[12] Note, however, that no singular behaviour can arise in this region because the approximations $U^{(k)}$ are unitary and therefore bounded, just as the exact expression (7).

[13] When the calculation is not restricted to the line wing, Eq. (5) involves $\bar{H}^0(F)$ instead of $H^0(0)$. However, in order that U^P be the exact solution, the dependence on F has to be suppressed.

[14] The other two forms have also been calculated and used as numerical tests for the first one.

[15] D. VOSLAMBER, Physics Letters 40 A, 266 [1972].

[16] N. TRAN MINH and H. VAN REGEMORTER, J. Phys. B 5, 903 [1972].

[17] J. T. GODFREY, C. R. VIDAL, E. W. SMITH, and J. COOPER, Phys. Rev. A 3, 1543 [1971]. — Natl. Bur. Stand. (U.S.) Monograph No. 121.

[18] It should be noted that when ω is not much smaller than $kT/\hbar$, a cut-off at $\hbar$ is not a realistic limitation of the region where the classical path approximation is valid. As pointed out in Ref. [1], for large ω the wave packet diffusion is required to stay small only during times ω^{-1} which may be smaller than the relevant collision times b/v. Correspondingly, the impact parameter b_c delimiting the classical domain is then $(\hbar/m\,\omega)^{1/2}$ instead of $\hbar$. Both become equal for $\omega = kT/\hbar$ (here the theory breaks down because it is based on a factorisation of the total density operator); however, b_c should be taken smaller than $\hbar$ already for $\omega \gtrsim \omega_W$ in order to have smooth transition between the two limiting expressions $\hbar$ and $(\hbar/m\,\omega)^{1/2}$.

[19] Direct integration methods have been used without employing the Monte Carlo method used in Ref. [1].

[20] G. BOLDT and W. S. COOPER, Z. Naturforsch. 19 a, 968 [1964].

[20a] G. FUSSMANN, Phys. Letters 41 A, 155 [1972].

[21] R. C. ELTON and H. R. GRIEM, Phys. Rev. 135 A, 1550 [1964].

[22] This result also clearly refutes the statement in Ref. [16] that *all* exponential forms of the *S*-matrix which do not take proper account of the time ordering operator are unable to give *any* information on strong collisions.

[23] Note that $I_1^{(2)}$ represents the corrected numerical result of Ref. [1].

[24] Small deviations were found within the numerical error limits.

[25] Note that the numerical integration of the Schrödinger equation in Ref. [17] is done only for impact parameters of the interval $0.3\,\hbar < b < 10\,\hbar$. — Outside this interval approximations are used. Also the Fourier transform in the collision operator is calculated with approximative methods.

[26] V. S. LISITSA and G. V. SHOLIN, J. Quant. Spectrosc. Radiat. Transfer 12, 985 [1972].

[27] V. I. KOGAN and V. S. LISITSA, J. Quant. Spectrosc. Radiat. Transfer 12, 881 [1972].

[28] H. R. GRIEM, Astrophys. J. 136, 422 [1962].

[29] H. R. GRIEM, Phys. Rev. 140 A, 1140 [1965].

Theory of Damped Polaritons

L. MERTEN * and G. BORSTEL *

Department of Physics, University of Southern California, Los Angeles, California 90007

The basic equations of damped polaritons in orthorhombic crystals and those of higher symmetry are set up. From these basic equations a general dispersion equation for the complex frequencies (real frequency and damping factor) is derived.

Essential differences of the dispersion curves are demonstrated for the case of purely temporally damped polaritons (ω complex, k real) and of purely spatially damped polaritons (ω real, k complex). A detailed discussion and numerical evaluations are given for ZnF_2 as an example.

1. Introduction

In the past the properties of polaritons in general have been treated in the harmonic approximation, i. e., the effect of damping has been neglected in theory. Nevertheless, the damping of polaritons is an important physical quantity which determines e. g., the natural line width of Raman lines, the losses in stimulated Raman effect or the detailed shape of the IR-spectra. A more exact investigation of damping of polaritons has also become of immediate interest because of a controversy which arose among several authors resulting from evident discrepancies between the hitherto existing theory and the experimental results [1-3]. Essentially these discrepancies lay in the existence of a limiting momentum k_c in the $\omega(k)$ diagram as well as a turnaround of the polariton branch at this k_c demanded by theory. In contrast to the experimental results, these conclusions from theory include the nonexistence of long optical phonons in the Raman effect as well as an additional polariton branch which never has been detected experimentally.

