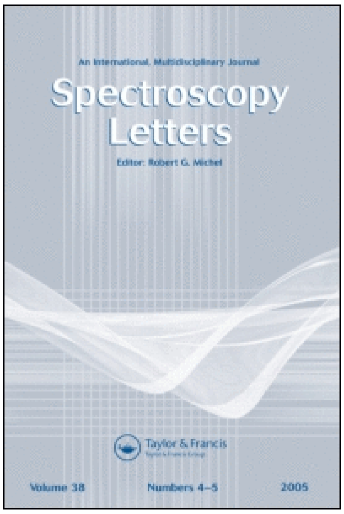

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ASPECTS ON APPLICATIONS OF IR REFLECTIVITY- AND RAMAN SCATTERING-EXPERIMENTS ON POLARITONS IN SOLID STATE CHEMISTRY AND BIOPHYSICS

Raman effect, lattice dynamics, crystal optics

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ABSTRACT

The coupled phonon-photon state called "polariton" is an elementary excitation which exists at all temperatures in single crystalline materials with well defined translational symmetries. In the view of this aspect polaritons turn out to be more important for the dynamics of crystal lattices in general than e.g. magnons or plasmons which normally can be excited only in certain low temperature ranges. The present article summarizes experimental results which all might be applied as analytical methods. An improved method for the determination of fundamental mode frequencies is described. Polariton interactions with localized modes, and second order phonons and the relation to the ferroelectric phase transition mechanism is reviewed. Furthermore experiments concerning parametric light scattering, the TM-reflection technique, the ATR-method, and nonlinear optical experiments are summarized. We finally discuss the question of mechanical-electromagnetic energy conversion and some tentative future aspects.

1. INTRODUCTION

Research in Solid State Physics over the last five decades has brought the detection of a large series of quasi particles such as phonons, excitons, magnons, polarons, plasmons or polaritons. Experimental investigations in order to establish their physical properties are associated with varying difficult problems. Some of them can be studied only at liquid Helium temperatures when simultaneously high magnetic or electric fields are applied, whereas others are easily investigated at room temperature. Thus conventional light scattering by optical and acoustical phonons has been used widely for many years in order to determine the frequencies of fundamental and higher order vibrational modes in crystalline materials, whereas e.g. the properties of magnons have been studied only by a relatively limited number of authors. Although polaritons are among the youngest of the particles cited above /1,2,3/ their observation by Raman-scattering or IR-reflection techniques has turned out to be rather simple. This has resulted in a rapidly increasing number of publications from all over the world since the first sucessful experiments about ten years ago /3,4,5/. A culmination of this development took place at the end of 1972 when a conference devoted only to polaritons was held in Taormina, Italy /6/. As a result the basic properties of polaritons are well understood in most crystal classes nowadays and relationships to other subjects such as the optical properties in the infrared, ferroelectric phase transitions or nonlinear optics have been recognized.

The experimental methods developed during the last decade offer themselves to be applied analytically in various fields of scientific research whenever condensed matter with a translational symmetry is to be studied. The development, however, took place rather quickly and could hardly be noted very much by others than solid state physicists directly involved in lattice dynamics or the optical properties of solids. It is therefore the aim of this article to draw some attention of chemists and biophysicists to polaritons. We are not going to present a summary of theories or a detailed description of experimental methods, we merely want to show what can be done by describing typical results and suggest some possible applications.

2. THE COUPLED PHONON-PHOTON STATES AND THEIR OBSERVATION BY LIGHT SCATTERING

From the viewpoint of the particle picture polaritons can be characterized as coupled quanta between photons and any elementary excitations in solids which are associated with an electric or magnetic (dipole) moment. Different types of polaritons are distinguished by terms as "phononlike", "excitonlike" or "magnetic". In the wave picture on the other hand polariton modes always appear when resonances take place between light waves and any polarization waves caused e.g. by lattice vibrations, excitons or other elementary excitations.

Because the greatest experimental progress has been achieved from studies of phonon-polaritons hitherto, our article shall be restricted to these. It should be noted, however, that the dispersion effects predicted for the other types of polaritons in principle are similar to those of phonon-polaritons, see /8/.

Phonon dispersion curves in the 1st Brillouin zone are normally calculated from rigid ion models, shell models, or breathing shell models. Near neighbor interactions are considered by introducing elastic forces between the particles. Long range electric fields in ionic crystals on the other hand are taken into account by calculating the local electric field ($\vec{E}_{loc}$) acting on an ion at a certain position by the Ewald method. The numerical determination of $\vec{E}_{loc}$ normally causes great problems in polyatomic anisotropic crystals. What is better known is the macroscopic electric field $\vec{E}$ which appears in Maxwell's equations. Generally the two fields are related to each other by an equation

$$\vec{E} = \vec{E}_{loc} - \beta\vec{P}$$

where $\vec{P}$ is the macroscopic polarization and β the "Lorentzfactor". From an electrostatic model it can be derived that long wave transverse optical vibrations (TO) in the centre of the 1.BZ. are not associated with a macroscopic field (div $\vec{E}_{TO}=0$) whereas longitudinal optical modes (LO) are. This causes an increase of the frequencies of LO-modes as there are additional restoring forces. The well known Lyddane-Sachs-Teller relation describes the effect quantitatively. Both types of waves are without dispersion around the centre of the 1.BZ. in the electrostatic model. Their group velocities vanish for $\vec{k} = 0$.

