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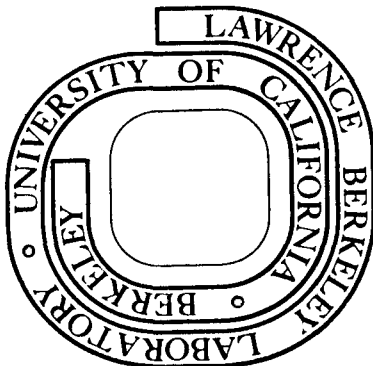
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In recent years, stimulated by the growing interest in surface phys-
ics, the problems of surface electromagnetic waves on metals and semicon-
ductors have attracted a great deal of attention.[1] By definition, a sur-
face em wave is an em wave propagating along the surface with its inten-
sity decaying exponentially away from the surface as is schematically
shown in Fig. 1. Since the exponential decay lengths into adjoining me-
dia are of the order of the optical wavelength, the surface wave charac-
teristics are in fact mainly determined by the bulk dielectric constants
of the two media. Nevertheless, they are sensitive to perturbations on
the surface. Thus, for example, surface em waves have been used to de-
tect the presence of a submonolayer of absorbed gas on metals.[2]

The propagation of the surface em wave is of course governed by the
wave equation together with the usual boundary conditions.[3] Consider,
for simplicity, two isotropic media bounded by an infinite plane surface.
The wave equation is

$$\nabla \times (\nabla \times \vec{E}) + (\omega^2 \epsilon / c^2)\vec{E} = \vec{S}(\omega) \tag{1}$$

where S is a source term for the $\vec{E}(\omega)$ field. With S = 0, the free wave
solution of the equation is

$$\vec{E} = (\hat{x}\mathcal{E}^o_{ax} + \hat{z}\mathcal{E}^o_{az})\exp(i\vec{k}_a \cdot \vec{r}) \qquad \text{in medium a}$$

$$= (\hat{x}\mathcal{E}^o_{bx} + \hat{z}\mathcal{E}^o_{bz})\exp(i\vec{k}_b \cdot \vec{r}) \qquad \text{in medium b}$$

assuming both $\vec{E}$ and $\vec{k}$ are in the $\hat{x} - \hat{z}$ plane (TM wave). The boundary

conditions at the surface are

$$\mathcal{E}^o_{ax} = \mathcal{E}^o_{bx}$$

$$\epsilon_a \mathcal{E}^o_{az} = \epsilon_b \mathcal{E}^o_{bz} \quad \text{or} \quad \epsilon_a \left(\frac{k_{ax}}{k_{az}}\right)\mathcal{E}^o_{ax} = - \epsilon_b \left(\frac{k_{bx}}{k_{bz}}\right)\mathcal{E}^o_{bx} \tag{2}$$

where $k_{ax} = k_{bx} \equiv k_x$, and $k_{az} = [k^2_a - k^2_{ax}]^{\frac{1}{2}} = i\alpha_a$ and $k_{bz} = [k^2_b - k^2_{bx}]^{\frac{1}{2}} = - i\alpha_b$ are both purely imaginary for a surface wave (see Fig. 1) if ϵ_a and ϵ_b are real, and $k^2_{a,b} = \omega^2 \epsilon_{a,b}/c^2$. In order to have nonzero solution of $\mathcal{E}^o_a$ and $\mathcal{E}^o_b$, Eq. (2) requires $\epsilon_a k_{bz} + \epsilon_b k_{az} = 0$ which can be rewritten in the form

$$k^2_x = K^2_x \equiv (\omega^2/c^2)[\epsilon_a \epsilon_b/(\epsilon_a + \epsilon_b)] \tag{3}$$

This is actually the dispersion relation for the surface wave provided $k^2_x > k^2_{a,b}$ or $\epsilon_a \epsilon_b/(\epsilon_a + \epsilon_b) > \epsilon_{a,b}$. The latter condition can be satis-fied if either ϵ_a or ϵ_b is negative. If $\epsilon_b < 0$, then $|\epsilon_b|$ must be larger than ϵ_a. A negative dielectric constant exists below the plasma frequency in metals or in the reststrahlung band of a solid. More generally, the source term S in Eq. (1) is nonzero. If S oscillating at frequency ω has a wave vector component along $\hat{x}$ equal to k_x given by Eq. (3), then the surface wave can be excited resonantly as we shall see later.

Since the surface em wave is confined to the surface, it will not leak out into bulk radiation unless the surface is subject to perturba-tion or imperfection. This follows directly from the requirement of matching of k_x along the surface. Conversely, it is also impossible to

excite the surface wave by shining a light beam of the same frequency directly on a smooth surface. Thus, in order to study the surface wave properties, various excitation and detection methods have been devised, namely, inelastic electron scattering,[4] Raman scattering,[5] and linear[6] and nonlinear[7-9] optical excitation and detection.

