

IV. OPTICAL AND INFRARED SPECTROSCOPY

Prof. C. H. Perry
Dr. R. Geick
D. P. Athans

W. J. Hakel
D. B. Hall

P. Lubitz
E. C. Reifstein III
E. F. Young

A. ANALYSIS OF REFLECTION SPECTRA BY MEANS OF A FIT WITH A CLASSICAL DISPERSION FORMULA

In the infrared region polar crystals exhibit a reflection spectrum with reststrahlen bands because of the infrared active lattice modes. These modes, which have a linear dipole moment with respect to the normal coordinate, cause the infrared dispersion. When the reflectivity of such a crystal has been measured over a sufficiently wide frequency range, two kinds of analyses are generally used to extract the available information, such as eigenfrequencies, oscillator strengths, and so forth. One method is the Kramers-Kronig analysis,¹ and the other is an optimum fit of the data by means of a classical dispersion formula. The latter method will be discussed in this report with respect to some theoretical aspects and its practical application.

Polar and cubic crystals with two particles per unit cell have one infrared active lattice mode. The classical treatment of the interaction of electromagnetic waves and this lattice mode yields the classical dispersion formula² for the complex dielectric constant of the crystal as a function of the frequency ω

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_{\infty} + \frac{s^2}{\omega_0^2 - \omega^2 + i\omega\gamma}, \quad (1)$$

where ϵ_{∞} is the contribution to ϵ of the UV-absorption and UV-dispersion which can be assumed to be constant in the infrared region; ω_0 is the eigenfrequency of the infrared active mode; s^2 is its oscillator strength; and γ is the damping constant.

If a more complicated crystal is considered with more than one infrared active mode that do not interact with each other, the dispersion formula contains a sum of dispersion terms, one for each active mode. In certain cases it may be necessary to take the interaction of at least two modes into account, and Barker and Hopfield³ have derived a dispersion formula for the case in which two modes strongly interact. In the equations of motion an interaction term was added:

$$\begin{aligned} \ddot{\vec{y}}_1 + \rho_{11}\dot{\vec{y}}_1 + a_{11}\vec{y}_1 + a_{12}\vec{y}_2 &= a_{13}\vec{E} \\ \ddot{\vec{y}}_2 + \rho_{22}\dot{\vec{y}}_2 + a_{21}\vec{y}_1 + a_{22}\vec{y}_2 &= a_{23}\vec{E}. \end{aligned} \quad (2)$$

The transformation diagonalizing the force constant matrix

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$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

yields off-diagonal terms for the damping constants:

$$\begin{aligned} \ddot{\vec{x}}_1 + \gamma_{11}\dot{\vec{x}}_1 + \gamma_{12}\dot{\vec{x}}_2 + \omega_1^2\vec{x}_1 &= b_{13}\vec{E} \\ \ddot{\vec{x}}_2 + \gamma_{21}\dot{\vec{x}}_1 + \gamma_{22}\dot{\vec{x}}_2 + \omega_2^2\vec{x}_2 &= b_{23}\vec{E}. \end{aligned} \quad (3)$$

From these two equations the following dispersion formula in which a third dispersion term is added for a third infrared active eigenvibration that does not interact with the two others⁴ is obtained:

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{s_1^2(\omega_2^2 - \omega^2 + i\omega\gamma_2) - 2is_1s_2\omega\gamma_{12} + s_2^2(\omega_1^2 - \omega^2 + i\omega\gamma_1)}{(\omega_1^2 - \omega^2 + i\omega\gamma_1)(\omega_2^2 - \omega^2 + i\omega\gamma_2) + \omega^2\gamma_{12}^2} + \frac{s_3^2}{\omega_3^2 - \omega^2 + i\omega\gamma_3}, \quad (4)$$

where the subscripts 1, 2, and 3 refer to the three active modes, and γ_{12} is the damping term arising from the interaction of modes 1 and 2.