The electrostatic model may be improved by taking into account retardation effects. This means that any electric interaction between others than near neighbours takes place with a finite velocity: the velocity of electromagnetic waves in the material. The dispersion curve of such waves is a straight line in the (ω, k)-diagram:

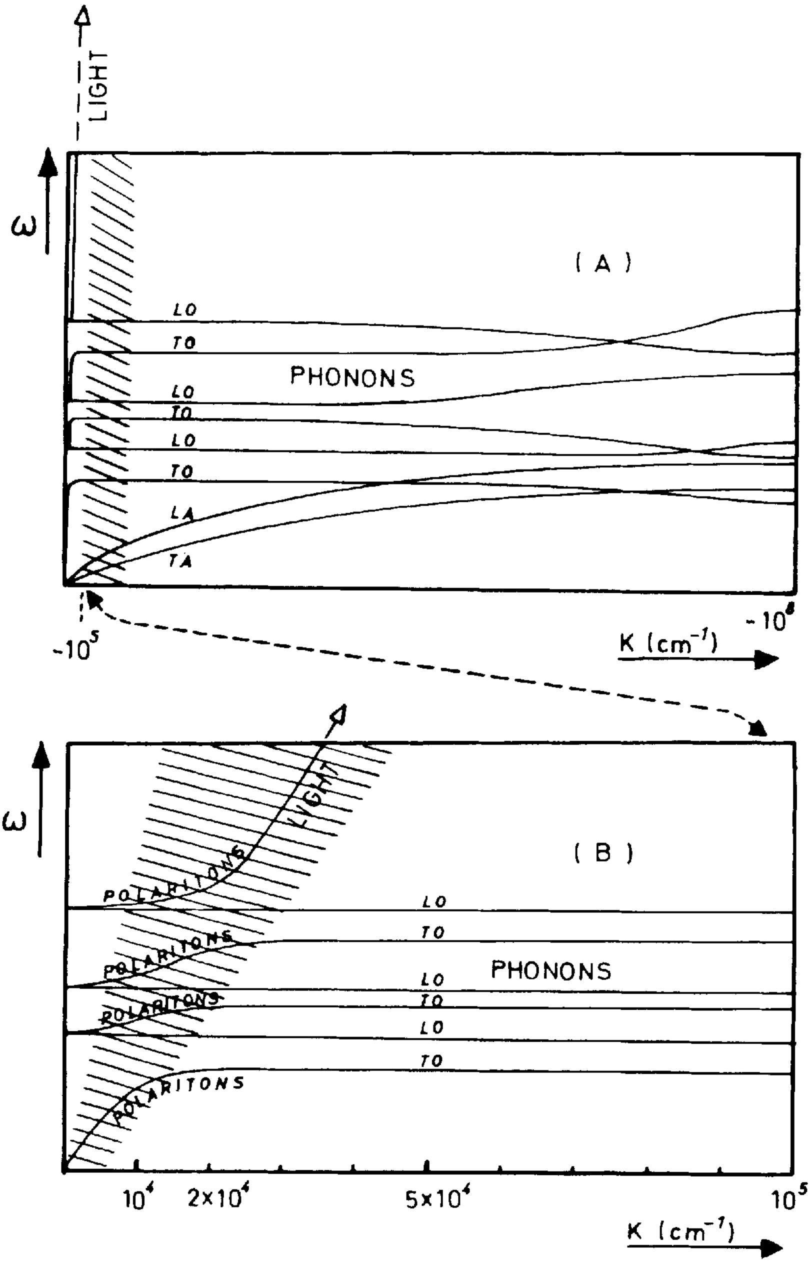
$\omega = (c/n)k$, n being the refractive index. Because of the large phase velocity of light waves (c/n) this line almost coincides with the ω-axis in a typical picture of the 1.BZ. ranging from k=0 to $k \approx 10^8\ cm^{-1}$. Fig. 1A illustrates this.

Raman scattering experiments performed by using conventional laser sources with lines in the visible and common right angle scattering techniques give information on phonons with wave vectors of the order of $k \approx 10^5\ cm^{-1}$, corresponding to the hatched area in Fig. 1A. This can easily be realized from the canonical momentum conservation law $\hbar\vec{k}_L = \hbar\vec{k}_R \pm \hbar\vec{k}$. $k_L = 2\pi n/\lambda_L$ is the laser photon wave vector magnitude, $k_R = 2\pi n/\lambda_R$ that of the Raman-photons in anti-Stokes or Stokes scattering processes, and $\vec{k}$ the wave vector of the observed elementary excitation in question. When, however, recording the scattered light in near forward directions at small angles away from the laser beam the magnitude of $\vec{k}$ becomes approximately one order of magnitude less than in right angle scattering experiments. In the k-region 10^3 to $\sim 2 \cdot 10^4\ cm^{-1}$ the retardation effects play an important role. As a result strong couplings between electromagnetic waves (in the infrared) and lattice waves are recorded. The dispersion curves of transverse modes remain no longer horizontal but show severe deviations from those of the pure phonons. Fig. 1B correspondingly shows the centre of the 1.BZ. in a larger scale. Because of the transverse character of photons couplingstake place only with TO-phonons or such which have at least a mixed TO-LO character (extraordinary modes in anisotropic materials). No coupling takes place with purely longitudinal modes. The energy quanta of the mixed modes are those which have become known as polaritons.