These discrepancies have caused some theoreticists to question fundamentally the justification of treating damping in the scope of a phenomenological theory. But the field theoretical methods developed by BENSON and MILLS [4] couldn't even clear up these discrepancies. Very recently ALFANO [5, 6] and GIALLORENZI [6] have shown for cubic crystals with one IR-active oscillator that the above mentioned fundamental discrepancies are not caused by the application of the phenomenological theory but by the uncritical transfer of the dispersion equation for IR-spectra to the dispersion measured by Raman effect. As shown in the following pages, the investigation of this problem is equivalent to the question of whether the wave vector k or the frequency ω or both have to be regarded as complex quantities.

In the following pages we shall derive general dispersion relations of polaritons including damping for orthorhombic crystals and those of higher symmetry with an arbitrary number of atoms in the unit cell. The treatment is based on the basic equations of long optical lattice vibrations combined with Maxwell's equations. The dispersion equations will be discussed in detail and evaluated numerically for ZnF_2 as an example. In doing so the essential differences between temporal and spatial damping are demonstrated.

2. Theory

As it has been shown elsewhere [7, 8], all properties of polaritons in the framework of harmonic approximation can be derived from the following three basic equations:

$$\ddot{Q} = -\omega^2 Q = B^{11} \cdot Q + B^{12} \cdot E , \qquad \text{(1 a)}$$

$$P = (B^{12})^+ \cdot Q + B^{22} \cdot E , \qquad \text{(1 b)}$$

$$E = \frac{4\pi}{n^2 - 1} (P - n^2 s\, s \cdot P) . \qquad \text{(1 c)}$$

Here ω denotes the frequency of the polariton, Q the r-dimensional vector of its quasi-normal coordinates, E its macroscopic electric field, P its electric polarization, $n = c\,k/\omega$ the refractive index and $s = (s_1, s_2, s_3) = k/k$ the wave normal vector. The coefficients B^{ik} in general are tensors, $(B^{12})^+$ denotes the transposed tensor of B^{12}.

Each of the quasi-normal coordinates Q_{aj} is damped by anharmonic interactions, interactions with impurities, etc. This damping can be described pheno-

menologically by a damping factor $\gamma_{aj}(\omega)$. If the coupling of the oscillators by the electric field is temporarily neglected, one gets a set of uncoupled damped oscillators **:

$$\ddot{Q}_{aj} + \gamma_{aj}(\omega)\, \dot{Q}_{aj} = -(\omega_{aj}^0)^2\, Q_{aj} . \qquad \text{(2 a)}$$

Here the index a is referring to the principal axes of the crystal. For anharmonic interactions this ansatz of a frequency dependent damping factor $\gamma_{aj}(\omega)$ can be well established by the quantum theory of anharmonic interactions [9, 10].

If finally a damping tensor $\Gamma(\omega)$ with the diagonal elements $\Gamma_{aj} \equiv \gamma_{aj}$ is introduced, the system (2 a) obviously can be combined to one vector equation:

$$\ddot{Q} + \Gamma(\omega) \cdot \dot{Q} = B^{11} \cdot Q , \qquad \text{(2 b)}$$

where the diagonal elements of B^{11} are the same as in the undamped case, that is $B_{aj}^{11} = -(\omega_{aj}^0)^2$.

Because the damped oscillators are in reality coupled by the electric field in the same manner as the undamped oscillators, the term $B^{12} \cdot E$ must be added again to the right side of Eq. (2 b):

$$\ddot{Q} + \Gamma(\omega) \cdot \dot{Q} = B^{11} \cdot Q + B^{12} \cdot E . \qquad \text{(3)}$$

An eventual damping of the electric field is not taken into account, because this damping is expected to be in general much smaller than the damping of the normal coordinates.