In the linear optical excitation and detection, the coupling between the surface wave and the bulk radiation mode is achieved through perturbation on the surface. The so-called Otto method[6] uses a prism to couple the surface wave and the bulk radiation. The prism sits on top of the surface with a small gap of the order of a wavelength. The coupling is established through the evanescent wave in the gap. A variation of the method is to use a grating deposited on the surface instead of the prism for the radiation coupling. In fact, surface roughness can be regarded as a random grating and is therefore also effective in establishing the coupling, although the coupling efficiency is rather small. An alternative method due to Kreschtmann[6] uses a film deposited on a prism. The surface wave on the surface between the film and the surrounding medium can be coupled to the bulk radiation mode in the prism through the film. In these linear methods, the surface is clearly perturbed; consequently, the surface wave becomes radiative and its dispersion curve is slightly modified. Such difficulty can in principle be avoided in the nonlinear optical excitation and detection method.[7-9] As we shall discuss here, the nonlinear optical method also offers the advantage of being able to measure directly the resonant frequency and the damping constant of the surface wave.

In the nonlinear optical scheme, the surface wave is excited by

beating of two laser beams at $(\vec{k}_1, \omega_1)$ and $(\vec{k}_2, \omega_2)$ which create a non-linear polarization P^{NL} $(\omega = \omega_1 \pm \omega_2)$ in, for example, medium "b". This nonlinear polarization acts as a source for the E field at ω, i.e., $\vec{S} = - 4\pi(\omega^2/c^2)P^{NL}(\omega)$ in Eq. (1). The general solution of Eq. (1) with the plane surface boundary conditions has been worked out by Bloembergen and Pershan for the case of sum- or difference-frequency generation near a plane boundary.[10] The solution consists of two parts: a particular solution $\vec{\mathcal{E}}_p \exp(i\vec{k}_s \cdot \vec{r})$ with $\vec{k}_s = \vec{k}_1 \pm \vec{k}_2$ representing the driven bulk wave at ω in medium "b" and a homogeneous solution $\vec{\mathcal{E}}_0^{(a)} \exp(i\vec{k}_a \cdot \vec{r})$ in medium "a" and $\vec{\mathcal{E}}_0^{(b)} \exp(i\vec{k}_b \cdot \vec{r})$ in medium "b". We have explicitly

$$\vec{\mathcal{E}}_p = - 4\pi \, \varepsilon_b^{-1}(k_s^2 - k_b^2)^{-1}\left\{\hat{x}[- P_x^{NL}k_{bz}^2 + P_z^{NL}k_x k_{sz}] + \right.$$

$$\left. \hat{z}[P_x^{NL}k_x k_{sz} + P_z^{NL}(k_{sz}^2 - k_b^2)]\right\}$$

$$\vec{\mathcal{E}}_0^{(a)} = \frac{- 4\pi(\hat{x}k_{az} + \hat{z}k_x)}{(\varepsilon_a k_{bz} + \varepsilon_b k_{az})(k_s^2 - k_b^2)} \, [P_x^{NL}(k_s^2 - k_b^2) - $$

$$(k_{bz} + k_{sz})(k_{sz}P_x^{NL} - k_x P_z^{NL})]$$

$$\vec{\mathcal{E}}_0^{(b)} = \frac{4\pi(\hat{x}k_{bz} + \hat{z}k_x)\varepsilon_a}{\varepsilon_b(\varepsilon_a k_{bz} + \varepsilon_b k_{az})(k_s^2 - k_b^2)} \, [P_x^{NL}(k_s^2 - k_b^2) - $$

$$\left(\frac{\varepsilon_b}{\varepsilon_a} k_{az} - k_{sz}\right)(k_{sz}P_x^{NL} - k_x P_z^{NL})] \tag{4}$$

Two denominator factors appear in the above equations. As is well known, the vanishment of $(k_s^2 - k_b^2)$ corresponds to the phase-matched generation of the field at ω in medium "b". The other denominator factor $(\varepsilon_a k_{bz} +$

$\epsilon_b k_{az}$) is usually always positive if ϵ_a and ϵ_b are both positive, and

therefore does not play any important role in the ordinary sum- and dif-

ference-frequency generation process. However, as we showed earlier,

$\epsilon_a k_{bz} + \epsilon_b k_{az} = 0$ actually describes the dispersion of the surface wave

when either ϵ_a or ϵ_b is negative. Therefore the vanishment of ($\epsilon_a k_{bz} +$

$\epsilon_b k_{az}$) in the denominator of $\vec{\epsilon}_0$ should correspond to the resonance exci-

tation of the surface wave.