An extensive tutorial introduction to light scattering experiments involving phonon-polaritons has recently been published /7/. We therefore omit any detailed discussion and refer the interested reader to this book for details. The basic result, namely the general dispersion relation, however, may directly be recognized also by combining two results well known from elementary physics courses: 1) The propagation of electromagnetic plane waves in anisotropic crystals is described by Fresnel's equation

$$(S_1\ S_2\ S_3)\begin{pmatrix} \varepsilon_1(\varepsilon_2-n^2)(\varepsilon_3-n^2) & & \\ & \varepsilon_2(\varepsilon_3-n^2)(\varepsilon_1-n^2) & \\ & & \varepsilon_3(\varepsilon_1-n^2)(\varepsilon_2-n^2) \end{pmatrix}\begin{pmatrix}S_1\\ S_2\\ S_3\end{pmatrix} = \begin{pmatrix}0\\ 0\\ 0\end{pmatrix}.$$

$\vec{s}$ is the wave normal vector = $\vec{k}/|\vec{k}|$, $n = ck/\omega$ the refractive index, and ε_1, ε_2, ε_3 are the dielectric


LIGHT
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(A)
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PHONONS
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LO
TO
POLARITONS
10⁴
2×10⁴
5×10⁴
10⁵
K (cm⁻¹)

constants for the principal crystallographic directions. These constants normally are assumed not to depend on frequency in crystal optics. 2) The classical dispersion theories determine the frequency-dependence $\varepsilon = \varepsilon(\omega)$. When substituting the corresponding expressions explicitely into Fresnel's equation the generalized relation obtained describes all polariton dispersion effects including photons and the directional dependence of extraordinary phonons in anisotropic crystals.

3. ON THE DETERMINATION OF FUNDAMENTAL MODE FREQUENCIES IN SINGLE CRYSTALLINE MEDIA

Besides of IR-spectroscopy inelastic light scattering still is the most important experimental technique used to determine the frequencies of fundamental and higher order vibrational modes in crystals. Raman scattering methods applied to molecules in liquids or gases only provide depolarization ratios which may give information on which modes are totally symmetric or not. Well defined

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FIG. 1

(A) Phonon dispersion curves in the 1. Brillouin zone of a crystal with three reststrahlenbands. The region normally observed by right angle light scattering (Raman scattering) is indicated by the hatched area.

(B) The long wave length part of the 1.B.Z. of this crystal in a larger scale showing the polariton region. The hatched area corresponds to the region observable by near forward scattering.

scattering geometries in single crystals on the other hand easily allow a detailed determination of modes belonging to all different symmetry species. The use of laser sources has made possible a great improvement of such experiments since the early 1960's. We illustrate this by one example.

The number of twofold degenerate modes in α-quartz observed by inelastic light scattering was found to exceed the number predicted by group theory. Several authors tried to explain this fact by different theoretical approaches until J.F. Scott and S.P.S. Porto in 1967 could unambiguously identify the Raman lines in excess to originate from longitudinal modes /9/. The TO-LO degeneracy of polar, IR-active modes is lifted for wave vectors $\vec{k} \neq 0$. A review of experimental methods for different crystal classes is given by Ref. /10/.

In spite of the progress that laser sources provided the experimentalist is still confronted with important problems when assignments are to be given: Which modes do originate from higher order processes (sum tones) or which are due to impurities or eventually reflections (ghosts)? We believe that a careful study of the polariton spectra in an easy way can help to solve such problems especially in anisotropic crystals.

It can be shown that the general polariton theory in the limit of large wave vectors, $k \approx 10^5$ cm^{-1}, in anisotropic materials describes the directional dependence of polar extraordinary phonons. In uniaxial crystals, for instance, it simply holds $tg^2\Theta = -\varepsilon_{\parallel}/\varepsilon_{\perp}$, Θ being the angle between the wave vector and the optic axis, and $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ the dielectric functions for directions parallel and perpendicular to this axis. Before a full development of the polariton theory was achieved for polyatomic crystals calculations of such directional dispersion branches were possible only by using expressions given e.g. by Loudon in 1964 /11/. These formulas, however, turned out to be relatively rough approximations of the correct theory and can not provide a check of assignments. We therefore suggest the following method.

For every principal direction in a crystal the modes of different polar species have to form sequences TO, LO, TO, LO ... up to the highest frequency LO-mode. Between two poles of the dielectric function there is always a zero determining an LO-frequency! Directional dispersion implies that a fundamental mode (of some symmetry species) showing a certain frequency when the wave vector propagates parallel to one of the principal axes will continuously change its frequency (as well as its symmetry) when the wave vector direction is changed until it propagates parallel to another principal axis. The frequency then observed is that of another fundamental mode in general belonging to another symmetry species. For arbitrary directions theextraordinary polar modes show a mixed symmetry- and TO/LO-character. When a total assignment of all fundamental vibrations has been worked out the directional dispersion branches can be calculated numerically from the rigorous theory and experimentally checked. Measurements exist, for instance, for α-quartz /12/ and for $LiNbO_3$ /13/. Erroneous assignments of course predict wrong angular dependences and may therefore be identified by such measurements.

This sort of experiments may be used advantageously also in order to find the position of weak LO-components e.g. disappearing in the wing of another strong fundamental by recording the changing position of the Raman lines for different wave vector directions.

It should be pointed out that a fitting of isolated dispersion branches will always affect the form of all the others. Fitting of single branches in general is not possible. This can be realized intuitively by regarding the Lyddane-Sachs-Teller relation. The TO-LO splittings for a certain direction determine the magnitude of the dielectric constant which in turn can be measured by other experimental techniques. Varying one certain TO-LO splitting therefore is not possible in an arbitrary way.

Directional dispersion measurements form a powerful complement to the conventional Raman spectroscopic methods used hitherto.

