quantities to be measured are usually larger, and hence more easily measured reliably than normal incidence data, and secondly that no approximations are involved ('normal' incidence measurements are usually taken only at 'near-normal' incidence). The latter approximation is often reasonable, as figure 1 shows, but may not be safe in regions where k is varying rapidly with frequency. The dependence of reflectance upon ϕ is very critical for certain values of k and indeed forms the basis of a method for evaluating n and k (Vincent-Geisse and Dayet 1965).

There is still a serious disadvantage of the method outlined above, namely the need for polarized light. Provided one is prepared to restrict the choice of ϕ to be 45° , however, this need is removed as completely unpolarized light may be used. Where the light available is partially polarized the degree of polarization must be known of course.

6. 45° incidence

Examination of equations (4) and (5) show that in the special case of $\phi = 45^\circ$, $R_p = R_s^2$ for all n and k . Since also the reflectance R_{45} for unpolarized incident radiation is given by the mean value of the two polarized components, we may write

$$R_{45} = \frac{1}{2}(R_s + R_p) = \frac{1}{2}R_s(1 + R_s). \quad (16)$$

Hence one may simply measure the reflectance at 45° incidence, and immediately calculate the value of R_s from equation (16). The remainder of the evaluation is then straightforward through equations (15), (13) and (14).

7. Application to magnesium oxide

In order to demonstrate the method, the reflectance of the freshly cleaved surface of a single crystal of magnesium oxide was measured. Initially the reflection spectrum at normal incidence was determined in the far ultra-violet for photon energies between 4 eV and about 14 eV. In practice the smallest incidence angle at which the experiment could be made was 15° , but according to figure 1 the reflection at 15° is very similar to that at normal incidence. The procedure was then repeated for an incident angle of 45° . The two spectra are presented for comparison in figure 2, where, as expected, R_{45} is seen to be

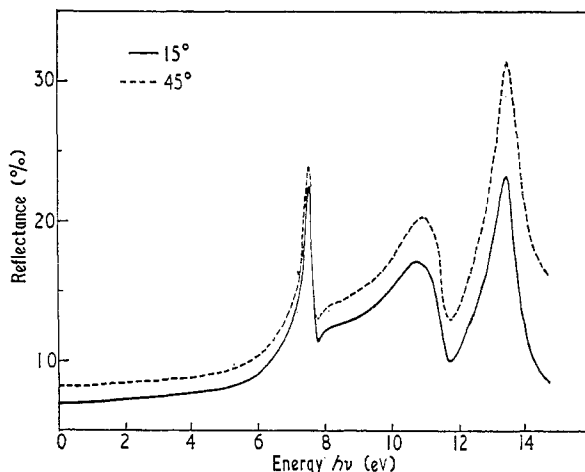


Figure 2. Reflectance spectra of a freshly cleaved single crystal of magnesium oxide. The full curve is that for unpolarized radiation incident at 15° ('normal') incidence; the broken curve refers to 45° incidence.

rather larger than the normal incidence data. The data have been extrapolated on the low energy side using known values of the refractive index in this region to calculate the theoretical reflectance. The use of a conventional hydrogen glow-discharge as a source for the ultra-violet incident radiation provided the high energy data limit at about 14 eV.

The normal incidence data were analysed using the Kramers-Kronig dispersion relation to compute $n^2 - k^2$ and $2nk$, the real and imaginary parts of the complex dielectric constant. The data at 45° were analysed by the method described in this paper and are presented in figure 3 for comparison. The details of the method of computation with respect to the

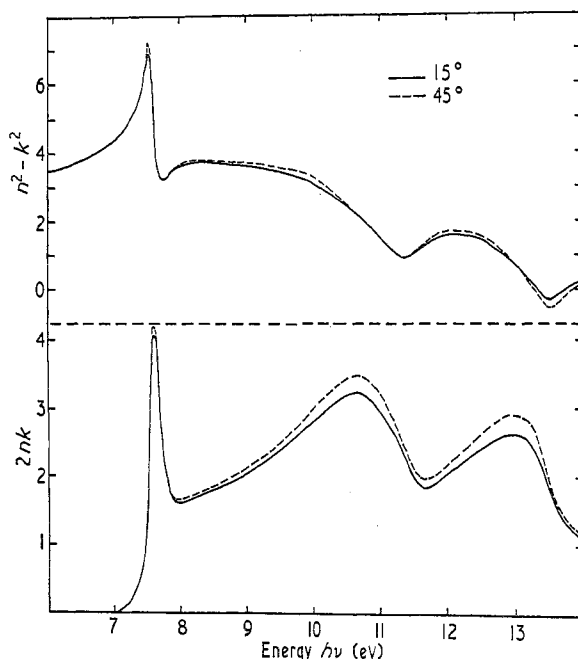


Figure 3. The real and imaginary parts of the complex dielectric constant, $n^2 - k^2$ and $2nk$, of magnesium oxide, as computed from reflectance data by the Kramers-Kronig analysis. The full curve corresponds to data measured at 15° , the broken curve to that at 45° .