More rigorously, since ϵ_a and ϵ_b are generally complex, we should

write

$$\epsilon_a k_{bz} + \epsilon_b k_{az} = [(\epsilon_a^2 - \epsilon_b^2)/(\epsilon_a k_{bz} - \epsilon_b k_{az})]2K_x'(-\Delta k_x + iK_x'')$$

where

$$K_x = K_x' + iK_x'' = (\omega/c)[\epsilon_a \epsilon_b/(\epsilon_a + \epsilon_b)]^{\frac{1}{2}}$$

$$\Delta k_x = k_{sx} - K_x' \tag{5}$$

Physically, Δk_x is the phase mismatch in the surface wave excitation,

$\Delta k_x = 0$, corresponds to exact resonance, and K_x'' is the damping constant

for the surface wave. The excited surface wave with the wavevector com-

ponent k_x along the surface has an amplitude

$$\mathcal{E}_0^{(a,b)} \propto (-\Delta k_x + iK_x'')^{-1} \tag{6}$$

Since $k_x = k_{1x} \pm k_{2x}$ is completely prescribed by the wavevectors of the

two input laser beams and can be different from the wavevector K'_x of the free surface wave, we call $\vec{E}_o^{(a,b)}$ in Eq. (6) a driven surface wave.

In the complete solution, we should however also include the free surface wave which is also a homogeneous solution of Eq. (1). Let the free surface wave be $\vec{E}_f^{(a,b)} \exp(iK_x x - \alpha_{a,b} z)$. Then the complete surface wave solution is

$$\vec{E}_{sur}^{(a,b)} = \vec{\mathcal{E}}_o^{(a,b)} \exp(i\vec{k}_{a,b} \cdot \vec{r}) + \vec{\mathcal{E}}_f^{(a,b)} \exp(iK_x x - \alpha_{a,b} z) \qquad (7)$$

Since $\vec{\mathcal{E}}_o^{(a,b)}$ is known, $\vec{\mathcal{E}}_f^{(a,b)}$ can be calculated from the boundary condition along $\hat{x}$ on the surface. For example, assuming P^{NL} = constant for $0 \leqslant x \leqslant \ell$ and $P^{NL} = 0$ elsewhere and assuming $k_x \cong K'_x$ so that $k_{az} \cong i\alpha_a$ and $k_{bz} \cong - i\alpha_b$, we find

$$\vec{E}_{sur}^{(a,b)} = 0 \qquad\qquad\qquad\qquad\qquad \text{for } x \leqslant 0$$

$$= \vec{\mathcal{E}}_o^{(a,b)} \left[e^{i\Delta k_x x} - e^{-K''_x x} \right] e^{iK'_x x - \alpha_{a,b} z} \qquad \text{for } 0 \leqslant x \leqslant \ell$$

$$= \vec{\mathcal{E}}_o^{(a,b)} \left[e^{i\Delta k_x \ell} - e^{- K''_x \ell} \right] e^{iK'_x x - K''_x (x-\ell) - \alpha_{a,b} z} \quad \text{for } x \geqslant \ell \quad (8)$$

where we have neglected the reflection of surface wave at $x = 0$ and ℓ. This result is quite similar to the result for sum- or difference-generation in the bulk. In the present case, however, the free wave contribution is often negligible because of the large K''_x. Then, following Eqs. (6) and (8), the excited surface wave is given, to a good approximation, by

$$\vec{E}_{sur}^{(a,b)} \propto (- \Delta k_x + iK''_x)^{-1} \exp(ik_x x - \alpha_{a,b}z) \text{ for } 0 \leqslant x \leqslant \ell$$

$$= 0 \qquad\qquad\qquad \text{otherwise} \qquad (9)$$

The excited surface wave can of course be detected by the linear optical coupling schemes we mentioned earlier, but it can also be detected by a nonlinear optical method. In the latter method, a probe beam $E_3 \times \exp(i\vec{k}_3 \cdot \vec{\gamma})$ at frequency ω is directed onto the surface excitation region to beat with the excited surface wave. The beating creates a nonlinear polarization $P^{NL}(\omega_4 = \omega \pm \omega_3)$ in medium "b". It then generates a coherent radiating field at ω_4 in the phase-matched direction determined by $k_{4x} = k'_x \pm k_{3x}$. Knowing the nonlinearity of the medium, the output power at ω_4 can easily be evaluated. This nonlinear detection method together with the nonlinear excitation constitutes a four-wave mixing process. Thus, in short, we have here a special case of the general four-wave mixing scheme for studying resonance excitations in a medium.[11]

Using either linear or nonlinear method to detect the nonlinearly excited surface wave, the output power is proportional to $|E_{sur}|^2$ or

$$I \propto [(\Delta k_x)^2 + K''^2_x]^{-1} \qquad (10)$$

which is a Lorentzian with its peak at $\Delta k_x = 0$ and its half width given by K''_x. Measurements of I versus k_x at various ω can therefore yield directly the dispersion characteristics $K'_x(\omega)$ and $K''_x(\omega)$ of the surface wave. Note that unlike the linear excitation method, the nonlinear excitation method allows us to map out the $\omega - k_x$ space by varying ω and k_x

independently.