4. OBSERVABLE INTERACTIONS WITH LOCALIZED MODES AND SECOND ORDER PHONONS

The conditions for observation of polariton modes originating from localized oscillators are: a) the concentration of the impurities must be small enough that they can still be regarded as isolated, and b) the concentration must be large enough that a sufficient number of centers is still found in a volume $= l^3$ where l is of the order of the polariton wave length. The latter condition allows the localized modes still to be described by plane waves which can interact with fundamental polaritons. It can easily be realized that a high homogeneity of distribution over a large volume of the sample will improve the observation of such polariton modes. First successful corresponding experiments have been carried out on modes originating from isotopic impurities in their natural abundance, see /7/. Typical concentrations which fulfill the above conditions are of the order of 1 %. As long as the modes are associated with a dipole moment they show interactions with fundamental polariton branches. Such interactions are recognized as resonance splittings i.e. a doubling of the Raman lines in question. Apparently small damping (small half-widths) improve the observation. The oscillator strengths of the localized modes may remain very weak as long as only the cross section of the fundamental polariton branch is large enough. Expressed by the magnitude of TO-LO splittings we find that beautiful effects on localized modes are observed for $\omega_{LO}-\omega_{TO}$ only = 0,05 cm^{-1}.

Raman spectroscopic studies in order to determine the energy of impurity modes certainly are not new. The basic problem well known to everybody who has ever performed such experiments is the low scattering intensity from such oscillators. This frequently prevented detailed investigations. The progress that polariton spectra provide is that an improvement of the scattering intensity of almost two orders of magnitude can be achieved in the resonance region, see again /7/. We therefore believe that such experiments may be used also in order to solve certain analytical problems.

Second order phonons with low cross sections can be studied in an analogons way. As long as second order phonons are IR-active resonance splittings of the fundamental polariton modes are expected in the same way.

The interactions in such cases can be interpreted as Fermi resonances well known to every Raman spectroscopist from the CCl_4-spectrum. The condition for Fermi resonance to take place is that a fundamental vibration accidentally coincides with a second order phonon of the same symmetry. This situation can be "constructed" when using a polariton mode because it can be moved continuously in the spectrum by varying the scattering angle. Weak higher order processes normally cause small splittings ($< 10\ cm^{-1}$). This frequently makes it possible to dinstinguish them from fundamentals.

It should finally be mentioned that Raman lines simply moved by directional dispersion as described in 3) may show such resonance splittings too when the positon of a second order phonon is being crossed /14/.

5. FERROELECTRIC PHASE TRANSITIONS RELATED TO POLARITONS

Over the last fifteen years the theory of ferroelectric phase transitions has been governed by the lattice dynamical model presented by Cochran in 1960 /15/. Very recently, however, new aspects have modified the picture somewhat /16/. Interactions between dipole relaxation modes and polaritons which have hitherto been left out of consideration seem to play an important role in the ferroelectric phase transition mechanism. We shall therefore shortly summarize the ideas of the lattice dynamical model and compare them with the relaxation-model in order to show what polaritons have to do with phase transitions.

The Cochran model in its simplest form is based on a diatomic elementary cell with a positive and a negative ion the latter consisting of a core and an electron shell which may move independently (electronic polarizability). Interactions between the oscillating cores are assumed to take place only via the electron shells. The cores are treated as elastically bound to an equilibrium position. Furthermore a time dependent local electric field in the equilibrium of every core is considered. This has necessarily to be done in ionic crystals. As is well known the local electric field can be separated into a part originating from oscillating near neighbours and another part representing the macroscopic electric field $\vec{E}$. $\vec{E}$ essentially summarizes Coulomb interactions with the rest of the lattice at larger distances. The macroscopic field of longitudinal modes can be determined to be $-4\pi\vec{P}$ in the center of the 1.BZ. $\vec{P}$ is the macroscopic polarization of the crystal. The macroscopic field of transverse modes on the contrary vanishes identically in an electrostatic model (div $\vec{D}_{TO} = 0$). From these basic assumptions Cochran succeeded in deriving the frequencies of TO- and LO-phonons. The important point of the result is that the frequencies of the LO-modes always have finite values whereas those of the TO-modes can vanish when short range elastic forces and long range Coulomb-forces are cancelled. A vanishing TO-mode frequency at some temperature indicates a partial instability of the crystal lattice and can be interpreted as the origin of a solid state phase transition. This requires either the next neighbour force constants, the long range Coulomb forces, or both to be temperature dependent. Generally the potential in which the core is oscillating has to be assumed as temperature dependent in such a way that the frequency softens to zero when the Curie point is reached (soft modes).

The limit of the Cochran model obviously lies in the assumption that transverse modes in the centre of the 1.BZ. generally are not associated with a macroscopic field. From the viewpoint of the polariton theory this is correct only in the phonon limit $k \gtrsim 2 \cdot 10^4$ but not in the region $k < 2 \cdot 10^4$ cm^{-1}. When taking into account the existence of polaritons deviations of the predictions from the classical Cochran model therefore occur.

Besides the fact that the construction of reasonable models providing temperature dependent potentials for the soft modes causes difficulties the temperature dependence of line widths were not described by the theory so far. A damped oscillator model presented by Cowley in 1963 /17/ brought a suitable generalization. In order to achieve an adequate description of the recorded spectra (frequencies and linewidths simultaneously) a complex damping function had to be introduced. This was justified by the success. The complex damping function , however, did hardly allow an easy physical interpretation.

It was not surprising that the relaxation model which shall be described henceforth led to similar formulas as Cowleys model /18/. The aim of both theories is to calculate the features observed in the spectra. The physical interpretation of the ansatz in the latter model, however, showed to be much more obvious. Furthermore the existence of "hard core frequencies" and the appearance of "central modes" near the Curie point in some crystals may be described by means of Cochrans and Cowleys theory only by introducing additional assuptions in the ansatz whereas they seem to follow from the relaxation model without any difficulties /16/.