Since the damping constants γ_ν and $\gamma_{\nu\mu}$ are introduced ad hoc in the classical treatment, this derivation of a dispersion formula cannot show the physical meaning of the damping terms. The results of a proper quantum mechanical treatment of the infrared dispersion, however, will show the damping related to the dissipation of energy from the active lattice modes (dispersion oscillators) to other lattice modes by means of anharmonic terms in the lattice potential.⁵ If third-order anharmonic potential only is taken into account and all nonlinear terms in the dipole moment are neglected, the following expression holds for the dielectric constant of a cubic crystal with two infrared active lattice modes⁶

$$\epsilon = \epsilon_\infty + \frac{s_1^2(\omega_2^2 - \omega^2 + i\delta_2) - 2is_1s_2\delta_{12} + s_2^2(\omega_1^2 - \omega^2 + i\delta_1)}{(\omega_1^2 - \omega^2 + i\delta_1)(\omega_2^2 - \omega^2 + i\delta_2) + \delta_{12}^2}. \quad (5)$$

This is the same formula that is obtained by the classical treatment, but instead of damping constants γ there are frequency-dependent damping functions δ :

$$\delta_j = \text{const} \sum_{j'j''} \int \left| \Phi \begin{pmatrix} 0 & k & -k \\ j & j' & j'' \end{pmatrix} \right|^2 \frac{\left[n' + \frac{1}{2} \right] \pm \left[n'' + \frac{1}{2} \right]}{\omega'\omega''} \Delta(\omega \pm \omega' - \omega'') dk^3$$

$$\delta_{j\ell} = \delta_{\ell j} = \text{const} \sum_{j'j''} \int \Phi \begin{pmatrix} 0 & k & -k \\ j & j' & j'' \end{pmatrix} \Phi \begin{pmatrix} 0 & k & -k \\ \ell & j' & j'' \end{pmatrix} \frac{\left[n' + \frac{1}{2} \right] \pm \left[n'' + \frac{1}{2} \right]}{\omega' \omega''} \Delta(\omega \pm \omega' - \omega'') dk^3, \quad (6)$$

where $\Phi \begin{pmatrix} 0 & k & -k \\ j & j' & j'' \end{pmatrix}$ is the third-order potential coefficient coupling modes $\begin{pmatrix} 0 \\ j \end{pmatrix}$ [wave vector 0, branch j], $\begin{pmatrix} k \\ j' \end{pmatrix}$ and $\begin{pmatrix} -k \\ j'' \end{pmatrix}$; ω' , ω'' , n' , and n'' are frequencies and the thermal averages of phonon occupation numbers of modes $\begin{pmatrix} k \\ j' \end{pmatrix}$ and $\begin{pmatrix} -k \\ j'' \end{pmatrix}$, respectively; Δ refers to the Dirac delta function; and the integrals are to be taken over the volume of the first Brillouin zone in reciprocal space.

Essentially, the damping functions δ_1 and δ_2 are the probabilities for all the 2-phonon summation processes (+ sign) or 2-phonon difference processes (- sign) via the dispersion oscillators 1 and 2 which are consistent with wave vector and energy conservation at a given photon frequency ω . δ_{12} is the interference of the processes contained in δ_1 and δ_2 .

For our purpose, the analysis of a reflection spectrum is carried out by means of the classical formula with constant damping terms. The reflection spectrum exhibits only the main features of the infrared dispersion and not the details of the absorption spectrum, especially outside the reststrahlen bands where the reflectivity is given mainly by the refraction index; even in the reststrahlen bands it is not possible to evaluate more than one damping function from the experimental data. Consequently, the use of the classical formula may be justified and the damping constants should be understood to be an average of the damping functions, mainly in the neighborhood of the eigenfrequencies. In the actual analysis, the constants in Eq. 4 have to be chosen by trial and error, and then ϵ is evaluated for the frequency range under consideration. From ϵ' and ϵ'' the optical constants n and k are obtained by means of the equations

$$\begin{aligned} \text{a) } \epsilon' > 0 \quad n &= \sqrt{\frac{1}{2} \left(\epsilon' + \sqrt{\epsilon'^2 + \epsilon''^2} \right)} & k &= \frac{\epsilon''}{2n} \\ \text{b) } \epsilon' = 0 \quad n = k &= \sqrt{\frac{\epsilon''}{2}} & & \\ \text{c) } \epsilon' < 0 \quad k &= \sqrt{\frac{1}{2} \left(-\epsilon' + \sqrt{\epsilon'^2 + \epsilon''^2} \right)} & n &= \frac{\epsilon''}{2k} \end{aligned} \quad (7)$$

The reflectivity (given only for normal incidence)

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$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (8)$$

can be evaluated and compared with experimental data. By variation of the constants in Eq. 4, an optimum fit to the experimental data is obtained, and this analysis yields the eigenfrequencies, the oscillator strengths, and the damping constants of the infrared active modes.