Study of surface em waves using the nonlinear optical method has
been demonstrated in two cases. In the first case,[8] the surface phonon-
polariton which lies in the phonon reststrahlung band was probed using
the nonlinear excitation and detection method. The crystal under inves-
tigation was GaP. The output signal at ω_4 was estimated to be of the
order of few tenths of a μW with 50 KW in the exciting and probe beams.
The experimental arrangement is shown in Fig. 2, and typical data of I
versus Δk_x fitted with Lorentzian curves shown in Fig. 3. The values of
$K_x'(\omega)$ and $K_x''(\omega)$ deduced from the experimental results are presented in
Fig. 4 in comparison with the theoretical curves derived from Eq. (5).
The solid and the dashed curves correspond to a single-oscillator model
and a multi-oscillator model for the dielectric constant of GaP respec-
tively. Deviation of the experimental points of $K_x''(\omega)$ from the theoreti-
cal curves at smaller ω is mainly due to the divergence of the focused
laser beams which sets a minimum to the width of the measured resonance
peak. We notice that if the damping constant K_x'' did not increase so ra-
pidly as ω approaches the longitudinal phonon frequency and the laser
beams used had sufficiently narrow linewidths, then we would be able to
probe the dispersion characteristics of the surface phonon-polaritons
over a wavevector range from $k_x = k_{1x} - k_{2x} \sim (\omega/c)\epsilon_b(\omega_1)$ to $k_x = (k_{1x} +
k_{2x}) \sim 2(\omega_1/c)\epsilon_b(\omega_1)$.

In the second case,[9] the surface exciton-polariton in ZnO was probed.
Since the exciton reststrahlung band of ZnO is in the ultraviolet, sum-
frequency excitation of the surface wave should be used. In our experi-
ment, we simply used one laser beam at ω_1 to excite the surface wave at

$\omega = 2\omega_1$. Then, because the surface always appears to be somewhat rough on the scale of the uv wavelength, a certain fraction of the excited surface wave is expected to be scattered out by the surface roughness. Even if it is only a small fraction, the photodetector is so sensitive in the uv that the scattered radiation can easily be detected. This was actually the detection scheme we used. With a 50-KW dye laser pumped by a Q-switched ruby laser, we estimated an output signal of 10^7 photons/ pulse assuming an output coupling coefficient of 1%. The experimental results connected to the C exciton in ZnO are shown in Figs. 5 and 6. Since ZnO is anisotropic, the dispersion relation of the surface wave takes a somewhat different form, e.g.,

$$K_x^2 = (\omega/c)^2[\epsilon_a\epsilon_{bz}(\epsilon_{bx} - \epsilon_a)/(\epsilon_{bx}\epsilon_{bz} - \epsilon_a^2)] \tag{11}$$

In this case, two points are worth mentioning. First, Fig. 5 shows that the widths of the resonance peaks $2K_x''$ are about two orders of magnitude smaller than K_x'. This means that even if the experimental data points are poorly scattered, the peak position K_x' can still be determined with an accuracy of about 1%. Second, since the surface exciton-polariton is only present at cryogenic temperature, application of the linear optical excitation and detection method is very difficult. The nonlinear optical excitation method we have described is, on the other hand, quite simple and straight forward.

The nonlinear optical method can of course also be used to study surface plasmons on metal surfaces. Simon and coworkers[12] have excited the surface plasmons at the fundamental frequency to enhance second-har-

monic generation from a metal surface. It is possible to nonlinearly ex-
cite the surface plasmon by sum-frequency mixing using the Otto or Kretch-
mann geometry[13] or by difference-frequency mixing using noncolinear la-
ser beams impinging on the surface from the non-metal side. The optical
nonlinearity of metals is generally small. Therefore, in order to en-
hance the nonlinear optical process, it is advisable to place a nonlinear
crystal with a large second-order nonlinear susceptibility $\chi^{(2)}$ on the
metal surface.[12,13]

With laser excitation, intense surface em wave can be propagated
along the surface. Then, observation of nonlinear interaction between
surface em waves becomes possible. Nonlinear optics of surface waves is
a field yet to be explored. Sum- and difference-frequency generation can
be easily observed, but exact phase matching of such process is usually
not possible in the case where the dispersion curve ω versus K'_x concaves
downward. Effects resulting from third-order nonlinear interaction be-
tween surface waves can also be observed. For example, using surface
plasmons in a four-wave mixing scheme, the Raman resonances in a liquid
film on the metal surface can be probed.[13]

The nonlinear optical method is probably most useful for studying
surface em waves at cryogenic temperature. This is because of the diffi-
culties inherent in the application of the linear method at low tempera-
ture. The surface wave characteristics are often very sensitive to the
change in the dielectric constants of the adjoining media. It has there-
fore been proposed as a means to study phase transitions.[14] Then, with
the nonlinear optical method, one can probably use the surface wave to
study phase transitions at low temperature, for example, the normal-super-

conducting phase transitions in solids.