Polaritons associated with purely transverse phonons are described by a dispersion relation of the simple type $(n^2=)\ c^2k^2/\omega^2 = \varepsilon(\omega)$. $\varepsilon(\omega)$ is the dielectric function in a direction parallel to the lattice displacement vector. This result can easily be derived from Fresnels equation cited in 2) above. All polariton dispersion effects thus are completely determined by the dielectric functions of a crystal. We therefore shortly recall which phenomena influence these. In the ultraviolet a contribution is given by the electrons, in the infrared by oscillating ions, and in the microwave region by dipole relaxations. The contribution giben by dipole relaxations is highly temperature dependent as can be seen from the Langevin-Debye-equation. Note that for the polarizability α in this equation holds $\varepsilon(\omega) = 1+4\pi\alpha(\omega)$). The possibility for a certain static dipole in a crystal to change its orientation from one potential minimum to another increases with temperature because of the higher Brownian motion. We now ask whether such dipole relaxations can influence the dynamical phonon spectrum of a crystal lattice. The answer is yes if we consider that the purely transverse modes show non vanishing macroscopic electric fields in the polariton region. Any temperature dependence of soft TO-phonons thus must not necessarily originate from a temperature dependence of long range or short range Coulomb forces as derived from Cochrans model. It may as well be caused by mode couplings between polaritons and relaxations, the latter becoming responsible for the strange temperature effects. A simple dielectric function written down by taking into account the three different kinds of contributions is

$$\varepsilon(\omega) = \varepsilon_\infty + 4\pi\rho\,\omega_T^2/(\omega_T^2 + i\gamma_T\omega - \omega^2) + 4\pi N\alpha_o/(1+i\omega\tau) \ .$$

$\sqrt{\varepsilon_\infty}$ stands for the high frequency refractive index, $4\pi\rho$ represents the mode strength of a polar phonon wave, γ_T the damping constant, and $4\pi N\alpha_o$ the static polarizability for $\omega=0$. The last term which was first derived by Debye in this form /20/ can strongly influence the polariton spectrum especially for small ω i.e. when ω becomes of the typical order of $1/\tau$. For $\tau \to 0$ calculations have shown that the dipole relaxation mechanism for the phase transition gives same results as Cochran's model /19/.

Dipole relaxations may exist due to impurities, dislocations, or other defects in an otherwise perfect lattice. Experiments concerning the phase transitions in $BaTiO_3$ and $SrTiO_3$ carried out over the last ten years did not provide coherent results. The features observed were highly dependent on the sample, i.e. its purity. This indicates at least qualitatively that the relaxation mechanism may cause an important progress in the understanding of phase transitions. Let us regard an intuitive view point. As is well known phase transitions between the solid, liquid and gaseous states are highly dependent on the existence of impurities (hysteresis of boiling and freezing points in extremely pure materials). Therefore it should not be surprising that impurities play an important role in solid state phase transitions too. The relaxation model thus may also here provide a reasonable description of hysteresis effects which in fact are observed.

Since the existence of polaritons is necessary for couplings between lattice waves and dipole relaxations to take place we finally see a principal possibility to influence such phase transitions by external electromagnetic radiation in a way that shall be described in more detail below, section 11.

6. PARAMETRIC LIGHT SCATTERING

When an intense laser beam with frequency ω_L enters a resonator containing a nonlinear optical crystal a second light beam with a lower frequency ω_s may be created an strongly amplified under certain conditions. Energy and the canonical momentum have to be preserved: $\hbar\omega_L=\hbar\omega_s+\hbar\omega_p$ and $\hbar\vec{k}_L=\hbar\vec{k}_s+\hbar\vec{k}_p$. This implies that simultaneously with the amplified wave ω_s a so called "idler wave" with frequency ω_p always will be created. Momentum conservation in such an experiment is equivalent to the well known phase matching condition from nonlinear optics. This can easily be realized when keeping in mind that the magnitudes of the wave vectors are given by $k_i=2\pi n_i/\lambda_i$, n_i being the refractive indices and λ_i the wave lengths in vacuum. Parametric amplification has first been observed in 1965 /21/. Because the refractive indices are temperature dependent a continuous variation of the phase matching condition and consequently the amplified wave frequency ω_s can be achieved by temperature tuning. Parametric oscillators are used as tunable lasers.

Before any parametric amplification takes place some initial energy quanta $\hbar\omega_s$ and $\hbar\omega_p$ have to be created by spontaneous scattering. In solids these are normally Stokes-processes associated with idler-phonons, polaritons or photons. The spontaneous scattering process is identical to inelastic Raman scattering. Best conditions for the construction of highly tunable light sources of this kind in general are provided by the upper photon-like polariton branches (see Fig. 1b) in anisotropic materials. The use of birefringence effects is important /7/. Strong dispersion of the "light branches" allows a remarkable frequency variation of the idler-quanta and consequently of the Stokes-light wave (ω_s). In suitable cases shifts within a range of almost 5000 cm^{-1} have been recorded.

Spontaneous creation of idler photons in the infrared in many cases turned out to be associated with surprisingly high scattering intensities at ω_s in the visible. These spontaneous processes have become known as parametric light scattering (or luminescence). The identity of parametric luminescence and Raman scattering at the upper polariton branch has first been shown by Klyshko and coworkers in 1970 /22/.

Besides that parametric light scattering can be used for the construction of tunable lasers it also represents a sensitive method for the determination of refractive indices in the band gap near the Reststrahlen region. One easily verifies this by a discussions of the canonical momentum conservation relation.

7. THE TM-REFLECTION TECHNIQUE APPLIED TO BULK POLARITONS

IR-reflection experiments performed in such a way that the electric vector of the incident and reflected rays lie in the plane determined by their wave vectors have become known as "transverse magnetic" (TM-reflection technique). A detailed understanding of such spectra was not achieved until very recently /23, 24/. Common IR-reflection spectra have been recorded only by the "proper" transverse-electric geometry hitherto.

