sistivity ($T \leqslant 3.5°$K for potassium) is dominated by phonon drag, leading to an exponential temperature dependence for $\rho(T)$ as $T \to 0$, rather than the T^5 dependence obtained without phonon drag. (ii) Our calculations, including phonon drag, are in excellent agreement with the recent resistivity measurement of Gugan for potassium in the temperature range $4.2 \geqslant T \geqslant 2.0°$K.

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Surface Phonons in the Oscillatory Photoconductivity of Zinc Oxide

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Photoconductivity on ($1\bar{1}00$) prism surfaces of ZnO crystals has been measured at low temperatures in ultrahigh vacuum. The spectral distribution between 0.2 and 0.7 eV exhibits two sequences of minima. The periods coincide with the energies of bulk LO phonons and of surface phonons, respectively. Additional evidence for the interaction with surface phonons is given by condensing xenon on the crystal surface. Thereby the period corresponding to the energy of surface phonons is decreased as expected.

Photoconductivity spectra of several semiconductors exhibit periodic sequences of minima. This so-called oscillatory photoconductivity was first observed in the intrinsic photoconductivity of GaSb and InSb.[1] The oscillations are explained by interaction of photoexcited carriers with phonons.[1] Oscillatory photoconductivity has been reported by Müller and Mönch[2,3] in connection with an excitation of holes out of surface states on (111) Si surfaces. Photoconductivity has also been detected on ZnO crystals, which is due to an excitation of electrons from surface states into the conduction band.[4] Oscillations in the spectral distribution of this process are treated in the present paper.

The ZnO crystals were grown from the vapor phase in this laboratory. They are hexagonal prisms with a diameter of about 2 mm. Undoped crystals have an n-type conductivity on the order of $10^{-2} \ \Omega^{-1} \ cm^{-1}$. The surfaces were cleaned by annealing at 400°C in an ultrahigh vacuum of about 10^{-10} Torr. Light is provided by a Globar followed by a double-pass grid monochromator (Perkin-Elmer E-1). The incidence of the light is perpendicular to a prism surface whereas the current flows parallel to this surface and to the c axis. Light modulation with 13 sec^{-1} allows phase-sensitive amplification of the photoconductivity signal (PAR lock-in amplifier HR-8).

Because of the dependence on dark surface conductivity $\Delta\sigma$, the data are given in terms of a photo surface conductivity $\delta\sigma$ (Fig. 1, upper). Curves b, c, and d are measured on surfaces cleaned by annealing. Transient exposure to atomic hydrogen at room temperature increases the dark surface conductivity[5] $\Delta\sigma$ as well as the photoconductivity $\delta\sigma$ (curve a). Independent of the surface conductivity $\Delta\sigma$ the curves show equal sequences
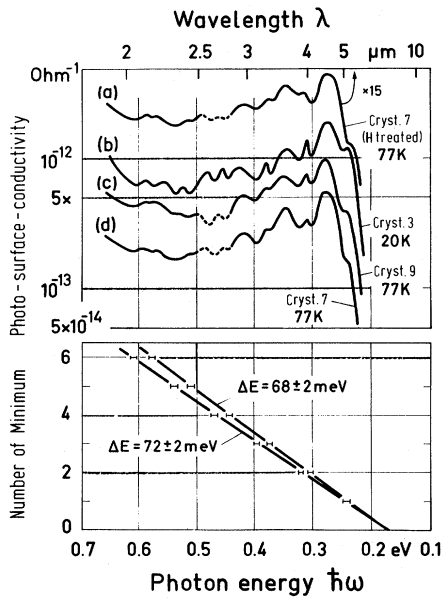
FIG. 1. Upper, photoconductivity spectra measured on prism surfaces as grown of undoped ZnO crystals. Dark surface conductivities $\Delta\sigma$: curve a, 1.6×10^{-6} Ω^{-1}; curve b, 1×10^{-8} Ω^{-1}; curve c, 3×10^{-9} Ω^{-1}; curve d, 1.4×10^{-9} Ω^{-1}. The spectra are related to an incident photon flux of 6×10^{14} cm^{-2} sec^{-1}. The dashed parts of the spectra are measured with lower accuracy because of the structured background absorption in the atmosphere. Lower, integral numbers of minima versus their energetic positions.
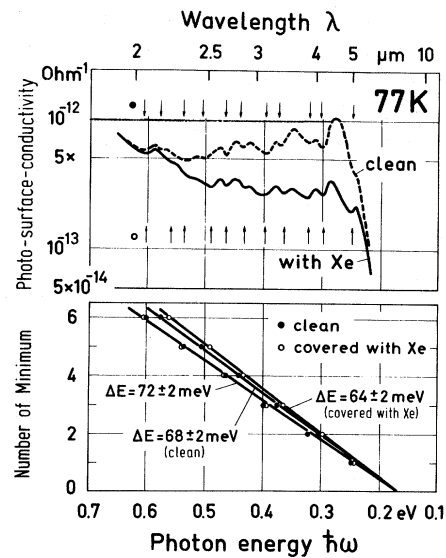

FIG. 2. Upper, influence of condensed xenon on the oscillatory photoconductivity. Crystal 8, dark surface conductivity $\Delta\sigma = 3.5 \times 10^{-9}$ Ω^{-1}. The spectra are related to an incident photon flux of 6×10^{14} cm^{-2} sec^{-1}. Arrows indicate the energetic positions of minima. Lower, integral numbers of minima versus their energetic positions.

of dips which are characteristic of oscillatory photoconductivity. At 20 K (curve b) the minima are more pronounced than at 77 K. There are five pairs of dips. The increasing distance within the pairs towards higher energies suggests two different series of oscillations. Integral numbers are attached to both series and are plotted versus the energetic positions of the minima. As seen from Fig. 1 (lower) two straight lines result. Their slopes characterize two different oscillation periods ΔE of 72 ± 2 and 68 ± 2 meV.