Acknowledgement:

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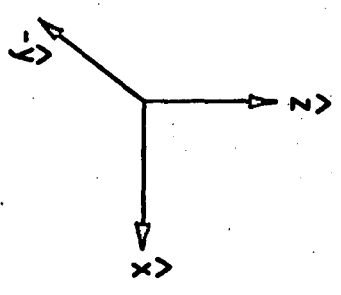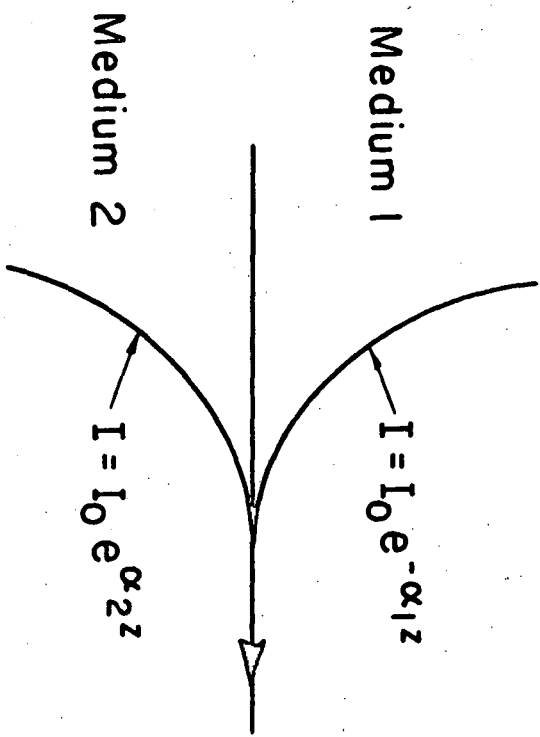11. See, for example, the lecture notes of Prof. S. A. Akhmanov in this
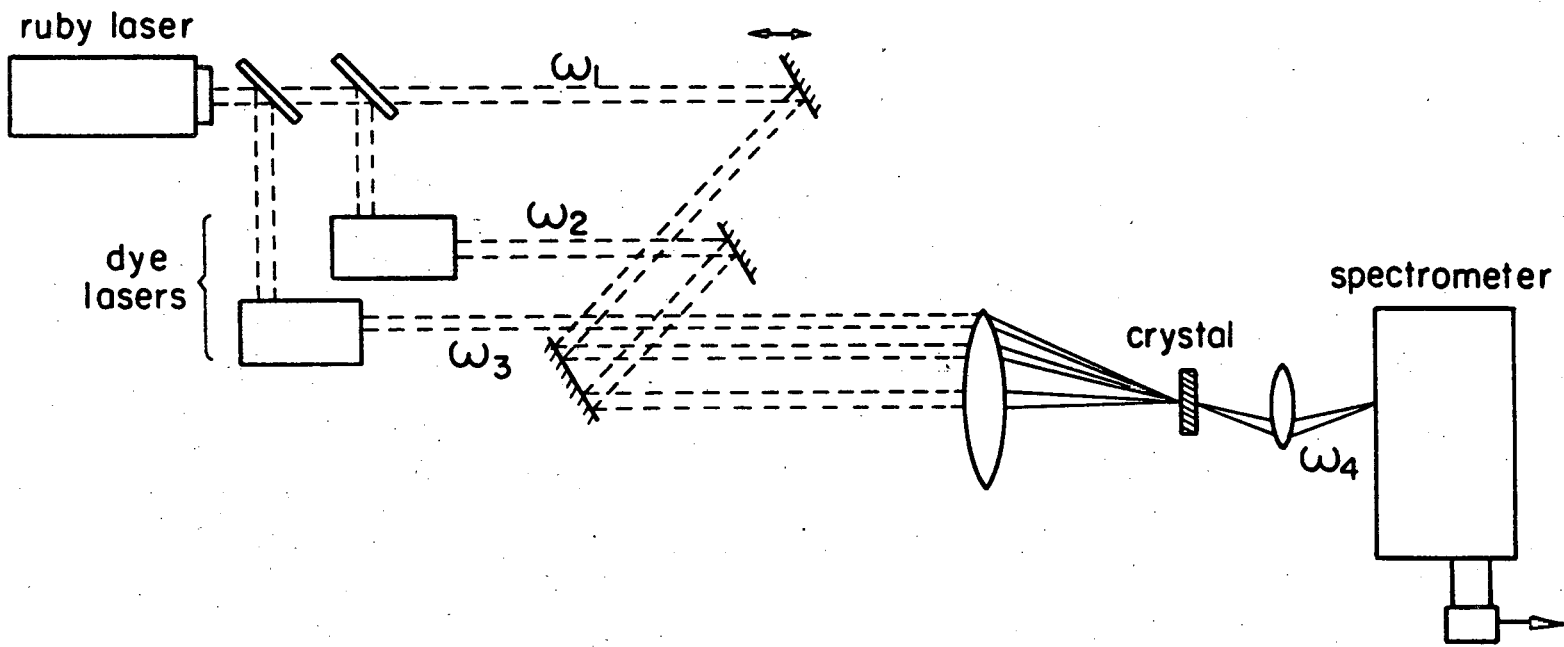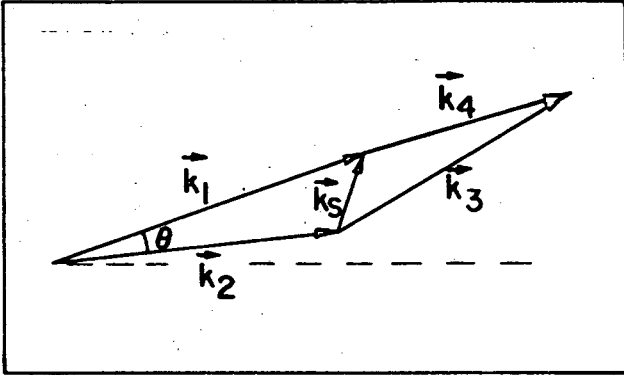