The TM-reflection method turned out to provide quite detailed information on the bulk polariton spectrum of insulating crystals, see /7/. From a qualitative view point this may be realized as follows. We have pointed out that the general dispersion relation of bulk polaritons is $c^2k^2/\omega^2=\varepsilon(\omega)$. The dielectric function $\varepsilon(\omega)$ thus contains the complete information on the dispersion of polaritons. $\varepsilon(\omega)$ on the other hand is also responsible for the line shapes in IR-reflection spectra. Therefore it is not surprising that certain experimental geometries provide an easy relation between the properties of bulk polaritons and those of the recorded IR-reflection bands. The result is that the turning points of the edges of the TM-reflection bands correspond to data points on the bulk polariton dispersion branches. Variation of k can be achieved by changing the angle of incidence (and consequently of reflection). The experimental set up is similar to that of the attenuated total reflection method which shall be described in the next section. The only difference is that the total reflection prism shown in Fig. 2 has direct contact with the material when bulk polaritons are studied.

The greatest advantage of the TM-reflection technique obviously is that polaritons in all crystal classes may be studied. We remember that light scattering experiments require a simultaneous IR- and Raman-activity. This

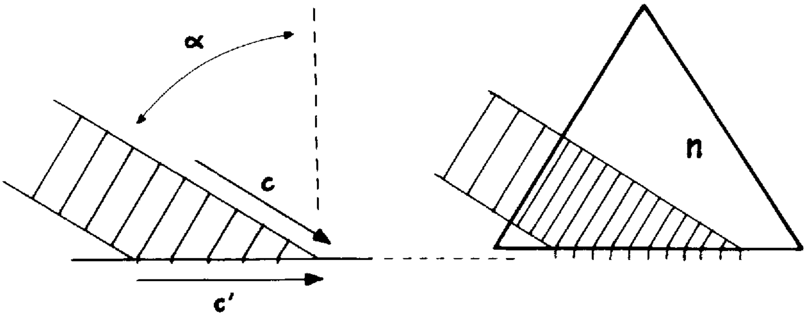

FIG. 2

On the excitation of surface waves by electromagnetic radiation, see text.

has prevented detailed studies of polaritons in e.g. alkali-halides, The TM-reflection method, however, should make possible such experiments.

In general the new method can be regarded as a suitable tool for complementary investigations relative to Raman studies. When, for instance, small LO-TO splittings are to be established experimentally the TM-reflection method was shown to be superior to light scattering experiments /24/.

8. THE ATR-METHOD APPLIED TO SURFACE MODES

Optical surface phonomena have become of great interest because of a rapid development of fiber optics within the last few years. Surface effects in general, however, play an important role also for catalysis and other fields of research in physical chemistry. We therefore want to draw some attention to a powerful experimental technique which allows detailed studies of surface waves. These may be surface-polaritons -plasma waves or others as well.

Let us shortly summarize what information can be obtained from surface polaritons. The basic difference to bulk modes is that surface modes propagate in an essentially two dimensional medium and that both the electric field vector component parallel to the surface and the displacement perpendicular to it have to alter continuously. The dispersion relation derived from the continuity conditions is $c^2k^2/\omega^2=\varepsilon(\omega)/(\varepsilon(\omega)+1)$ for a simple isotropic crystal. The difference to the bulk polariton dispersion formula lies in the appearance of the denominator $\varepsilon(\omega)+1$. This denominator causes the dispersion branches of surface polaritons to lie in the reststrahlen regions between TO and LO modes where no bulk polariton propagation is allowed, see Fig. 1. Bulk- and surface-polaritons together cover the complete energy spectrum.

Although there have been some sucessful Raman scattering experiments on surface polaritons /27/ the attenuated total reflection method (ATR) still seems to be simpler to handle. Raman scattering from surface polaritons was observed only on thin crystalline films hitherto whereas the ATR-technique easily allows investigations also on surfaces of "semi infinite" samples. Let us study under what conditions an electromagnetic wave reflected on a surface can be used to excite polar surface waves. The upper medium in the left drawing of Fig. 2 is assumed to be vacuum with the refractive index n=1. As can easily be seen from this figure the phase velocity c' along the surface exeeds the vacuum velocity c because $c' = c/\sin\alpha$. An excitation of surface waves by simply reflecting light thus is impossible. The situation is changed, however, when vacuum is replaced by a medium with a refractive index n>1. The phase velocity in the medium is then c/n and the component $c' = c/n\cdot\sin\alpha$. c' can now be arranged to coincide with the phase velocity of a surface mode by varying α in a suitable way. Experiments of this kind are carried out with a total reflection prism as shown in the right figure. The prism has to be located at a distance less than one vacuum wave length away from the surface active medium. The contact medium at the surface then is still vacuum (or air). The electric field of the "totally" reflected wave outside the prism, however, can easily interact with surface waves. We thus observe "frustated" of attenuated total reflection which is easily monitored. For detailed discussions and references, see refs /7,25,26/.

It should finally be pointed out that complete ATR-equipments are available commercially nowadays.

9. A CRITICAL VIEW ON TUNABLE POLARITON LASERS

Polariton frequencies observed by sponaneous Raman scattering dependon the scattering angle ρ between the laser beam and the direction of observation. For polariton branches with strong dispersion where ω changes rapidly with k a large frequency spectrum of Stokes-(or anti-Stokes)radiation is covered when ρ is varied within a range of 0° to approximately 10° away from the straight forward direction. When the intensity of the exciting laser beam becomes extremely high (giant puls lasers) stimulated Raman scattering takes place.