As the remaining basic equations (1 b) and (1 c) are not influenced by damping, the complete system of basic equations of damped polaritons reads, if simultaneously the time dependence $e^{-i\omega t}$ of Q is noticed:

$$-\omega^2 Q = B^{11} \cdot Q + i\,\omega\, \Gamma(\omega) \cdot Q + B^{12} \cdot E , \qquad \text{(4 a)}$$

$$P = (B^{12})^+ \cdot Q + B^{22} \cdot E , \qquad \text{(4 b)}$$

$$E = \frac{4\pi}{n^2 - 1} (P - n^2 s\, s \cdot P) . \qquad \text{(4 c)}$$

The dispersion relation of damped polaritons results from the condition that the determinant of the sys-

** Here and in the following the resonance frequency *without* damping ($\gamma_{aj} = 0$ for all aj) is denoted by ω_{aj}^0 instead of ω_{aj}, because in the following ω_{aj} means the complex frequency $\omega_{aj} = \overline{\omega}_{aj} - i(\gamma_{aj}/2)$, whose real and imaginary parts and whose magnitude $|\omega_{aj}|$ are connected with ω_{aj}^0 by

$$\overline{\omega}_{aj} = \mathrm{Re}(\omega_{aj}) = \pm \sqrt{(\omega_{aj}^0)^2 - (\gamma_{aj}/2)^2}$$

and $|\omega_{aj}| = \omega_{aj}^0$,

which follows directly from (2 a).

tem (4) vanishes. As it is shown in [7], the analogous condition for the system (1) of undamped polaritons leads to a dispersion relation in the form of a generalized Fresnel's equation

$$\varepsilon_1 (\varepsilon_2 - n^2)(\varepsilon_3 - n^2) s_1{}^2 + \varepsilon_2(\varepsilon_3 - n^2)(\varepsilon_1 - n^2) s_2{}^2$$
$$+ \varepsilon_3 (\varepsilon_1 - n^2)(\varepsilon_2 - n^2) s_3{}^2 = 0 . \qquad (5)$$

Here the dielectric function $\varepsilon_a(\omega)$ $(a = 1, 2, 3)$ is determined by the frequencies $\omega_{\alpha j}^0$ and mode strength $\varrho_{\alpha j}$ of the transversal and the frequencies $\omega_{\alpha j}^1$ of the longitudinal long optical phonons:

$$\varepsilon_a(\omega) = \varepsilon_a{}^\infty + \sum_j \frac{4\pi \varrho_{\alpha j}(\omega_{\alpha j}^0)^2}{-B_{\alpha j}^{11} - \omega^2}$$
$$= \varepsilon_a{}^\infty \frac{\prod_j ((\omega_{\alpha j}^1)^2 - \omega^2)}{\prod_j ((\omega_{\alpha j}^0)^2 - \omega^2)} . \qquad (6)$$

Comparing the system (1) of undamped polaritons with the system (4) of damped polaritons the diagonal tensor B^{11} with elements $B_{\alpha j}^{11} = -(\omega_{\alpha j}^0)^2$ is to be replaced by the diagonal tensor

$$\tilde{B}^{11} \equiv B^{11} + i\,\omega\, \Gamma(\omega)$$

with elements

$$\tilde{B}_{\alpha j}^{11} = -(\omega_{\alpha j}^0)^2 + i\,\omega\,\gamma_{aj}(\omega) .$$

This substitution has to be made in all relations derived from the system (1) of undamped polaritons, especially in Eqs. (5) and (6), i. e., $\varepsilon_a(\omega)$ now takes the form

$$\varepsilon_a(\omega) = \varepsilon_a{}^\infty + \sum_j \frac{4\pi \varrho_{aj}(\omega_{\alpha j}^0)^2}{-\tilde{B}_{\alpha j}^{11} - \omega^2} \qquad (7\,\text{a})$$

$$= \varepsilon_a{}^\infty + \sum_j \frac{4\pi \varrho_{aj}(\omega_{\alpha j}^0)^2}{(\omega_{\alpha j}^0)^2 - i\,\omega\,\gamma_{aj}(\omega) - \omega^2} . \qquad (7\,\text{b})$$

Equation (5) together with Eq. (7) represents the general dispersion relation of damped polaritons.

In the case of uniaxial crystals, the Fresnel's equation (5) splits into

$$n^2 = \varepsilon_\perp , \quad (\varepsilon_\perp \equiv \varepsilon_1 = \varepsilon_2) \qquad (8\,\text{a})$$

for the ordinary and

$$n^2 = \frac{\varepsilon_\perp \varepsilon_\parallel}{\varepsilon_\perp s_\perp{}^2 + \varepsilon_\parallel s_\parallel{}^2} \quad (\varepsilon_\parallel \equiv \varepsilon_3 ;$$
$$s_\perp{}^2 \equiv s_1{}^2 + s_2{}^2 , \; s_\parallel \equiv s_3) \qquad (8\,\text{b})$$

for the extraordinary polaritons.