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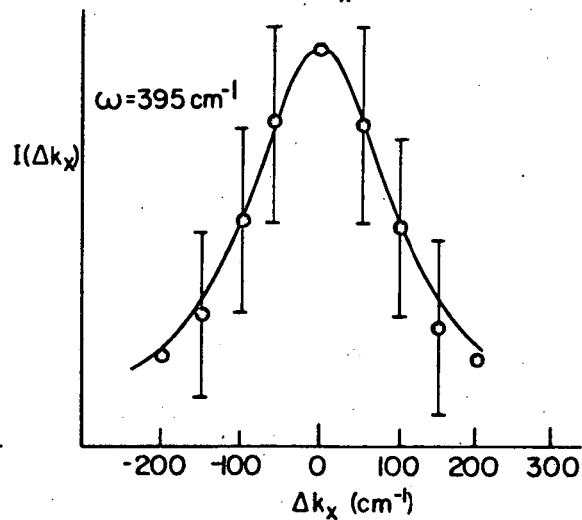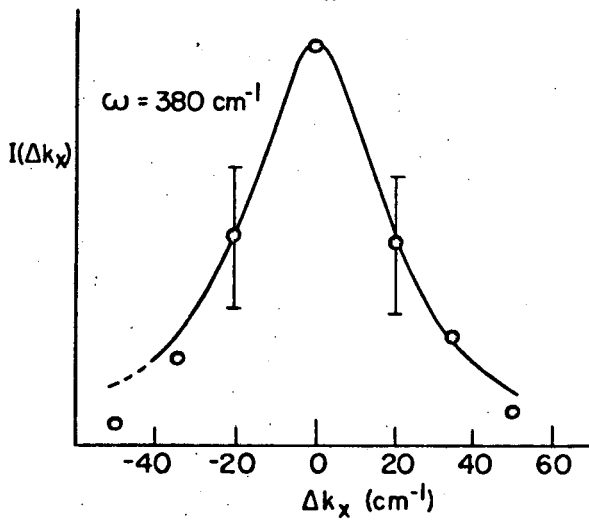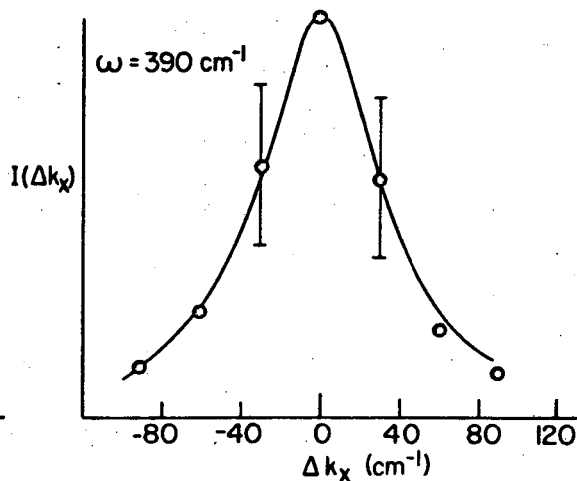
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Figure Captions

Fig. 1   Schematical drawing showing a surface wave propagating on a

plane surface. The intensity of the surface wave decays expo-

nentially away from the surface.