restricted energy range used are given in a previous paper (Roessler 1965). The ultra-violet reflection spectrum of magnesium oxide has already been reported by Nelson (1955), Reiling and Hensley (1958) and Harris (1963 Ph.D. Thesis, University of London). It is believed, however, that this paper presents the first analysis of the optical parameters of MgO from its reflection spectrum. Details of the other optical and dielectric properties, together with a discussion of their significance, have been given in a report to the U.S. Army (1964, unpublished).

8. Discussion of results

In figure 3 the full lines refer to data obtained from the 15° incidence reflectance, and the broken curves correspond to the 45° incidence reflectance. The spectral shape of the curves is identical and the only discrepancy lies in the absolute magnitudes where small differences are observed. However, there are several reasons which may be advanced to explain the differences.

(i) As has been mentioned above, the ultra-violet reflectance of a material is very critically dependent upon the nature of the surface examined. Since the crystal used was examined at two angles of incidence it is very probable that slight imperfections in the surface may appear more prominently at 45° than at 15° and vice versa, or even that a slightly different area of the surface was examined in the two cases.

(ii) It was assumed that the incident light used in both measurements was completely unpolarized. In practice the concave reflection grating used as the disperser partially polarizes the light before the latter is incident upon the sample. The grating is used at near-normal incidence and the degree of polarization produced is therefore probably quite small, but may have been sufficient to produce the observed differences in the spectra. It should also be noted that, quite apart from the effect of the grating, many sources of ultra-violet emit partially polarized radiation.

(iii) In the Kramers-Kronig analysis of the 15° reflectance it was assumed that this was in fact 'normal' incidence. There is a small difference, however, between the reflectance at 15° and at normal incidence, as figure 1 indicates, though the extent of this difference will vary over the spectral range with the values of n and k .

(iv) A certain amount of error is always possible in the actual computation of parameters by means of the Kramers-Kronig transform owing to the difficulty in the exact evaluation of the phase angle θ throughout the spectral range. This point has already been discussed in greater detail in §4 of this paper.

9. Conclusions

The extent of agreement between the parameters obtained from the near normal incidence and 45° reflection data, indicates the validity of the above method. Unlike the analysis of normal incidence data, no approximations or assumptions have to be made concerning the angle of incidence when the latter is 45° . Further, unlike conventional methods of obtaining non-normal incidence data, it is not necessary to use polarized radiation, and only a single measurement of the reflection spectrum is required, rather than the use of two or more measurements at varying angles of incidence. It should be observed of course that, if polarized radiation is available, the method can still be used, and the intermediate calculation indicated in equation (16) is simply by-passed. The use of 45° incidence may also permit the use of a rather simpler experimental arrangement, as the detector used to measure the reflectance lies exactly perpendicular to the direction of the incident radiation. There is also the advantage that in general the reflectance at 45° is rather higher than that at normal incidence (the extent again depending on the values of n and k), and hence permits more accurate measurement in regions of low reflectance.

As was mentioned in §7, the surface examined was of a freshly cleaved single crystal of magnesium oxide. The sample was in fact cleaved in air, but then immediately transferred to the reflectometer and maintained in a vacuum of about 10^{-5} torr. The measurements at 15° and at 45° incidence were performed in quick succession under vacuum, and thus it was not expected that the surface conditions altered significantly during the experiment. Thus even if surface contamination appeared before transfer of the crystal to the vacuum system, both reflectance measurements were made on the same surfaces under identical conditions.

It is not claimed that the Kramers-Kronig technique is the best method of determining optical parameters, but that where it is used the analysis need not be restricted to normal incidence data. Where it is difficult to obtain and examine 'pure' surfaces a different method is probably desirable. For example if it is conveniently possible to make reflectance measurements over a range of angles, the effect of any surface films can be determined and hence eliminated.

The method has been described with particular reference to the far ultra-violet region, but it will be clear that it applies equally well to any other spectral region.

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