To calculate the dispersion branches $\omega = \omega_i(\boldsymbol{k})$ of polaritons as the roots of Eqs. (5) or (8) for real crystals, the damping factors $\gamma_{aj}(\omega)$ of the uncoupled oscillators in Eq. (2) must be known nu-

merically. In general, however, only the damping factors $\gamma_{aj}(\omega_{aj})$ at the resonance frequencies ω_{aj} are known from measurements. But it seems already to be a very good approximation to replace the damping factors $\gamma_{aj}(\omega)$ in Eq. (7 b) by the constant values $\gamma_{aj} \equiv \gamma_{aj}(\omega_{aj})$. This is because the main contributions to the damping of polaritons come from the damping of those oscillators (aj) [cf. Eq. (2 a)] which are most strongly excited at the given frequency of the polariton. These are those oscillators, whose resonance frequencies ω_{aj} are near the polariton frequency. With this substitution of $\gamma_{aj}(\omega)$ by $\gamma_{aj}(\omega_{aj})$ now Eq. (7 b) can be written in an equivalent form [11,12]

$$\varepsilon_a(\omega) = \varepsilon_a{}^\infty \frac{\prod_j (|\omega_{\alpha j}^1|^2 - i\,\omega\,\gamma_{\alpha j}^1 - \omega^2)}{\prod_j ((\omega_{\alpha j}^0)^2 - i\,\omega\,\gamma_{aj} - \omega^2)} . \qquad (7\,\text{c})$$

In this formula, which is an extension of the well-known Kurosawa formula [13], $\omega_{\alpha j}^1 = \bar{\omega}_{\alpha j}^1 - i(\gamma_{\alpha j}^1/2)$ is the complex frequency of the longitudinal long optical phonons in the principal direction a. Herein $\bar{\omega}_{\alpha j}^1 = \mathrm{Re}(\omega_{\alpha j}^1)$ has the physical meaning of the real phonon frequency and $\gamma_{\alpha j}^1 = -2\,\mathrm{Im}(\omega_{\alpha j}^1)$ of the phonon damping factor (for pure temporal damping). $|\omega_{\alpha j}^1|$ denotes the magnitude of the complex frequencies $\omega_{\alpha j}^1$. The $\bar{\omega}_{\alpha j}^1$'s and $\gamma_{\alpha j}^1$'s are completely determined by the knowledge of the ϱ_{aj}'s ω_{aj}'s and γ_{aj}'s. For details cf. [12]. Formula (7 c) is very useful for numerical evaluations as given below.

Because of the imaginary parts appearing in Eq. (7 b), $n = c\,|\boldsymbol{k}|/\omega$ must be a complex quantity, with the consequence that the frequency $\omega(\boldsymbol{k})$ and/or the wave vector $\boldsymbol{k}$ itself now must be complex quantities. The details of the complex character of ω and $\boldsymbol{k}$ are determined by the boundary conditions of the specific problem. The two special cases are the cases of *pure temporal damping* and of *pure spatial damping*.

Table 1. Input frequencies [11,12] in cm^{-1} and dielectric constants [11] of ZnF$_2$.

E (T)	E (L)
$\omega_{\perp 1} = 173.00 - 3.03\,i$	$\omega_{\perp 1}^1 = 226.58 - 4.19\,i$
$\omega_{\perp 2} = 244.00 - 4.51\,i$	$\omega_{\perp 2}^1 = 265.13 - 5.62\,i$
$\omega_{\perp 3} = 380.00 - 16.7\,i$	$\omega_{\perp 3}^1 = 503.85 - 14.4\,i$
A (T)	A (L)
$\omega_{\parallel 1} = 294.00 - 13.5\,i$	$\omega_{\parallel 1}^1 = 489.58 - 13.5\,i$
$\varepsilon_\perp^\infty = 2.1$	$\varepsilon_\parallel^\infty = 2.6$

3. Pure Temporal and Pure Spatial Damping with Application of ZnF₂

For illustration of the essential differences of *pure temporal* and *pure spatial damping* we treat ZnF$_2$ as an example. The input data for the numerical calculations are given in Table 1. For determination of the $\omega_{\alpha j}^1 = \overline{\omega}_{\alpha j}^1 - i(\gamma_{\alpha j}^1/2)$ from the measured ω_{aj}, ϱ_{aj} and γ_{aj} see [11, 12].