Fig. 2   Experimental setup. The inset shows the wavevector diagram for

the four-wave mixing process.

Fig. 3   Experimental results of normalized $I(\omega_4, \Delta k_x)$ versus Δk_x at $\omega =$

370, 380, 390, and 395 cm^{-1} in GaP. The solid curves are Lorentz-

ian used to fit the data points.

Fig. 4   Measured dispersion characteristics of surface polaritons in

GaP. (0 —— K'_x versus ω; Δ —— $2K''_x$ versus ω). The solid curves

are calculated from Eq. (5) using a single-oscillator model.

The dashed curves are calculated from the multi-oscillator model

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Fig. 5   Experimental results of normalized $I(\omega, \Delta k_x)$ versus Δk_x at four

output frequencies in ZnO. The solid curves are Lorentzian used

to fit the data points.

Fig. 6   Measured dispersion and damping characteristics of surface exci-

ton-polariton in ZnO. (—— K'_x versus ω; + —— K''_x versus ω).
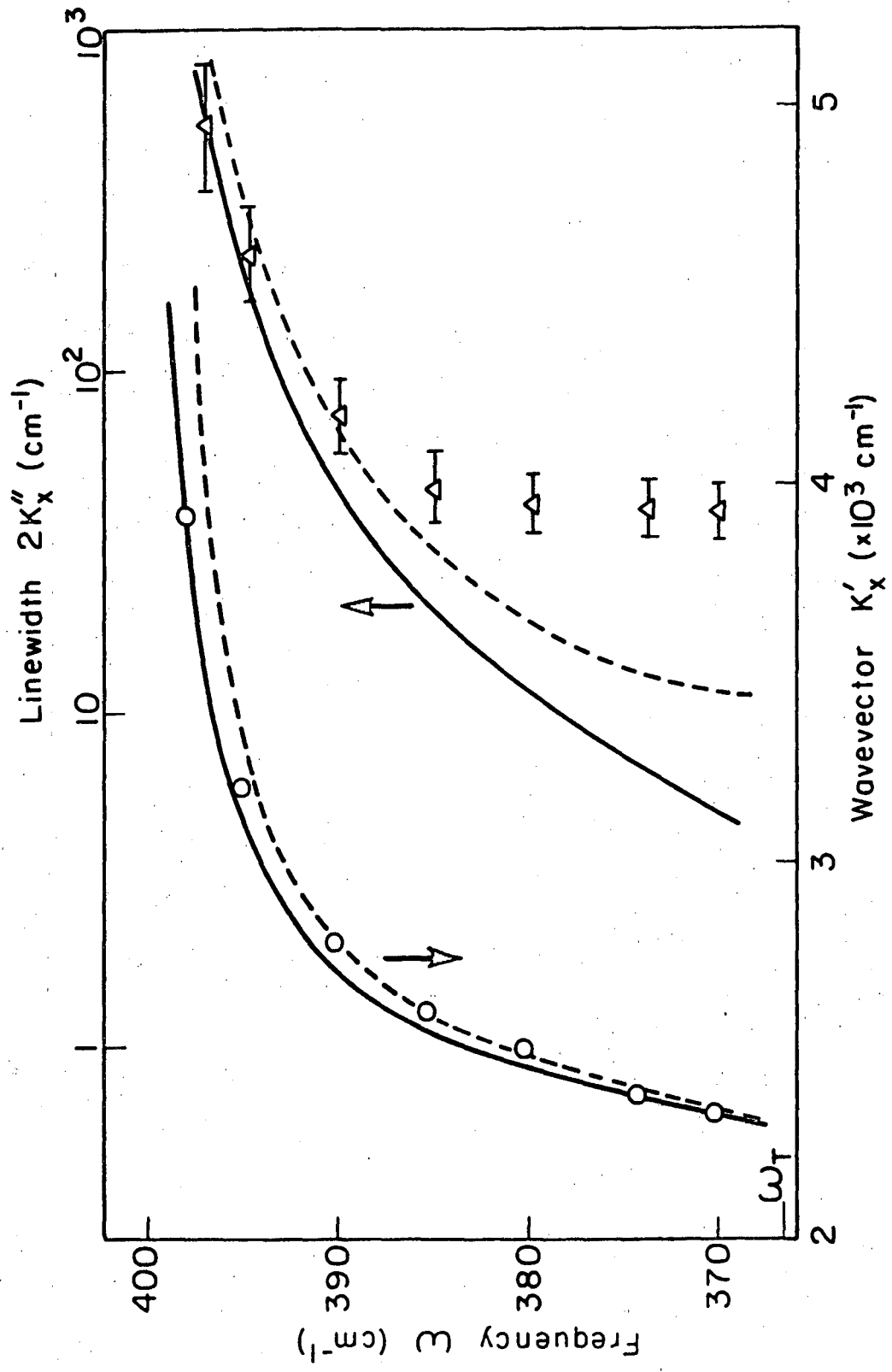
The solid curves are calculated from Eq. (11).