Note that Eq. 4 can be used also in the case of a crystal having two interacting eigenvibrations and additional dispersion and absorption caused by free carriers (for example, semiconductors). By setting $\omega_3 = 0$, the last dispersion term in Eq. 4 is converted into a Drude-term, and s_3 and γ_3 are determined by the carrier concentration N , the effective mass m^* , and the mobility μ of the free carriers

$$s_3 = \sqrt{\frac{N}{m^* \epsilon_{\text{vac}}}} \frac{e}{2\pi c} [\text{cm}^{-1}] \quad \gamma_3 = \frac{e}{2\pi c m^* \mu} [\text{cm}^{-1}],$$

where e is the electron charge, c is the light velocity in vacuum, and ϵ_{vac} is the dielectric constant in vacuum.

As examples of this analysis we shall describe the fit to the reflection spectra of BN and KNiF_3 . BN is a uniaxial anisotropic crystal with a layer structure similar to graphite. The reflectivity has been measured with linearly polarized light with the E-vector parallel and perpendicular to the c-axis (See Figs. IV-1 and IV-2). KNiF_3 has the perovskite structure and its experimentally determined reflectivity is shown in Fig. IV-3. From the experimental data, it appears that there are two infrared active lattice modes causing reststrahlen bands in both cases for BN, and three active modes in KNiF_3 . The initial values for the various constants in the classical dispersion formula (Eq. 4) were obtained from the results of a Kramers-Kronig analysis (see Figs. IV-4, IV-5 and IV-6).

BN	E c				
$\epsilon_\infty = 3.06$	$s_1 = 771$	$\omega_1 = 783$	$\gamma_1 = 15.0$		
$\gamma_{12} = 0$	$s_2 = 1585$	$\omega_2 = 1510$	$\gamma_2 = 146$		
$\epsilon_0 = 5.13$	$s_3 = 0$	$\omega_3 = 0$	$\gamma_3 = 0$		(10a)

BN	E \perp c				
$\epsilon_\infty = 5.36$	$s_1 = 351$	$\omega_1 = 767$	$\gamma_1 = 35.0$		
$\gamma_{12} = 0$	$s_2 = 1850$	$\omega_2 = 1367$	$\gamma_2 = 31.0$		
$\epsilon_0 = 7.45$	$s_3 = 0$	$\omega_3 = 0$	$\gamma_3 = 0$		(10b)

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<u>KNiF₃</u>	(isotropic crystal)			
$\epsilon_{\infty} = 2.47$	$s_1 = 233$	$\omega_1 = 152$	$\gamma_1 = 19.5$	(10c)
$\gamma_{12} = 0$	$s_2 = 355$	$\omega_2 = 245$	$\gamma_2 = 15.0$	
$\epsilon_0 = 8.13$	$s_3 = 483$	$\omega_3 = 447$	$\gamma_3 = 32.5$	

The units for s_{ν} , ω_{ν} , γ_{ν} and $\gamma_{\mu\nu}$ are in cm^{-1} , and ϵ_{∞} is the dielectric constant relative to that of vacuum. The reflectivity computed with these sets of constants has to be compared with the experimental data (see Figs. IV-1, IV-2 and IV-3), and the agreement at first is still rather poor for most of the reststrahlen bands. The computed values of ϵ' and ϵ'' can be compared with the Kramers-Kronig data (see Figs. IV-4, IV-5 and IV-6). In order to improve the fit, it is often advisable to make use of the following rules.

1. The static dielectric constant which determines the reflectivity at the low-frequency end of the spectrum outside the reststrahlen bands is given by

$$\epsilon_0 = \epsilon_{\infty} + \frac{s_1^2}{\omega_1^2} + \frac{s_2^2}{\omega_2^2} + \frac{s_3^2}{\omega_3^2}$$

2. Where the real part ϵ' changes from positive to negative values, the reflectivity exhibits a pronounced minimum and a sharp rise to high values with decreasing frequencies, provided ϵ'' is sufficiently small.

3. The height of a reststrahlen band is determined by ϵ'' , that is, mainly by the damping γ_{ν} , while the interaction damping $\gamma_{\mu\nu}$ becomes significant in the region between two eigenvibrations.