Pure Temporal Damping

E x a m p l e : Spontaneous Raman effect

In the classical spontaneous Raman effect the scattering takes place at thermally excited polaritons with pure temporal damping [2]. In this case in Eq. (5) $\omega_i(\boldsymbol{k})$ must be treated as a complex quantity, $\boldsymbol{k}$ as a real one: $\omega_i(\boldsymbol{k}) = \mathrm{Re}\,(\omega_i(\boldsymbol{k})) - i\,\gamma_i(\boldsymbol{k})/2$ where $\gamma_i(\boldsymbol{k})$ is the damping factor of the polariton. According to Eq. (5) and (7) the frequencies $\omega_i(\boldsymbol{k})$ of the different polariton branches can then be calculated for each real value of $\boldsymbol{k}$.

Figures 1 a – 1 d show the $\omega(\boldsymbol{k})$ diagram for ZnF$_2$ for different orientations ϑ of the wave normal vector $\boldsymbol{s}$ relative to the optic axis of the crystal. As it is seen, the real part as well as the imaginary part of ω_i shows partially strong dispersion according to modulus and direction of the wave vector. Starting from the values at $\boldsymbol{k} = 0$ which are equal for all ϑ the values show strong dispersion in the region at about $k = 0.4 \times 10^4$ cm^{-1} and then approach asymptotically the respective values at $k = \infty$ which are only dependent on ϑ. For $k = \infty$ the damping of the highest (light) branch (branch 5) vanishes because we have not taken into account any damping of the electric field. Table 2 gives the

Table 2. Frequencies $\mathrm{Re}\,\omega_i$ (in cm^{-1}) without and with damping for $\vartheta = 30°$.

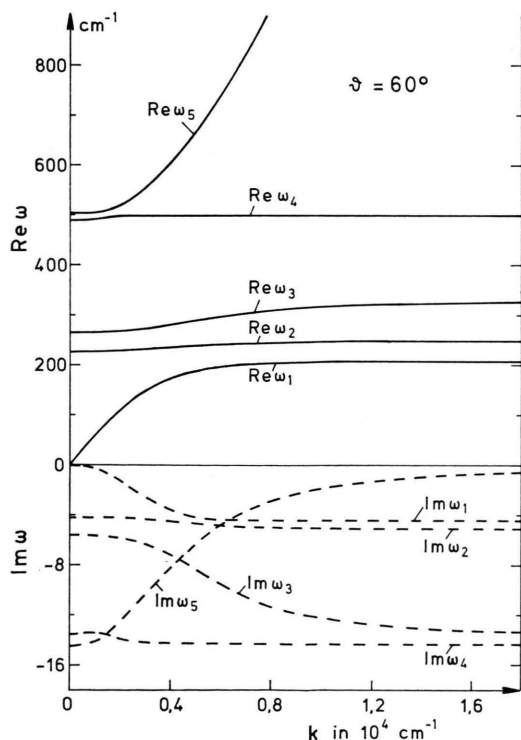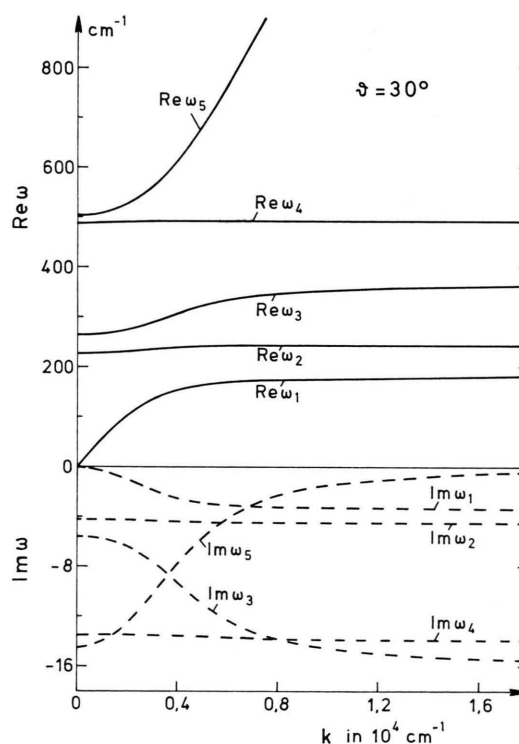| branch i	$k = 5000$ cm^{-1}		$k = \infty$	
	$\mathrm{Re}\,\omega_i$ $\Gamma = 0$	$\mathrm{Re}\,\omega_i$ $\Gamma \neq 0$	$\mathrm{Re}\,\omega_i$ $\Gamma = 0$	$\mathrm{Re}\,\omega_i$ $\Gamma \neq 0$
1	164.77	164.76	182.81	182.79
2	241.10	241.07	244.60	244.56
3	323.06	322.97	366.96	366.63
4	493.38	499.15	493.64	493.64
5	685.35	685.13	∞	∞