Medium 1

Medium 2

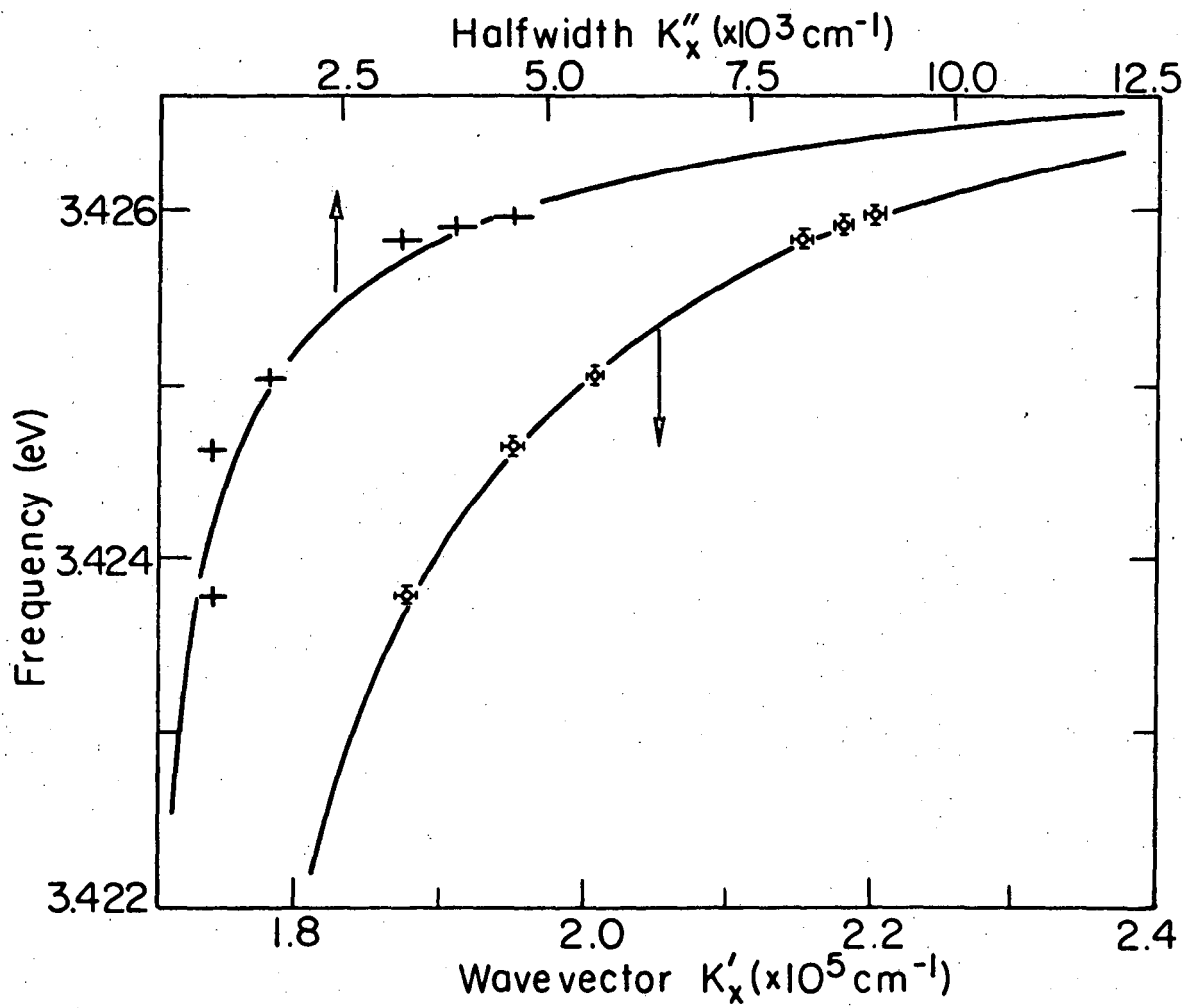$I = I_0 e^{-\alpha_1 z}$

$I = I_0 e^{\alpha_2 z}$

$\hat{z}$

$-\hat{y}$

$\hat{x}$

XBL 789-5817

$\vec{k_4}$

$\vec{k_1}$

$\vec{k_S}$

$\vec{k_3}$

θ

$\vec{k_2}$

ruby laser

ω_L

dye
lasers

ω_2

spectrometer

ω_3

crystal

ω_4

XBL 764-6740

XBL 764 - 6741

XBL 764- 6739

Halfwidth K_x'' ($\times 10^3$ cm^{-1})

Frequency (eV)

Wave vector K_x' ($\times 10^5$ cm^{-1})

XBL 772-5094

XBL 772-5093