In this way, the best fit for BN was obtained with the following sets of constants:

<u>BN</u> <u>E c</u>				
$\epsilon_{\infty} = 4.10$	$s_1 = 572$	$\omega_1 = 783$	$\gamma_1 = 8.0$	(11a)
$\gamma_{12} = 0$	$s_2 = 1020$	$\omega_2 = 1510$	$\gamma_2 = 80.0$	
$\epsilon_0 = 5.09$	$s_3 = 0$	$\omega_3 = 0$	$\gamma_3 = 0$	

<u>BN</u> <u>E ⊥ c</u>				
$\epsilon_{\infty} = 4.95$	$s_1 = 351$	$\omega_1 = 767$	$\gamma_1 = 35.0$	(11b)
$\gamma_{12} = 0$	$s_2 = 1870$	$\omega_2 = 1367$	$\gamma_2 = 29.0$	
$\epsilon_0 = 7.04$	$s_3 = 0$	$\omega_3 = 0$	$\gamma_3 = 0$	

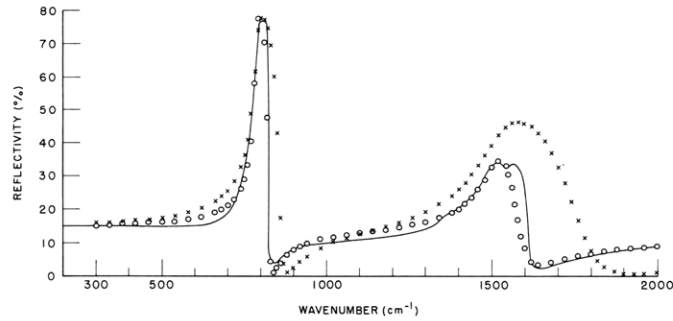


Fig. IV-1. Reflectivity of BN, E || c. Experimental (—), computed by using the classical dispersion formula and the values for the constants given in (10a) (X X X) and (11a) (O O O).

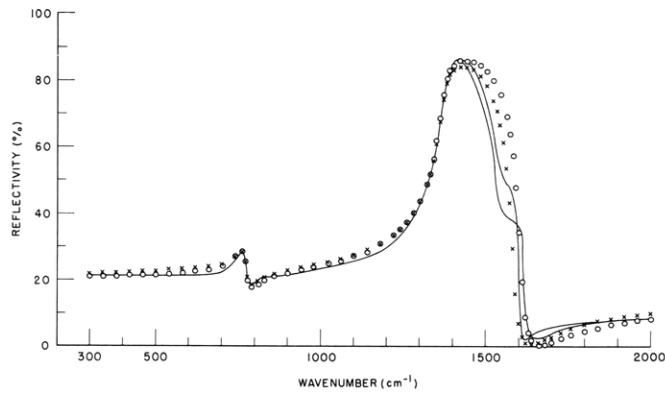


Fig. IV-2. Reflectivity of BN, E ⊥ c. Experimental (—), computed by using the classical dispersion formula and the values for the constants given in (10b) (X X X) and (11b) (O O O).

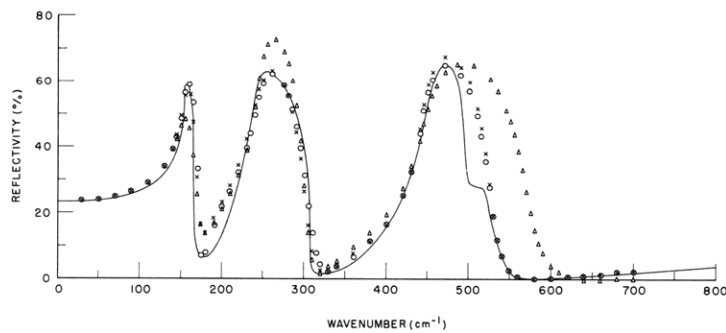


Fig. IV-3. Reflectivity of KNiF_3 . Experimental (—), computed by using the classical dispersion formula and the values for the constants given in (10c) ($\Delta\Delta\Delta$), (12) (X X X) and (13) (O O O).

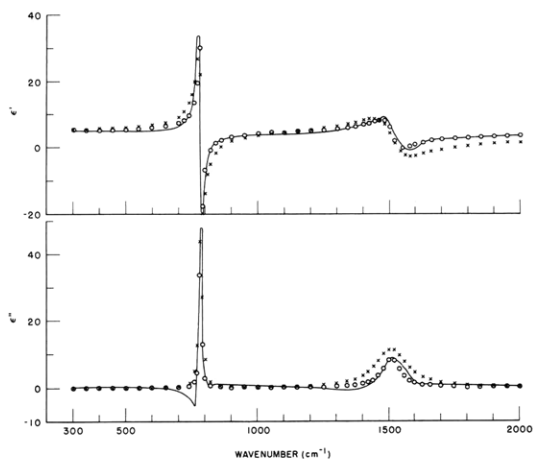


Fig. IV-4. Real part ϵ' and imaginary part ϵ'' of the dielectric constant of BN for $E \parallel c$ obtained by Kramers-Kronig analysis (—), computed by using the classical dispersion formula and the values for the constants given in (10a) (XXX) and (11a) (OOO).