Fig. 1 a.

Fig. 1 b.
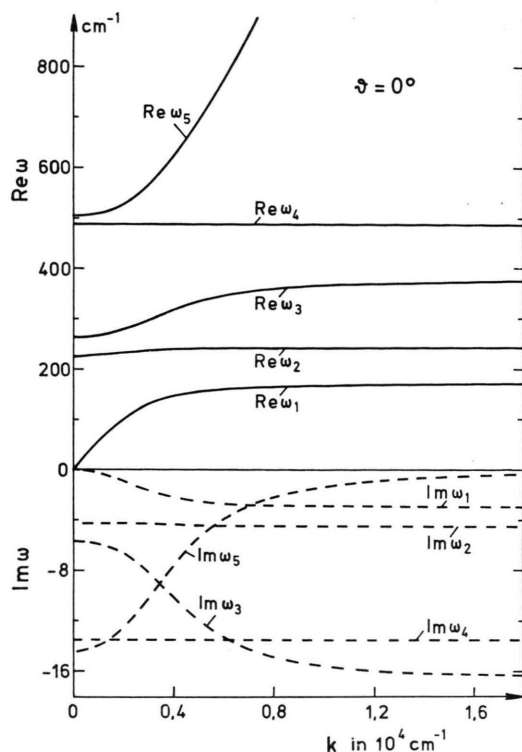
Fig. 1 c.
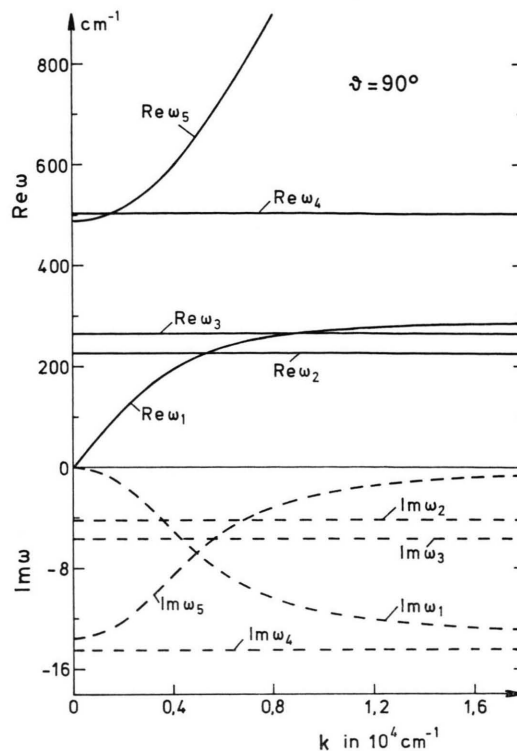
Fig. 1 d.

Fig. 1 a—d.
Dispersion branches Re $\omega_i(k)$ and Im $\omega_i = -\gamma_i(k)/2$ for various angles ϑ in ZnF$_2$.

values of the real part of ω_i for $\vartheta = 30°$ without damping ($\Gamma = 0$) and with inclusion of damping ($\Gamma \neq 0$) for $k = 5000$ cm^{-1} and $k = \infty$. Obviously the influence of damping on the values of the eigenfrequencies is extremely low in the present case and may therefore in general be neglected for calculating dispersion branches of thermally excited polaritons.

Pure Spatial Damping

Example: IR-absorption

In an IR-absorption experiment the excitement of the polariton is forced by the electromagnetic wave radiated into the crystal. This is a case of a pure spatial damped wave. Therefore the wave vector $\boldsymbol{k}$ must be treated as a complex quantity whereas ω is a real one. According to Eqs. (5) and (7) the complex wave vector can be calculated for each real value of ω.