In a further experiment the photoconductivity was measured with xenon condensed on the surface at 10^{-3} Torr pressure (Fig. 2). No change in dark surface conductivity was observed after xenon condensation. Also the period $\Delta E = 72$ meV for one series of oscillations remained unchanged. The other oscillation period, however, decreased from 68 to 64 meV, as is seen from the different slopes of the corresponding straight lines in Fig. 2 (lower). This shift is beyond the margin of error.

The oscillation period $\Delta E = 72 \pm 2$ meV (Fig. 1) nearly coincides with the energies of the bulk in-

frared longitudinal optical (LO) phonons in ZnO: 71.5 meV (vibration parallel to the c axis) and 73.1 meV (vibration normal to c).[6] Oscillations in photoconductivity which have been found up to now are mostly due to LO phonons. The reason is the extraordinarily strong coupling (compared with all other phonons) of these phonons to the electron system because of the macroscopic electric field of LO phonons with long wavelength. Because of this strong coupling, the relaxation time for electron scattering by LO phonons is short compared to other relaxation times and to the lifetime of excited carriers in most cases. Hot electrons which have been excited from states, in the forbidden band into the conduction band by a photon of the energy $\hbar\omega$ can be scattered to the bottom of the conduction band by multiple emission of LO phonons (energy $\hbar\omega_{LO}$) under the condition

$$\hbar\omega = E_0 + n\hbar\omega_{LO}, \quad n = 1, 2, 3, \ldots . \tag{1}$$

E_0 is the threshold energy of photoconductivity, i.e., the minimal transition energy from the surface states[4] into the conduction band. If the fast scattering process between hot electrons and LO phonons ends in recombination centers instead of the conduction band, then E_0 must be replaced by the energetic distance between photoactive surface states and recombination centers.[7] By the

phonon emission the carriers lose net momentum in the field direction. Thus, a decrease of photo-conductivity is caused.[8,9]

The other oscillation period of $\Delta E = 68 \pm 2$ meV which is sensitive to xenon condensation agrees with the energy of 68.8 meV for Fuchs-Kliewer surface phonons[10] found by Ibach from inelastic scattering of low-energy electrons.[11] Except for bulk LO phonons, only these optical surface pho-nons—in the case of long wavelengths—are ac-companied by a macroscopic electric field. This is caused by a dipole moment within the elemen-tary cell arising from oscillations of the sublat-tices of zinc and oxygen against each other. The macroscopic field of the dipole moment decays exponentially with k^{-1} as penetration depth (k is the wave vector of the phonon) from the surface into the bulk of the crystal and symmetrically in-to the vacuum or an adjacent medium.[12] The vac-uum part of the field causes the strong inelastic scattering of external electrons, whereas the field below the crystal surface must interact in the same way with photocarriers in the space-charge layer. This interaction explains the ob-servation of Fuchs-Kliewer surface phonons in photoconductivity. In the scattering process be-tween hot electrons and surface phonons, momen-tum and energy are conserved. Therefore, from the energy of the exciting light at the first oscil-lation minimum and the effective mass in the con-duction band,[5] the penetration depth k^{-1} of the sur-face phonons can be estimated to be about 15 Å.

Further evidence for this interpretation is giv-en by the experiments with xenon. Because of its high polarizability, xenon condensed on the sur-face changes the electric field of the phonons out-side the crystal and, thus, their frequency. Ac-cording to the dielectric theory[12] the frequency ω_s of Fuchs-Kliewer surface phonons is related to the Reststrahlen frequency ω_{TO} by

$$\omega_s^2 = \frac{\epsilon_0 + \epsilon_{ad}}{\epsilon_\infty + \epsilon_{ad}} \omega_{TO}^2, \qquad (2)$$

where ϵ_{ad} is the dielectric constant of the medium adjacent to the crystal surface. By means of the Lorentz-Lorenz formula ϵ_{ad} for the condensed xenon is calculated to be 2.25 from atomic data. With Eq. (2) an energy of 64.5 meV follows for

the surface phonon, in good agreement with the experimental result. Equation (2) is derived un-der the premise of a semi-infinite adjacent medi-um. This should be a reasonable approximation, however, if the unknown thickness of the xenon layer exceeds the penetration depth of the phonon (15 Å).

Minima which belong to a combined scattering of electrons with LO phonons and surface phonons are not found in the spectra. Therefore, these combination processes must be less probable than the emission of only one type of phonon. There is no explanation for this fact at present. Also the decrease of the photoconductivity to-wards longer wavelengths after xenon condensa-tion (Fig. 2, upper) is not yet understood.

The present paper shows that photoconductivity measurements might be another experimental method for studying surface phonons besides spectroscopy with low-energy electrons.

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