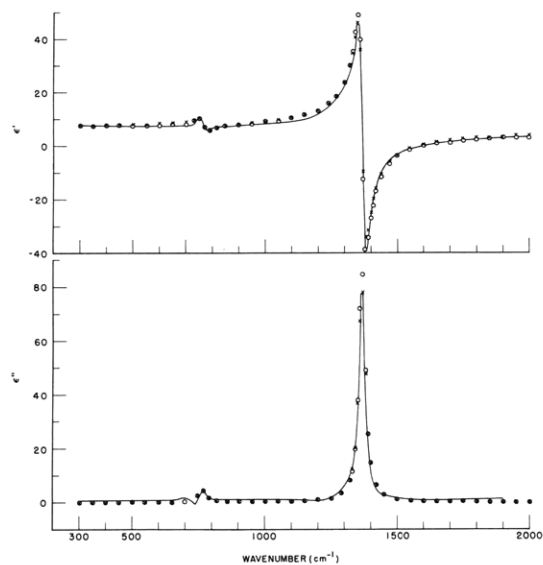


Fig. IV-5. Real part ϵ' and imaginary part ϵ'' of the dielectric constant of BN for $E \perp c$ obtained by Kramers-Kronig analysis (—), computed by using the classical dispersion formula and the values for the constants given in (10b) (XXX) and (11b) (OOO).

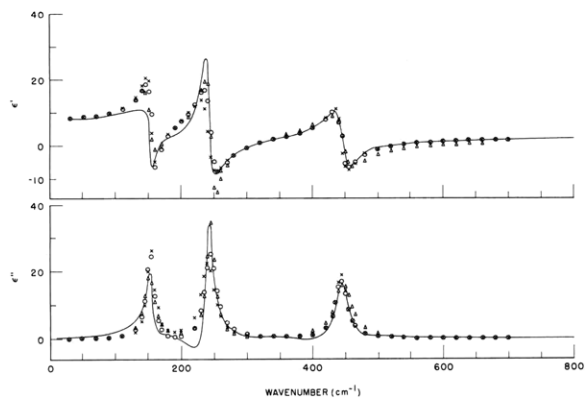


Fig. IV-6. Real part ϵ' and imaginary part ϵ'' of the dielectric constant of KNiF_3 obtained by Kramers-Kronig analysis (—), computed by using the classical dispersion formula and the values for the constants given in (10c) ($\Delta\Delta\Delta$), (12) (XXX) and (13) (OOO).

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In these cases it was not necessary to use the interaction damping. The computed data are shown in detail in Figs. IV-1, IV-2, IV-4 and IV-5.

For KNiF_3 the best fit without interaction damping was obtained with the following

$$\begin{array}{llll} \epsilon_{\infty} = 2.85 & s_1 = 230 & \omega_1 = 154 & \gamma_1 = 13.0 \\ \gamma_{12} = 0 & s_2 = 365 & \omega_2 = 241 & \gamma_2 = 25.0 \\ \epsilon_0 = 8.21 & s_3 = 408 & \omega_3 = 444 & \gamma_3 = 20.0 \end{array} \quad (12)$$

The agreement of computed and experimental data is quite reasonable in the region of the reststrahlen bands (Fig. IV-3) but the computed reflectivity is too high in the frequency region $170\text{-}220 \text{ cm}^{-1}$. Therefore better agreement is reached with $\gamma_{12} \neq 0$ (Fig. IV-3).

$$\begin{array}{llll} \epsilon_{\infty} = 2.85 & s_1 = 230 & \omega_1 = 154 & \gamma_1 = 13.5 \\ \gamma_{12} = 12.0 & s_2 = 371 & \omega_2 = 245 & \gamma_2 = 22.5 \\ \epsilon_0 = 8.21 & s_3 = 408 & \omega_3 = 444 & \gamma_3 = 22.0 \end{array} \quad (13)$$

The computed values of ϵ' and ϵ'' are shown in Fig. IV-6.

The computations for this work were performed at the Computation Center, M. I. T., and the authors wish to thank S. A. Rappaport of the RLE Computation Group for writing the program.

R. Geick, C. H. Perry

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