The mechanism of stimulated scattering is described classically as follows. A strong exciting laser causes strong Raman scattering. At high intensities the exciting light wave and the scattered, frequency shifted wave do not propagate independently through the crystal. The principle of superimposition known from linear optics does not hold any longer. Interactions take place due to nonlinearities of the optical susceptibility. As a result an electromagnetic wave at the difference frequency is generated. This wave can drive the original lattice wave because their frequencies (trivially) are identical and consequently cause further amplified scattered radiation (optical feedback). A remarcable percentage of the incident radiative energy can be transferred to the frequency shifted wave in this way. The power of stimulated Raman scattering becomes of the same order as the exciting laser. Stimulated scattering by polaritons therefore can be used for the construction of tunable lasers. In fact there are experiments showing that such lasers work at the frequency of the scattered light in the visible as well as in the infrared at the difference frequency between the incident laser and the frequency shifted wave /28,29/.

The polariton laser has been predicted to become one of the most important applications of polaritons in practice by several physicists especially in the late 60'th. Nowadays, however, we realize that dye lasers and spin-flip lasers are much more efficient. The former cover large regions in the visible and the latter in the infrared. The difficulties for the construction of polariton lasers are obvious. In order to obtain a narrow polariton laser line the aperture determining the divergence of the stimulated scattered beam has to be kept very small. The divergence directly determines the error of the polariton wave vector in k-space and thus the half width of the emitted radiation. The efficiency of such lasers is reduced enormously by the aperture. Narrow laser lines and a high tunability are properties which cannot be controlled independently from each other.

Although the parametric oscillator in principle is based on polariton scattering too, see again 6) it provides much better conditions. The use of photon like dispersion branches allows tuning within a large frequency range. The half width of the emitted radiation on the other hand is independently determined by the resonator.

In summary we believe that polariton lasers will not become of great technical importance in a near future.

10. NONLINEAR OPTICAL EXPERIMENTS WITH POLARITONS

The parametric oscillator and stimulated Raman scattering described above are two examples of nonlinear optical experiments involving polaritons. A third group of experiments is concerned with mode mixing. The principle is the following: Two strong incident laser beams at different frequencies enter a nonlinear optical medium without a resonator. A new wave at the sum or the difference frequency is generated. The conditions for such experiments again are derived from energy conservation $\hbar\omega_L = \hbar\omega_s + \hbar\omega$ and the wave vector relation $\vec{k}_L = \vec{k}_s + \vec{k}$. The two incident laser beams have to form an angle so that the canonical momentum is preserved. Radiation at the difference frequency ω then leaves the medium in direction of the third wave vector.

Three typical experiments are sketched in Fig. 3. In the geometry 3a the incident laser beams (full arrows!) operate at frequencies ω_L and ω_s, the latter being identical to the Stokesshifted frequency of a polariton. As a result strong radiation is generated in the infrared at the polariton frequency. Emission appears in direction of $\vec{k}$ as indicated in the figure /30/. Geometry 3b corresponds to mixing of visible (ω_L) and infrared (ω) light, the latter at some polariton frequency. In this case strong radiation at the visible Stokes-frequency ω_s is generated /31/. Experiments corresponding to Fig. 3c finally have become known as "coherent anti-Stokes Raman spectroscopy" (CARS). Both a Stokes and an anti-Stokes wave vector relation are combined to $2\vec{k}_L = \vec{k}_s + \vec{k}_A$ which is the well known condition for the appearance of stimulated Raman scattering at the anti-Stokes

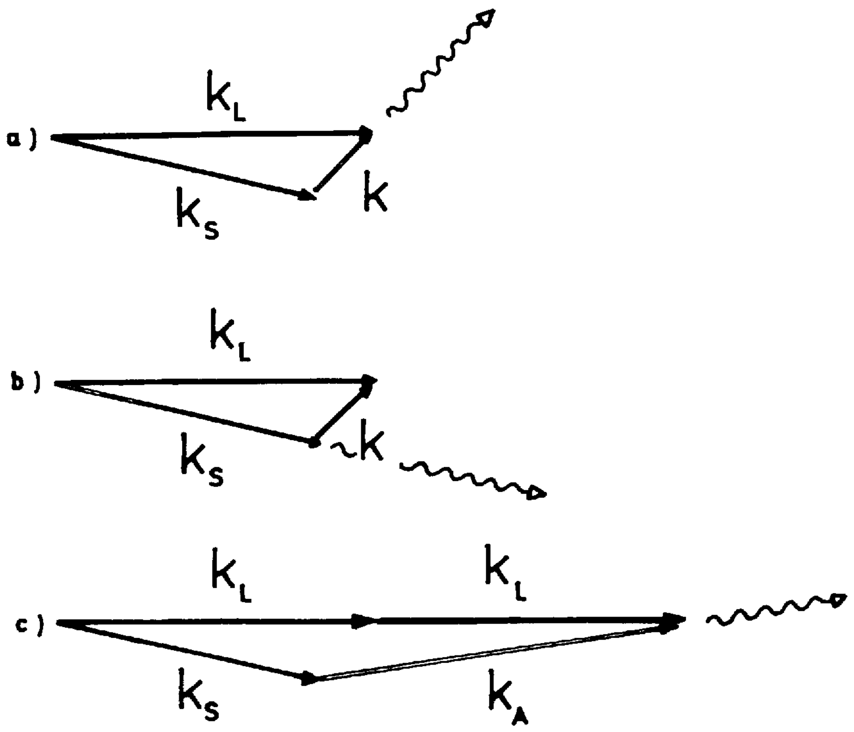

FIG. 3

Nonlinear optical experiments involving polaritons: Generation of difference frequencies in the visible a), and infrared b), and the excitation of coherent anti-Stokes radiation c).

frequency ω_A. Two laser quanta $\hbar\omega_L$ and a Stokes-quantum $\hbar\omega_s$ are combined to an anti-Stokes quantum $\hbar\omega_A = 2\hbar\omega_L - \hbar\omega_s$. The direction of the emitted radiation again is shown in figure 3c /32/.