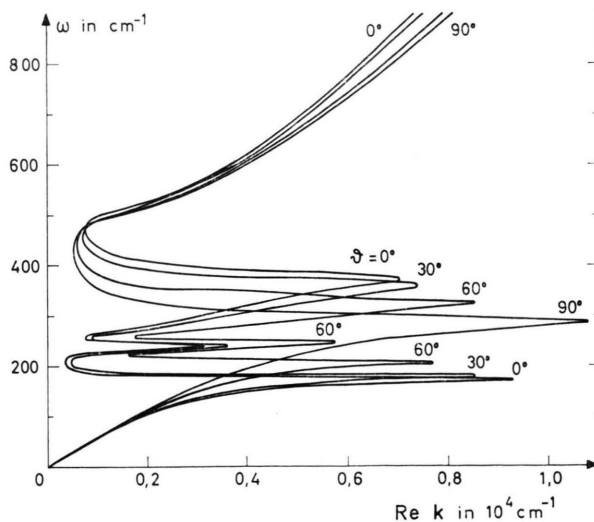For ZnF$_2$ the results are shown in Figs. 2 and 3. Evidently we now obtain limiting momenta of $\boldsymbol{k}$

Fig. 2. Dispersion curves $\omega = \omega(\text{Re } k)$ for various angles ϑ in ZnF$_2$.

and turnarounds described by other authors [5, 6]. Finally the direct relation of Figs. 2 and 3 to IR-experiments should be emphasized, for the real part
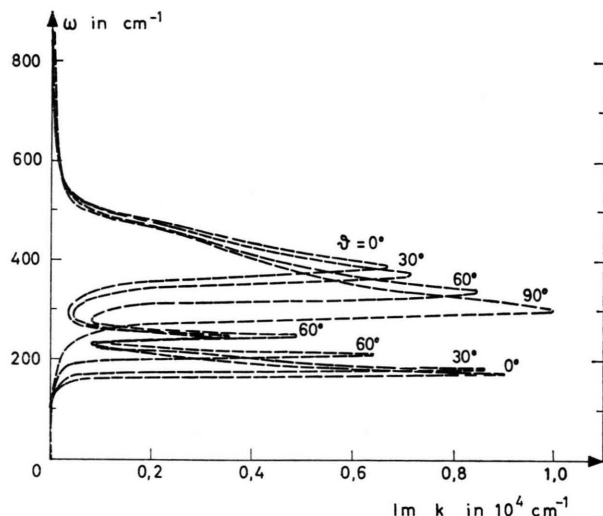
Fig. 3. Dispersion curves $\omega = \omega(\mathrm{Im}\,k)$ for various angles ϑ in ZnF_2.

of the refractive index $\mathrm{Re}\,n = (c/\omega) \cdot \mathrm{Re}\,k$ and the absorption coefficient $\mathrm{Im}\,n = (c/\omega) \cdot \mathrm{Im}\,k$ for IR-experiments of ZnF_2 are directly obtained from them.

[1] H. E. PUTHOFF, R. H. PANTELL, B. G. HUTH, and M. A. CHACON, J. Appl. Phys. 39, 2144 [1968].
[2] L. RIMAI. J. L. PARSONS, H. T. HICKMOTT, and T. NAKAMURA, Phys. Rev. 168, 623 [1968].
[3] A. S. PINE and P. E. TANNENWALD, Phys. Rev. 178, 1424 [1969].
[4] H. J. BENSON and D. L. MILLS, Phys. Rev. B 1, 950 [1970].
[5] R. R. ALFANO, J. Opt. Soc. Amer. 60, 66 [1970].
[6] R. R. ALFANO and T. G. GIALLORENZI, Opt. Comm. 4, 271 [1971].

[7] L. MERTEN, Z. Naturforsch. 22 a, 359 [1967].
[8] L. MERTEN, Z. Naturforsch. 23 a, 1183 [1968].
[9] H. BILZ, L. GENZEL, and H. HAPP, Z. Phys. 160, 535 [1960].
[10] R. A. COWLEY, Adv. Phys. 12, 427 [1963].
[11] A. S. BARKER, Phys. Rev. 136 A, 1290 [1964].
[12] G. LAMPRECHT and L. MERTEN, Phys. Stat. Sol. [1972], to be published.
[13] T. KUROSAWA, J. Phys. Soc. Japan 16, 1298 [1961].