Mode mixing of the above types advantageously can be used for the construction of laser sources with variable frequencies in the visible as well as in the infrared. We beliebe that especially in the infrared region this type of sources may be able to compete with spin-flip lasers because no Helium-cooling of the arrangement is necessary. The growing interest in laser induced chemical reactions might support corresponding developments.

11. THE QUESTION OF ENERGY CONVERSION AND SOME TENTATIVE FUTURE ASPECTS

The mixed electromagnetic/mechanical character of polaritons induces the question whether such systems can be used for energy conversion. From the hamiltonian of polaritons the percentage of mechanical and electromagnetic energy can be calculated as a function of k /7/. The experiment by Faust and Henry /31/, Fig. 3b, described above on the other hand shows that polaritons may be heated up remarkably by external infrared radiation. What is unambiguously observed in this experiment, however, is critically spoken only a drastically enlarged scattering cross section which does not make sure that a remarcable part of the incident radiative energy is converted to mechanical energy. Corresponding recent experiments by Hwang and Solin /33/ indicate that most of the energy possibly remains in the electronic system. No decay products of the hot polaritons could be identified among the phonons by these authors. Since the decay mechanism of polaritons in real crystals is hardly known, however, any search for such products remains accidental. Raman scattering experiments give information only on a very narrow region of k-space near the centre of the first Brillouin zone, Phonons with larger wave vectors may be detected only as second order processes by light scattering. Further systematical experiments of this kind and neutron scattering therefore should throw more light on the energy conversion mechanism in the future.

From an analogy in molecular physics we conclude that energy conversion should be possible also in solids. As already indicated above the last few years brought an increasing interest in laser induced chemical reactions. Molecules in the gaseous state are irradiated by an IR-laser of some watts power. Chemical reactions which take place under such circumstances in many cases were found to be different from simple thermal reactions /34/. The molecules seem to react on the well defined frequency of the incident laser radiation in a specific way.

It is known furthermore that intense laser radiation can cause local alterations and defects in crystal lattices. We therefore ask on what conditions external electromagnetic radiation can interact with polar lattice vibrations.

The characteristic differences between the dynamics of a molecule and a crystal lattice are caused by the latter being an almost infinite system of coupled identical oscillators whereas the former represent isolated oscillators. As a result energy is transmitted through a crystal by waves with different wave lengths and frequencies. Obviously the frequency of the external radiation most coincide with an eigenfrequency of the system in both cases for resonance to take place. This remains the only condition for molecules. In a solid the wave length of the incident radiation and the lattice wave in addition have to coincide. This is equivalent to the well known condition that the canonical momenta $\hbar k_i$ have to be of the same order.

Let us regard lattice vibrations at the border of the 1.BZ ($k \approx 10^8$ cm^{-1}) where oscillations in neighboring elementary cells are in opposite phase. Dipolemoments in every pair of neighboring cells are cancelled in this case and no macroscopic electric polarization is built up. Macroscopic fields appear only when cells at approximately half a wave length distance from each other oscillate in opposite phases, the wave length in question being that of the free electromagnetic wave in the material. It turns out that this is exactly what happens in the polariton region $10^3 \lesssim k \lesssim 2 \cdot 10^4$ cm^{-1}. We realize that excitations in the real phonon region $k \approx 10^5$ cm^{-1} are not associated with electric fields and cannot interact with external radiation. "Polar phonons" (with frequency ω_T) cannot directly be excited externally by IR-lasers. This is an important difference to molecular vibrations. From Fig. 1b it can be seen that only slightly below any limiting phonon frequency ω_T there are always polaritons which easily fulfil the momentum conservation. External electromagnetic energy therefore is transferred into a crystal only via polaritons. Polaritons cause the thermal equilibrium between a crystal and its radiative surrounding. The energy flux between different vibrational modes on the other hand is made possible by anharmonic couplings. These are taken into account by damping terms in the macroscopic theory. Laser-induced reactions in solids thus generally are governed by the physics of polaritons.

Because the polariton theory in its simplest form is essentially onedimensional we realize that the wave like character of vibrations in suitable linear macromolecules strictly should not be neglected but correctly described in an analogous way too.

Most basic research concerning energy conversion by polaritons still is missing. There are lots of open questions starting from problems around the elementary mechanism of electron-lattice-interaction and ending somewhere in the neighborhood of laser induced reactions in macromolecules.

12. CONCLUSION

In the preceeding ten sections we have presented a rather broad spectrum of possible applications of polaritons. Some of them represent refined techniques for conventional Raman scattering experiments others suggest connections between different fields of research and some finally might turn out to be only fata morganas. The aim of this article was to show that polaritons should be of interest not only to solid state physicists but also to those working in neighboring fields. A large number of papers on biological materials contributed to the "Fourth International Conference on Raman Spectroscopy" in Brunswick, Maine 1974 clearly demonstrated this. It furthermore showed that a better flux of information might increase the efficiency of research work of this kind.

Classical Raman spectroscopic methods normally provide an extremely large number of lines from biological systems in the liquid state. The only parameter giving information on assignments is the depolarisation ratio. A straight forward examination of Raman spectra from a biological system should start with detailed studies of its single crystalline amino acids or even simpler parts in the opinion of this authors. Directional dispersion and polariton measurements applied to these provide detailed information because only one additional parameter (the scattering angle) allows a multiple number of eigenfrequencies to be determined. Only when the frequency spectra of the "bricks" are understood in detail an analysis of spectra from the complete system will give applicable information. A new journal dedicated to chemistry and lasers might induce some new work in this direction.

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