band calculation, we are able to state that we have found indeed very large excitonic shifts (10 eV!).

It has been shown that the electron-hole interaction cannot be considered to be a weak perturbation for core excitations in insulators like LiF. We believe that further progress in calculating core absorption spectra could start from atomic and molecular theory rather than band calculations. In order to stress this point we show the long-noted coincidence between the lowest excited levels[12] of the Li^+ free ion and the LiF excitations in Fig. 1.

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[11]It is possible, in principle, to ascribe the weak structures in the range 54 to 60 eV to F^- 2*s* or valence-band transitions. Usually, however, such structures far above threshold are much broader. Moreover, the fact that we would then find a very prominent peak at the onset would not agree with the general expectation that the lowest excited states are of the forbidden *s*-*s* type.

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Nonlinear Optical Response of Mobile Holes in Tellurium

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Nonlinear and linear optical responses of mobile holes in the "camelback"-shaped valence band of tellurium are calculated without expansion in powers of electric field of the wave. We predict unusual nonlinear properties depending on intensity, frequency, and polarization of the driving field, as well as on the free-hole concentration and hydrostatic pressure.

Optical nonlinearities due to mobile carriers in nonparabolic energy bands of III-V semiconducting compounds are known to be among the strongest ever observed. This effect was first proposed by Butcher and McLean[1] and Lax, McWhorter, and Mavroides,[2] observed by Patel, Slusher, and Fleury,[3] and described by Wolff and Pearson.[4] As always, when dealing with a free-electron system, one can influence it easily by external factors like magnetic field,[5] pressure, doping, and temperature. All theories of the effect (cf. also Jha and Bloembergen[6] and Wang and Ressler[7]) use an expansion of nonlinear current in powers of the driving electric field. In this note we consider nonlinear and linear optical responses of free holes in the "camelback"-shaped upper valence band of tellurium and demonstrate that, in this case, one has to go beyond the usual expansion. This results in a number of new possibilities. Our treatment is in the spirit of that used by Keldysh[8] to calculate multiphoton absorption and tunneling in the field of a strong electromagnetic wave.

The upper valence band of tellurium is described

by a dispersion relation proposed by Betbeder-Matibet and Hulin[9]:

$$\epsilon(\vec{k}) = -\alpha k_z^2 + (A^2 + B^2 k_z^2)^{1/2} - \hbar^2 k_\perp^2/2m_\perp - C, \quad (1)$$

where $\vec{k}$ is counted from the corner H of the Brillouin zone, k_z and $k_\perp$ denoting components parallel and perpendicular to the trigonal axis, respectively. The band parameters determined from the cyclotron-resonance experiments by Couder, Hulin, and Thomé[10] give $\alpha = 4.23\times10^{-15}$ eV cm^2, $A = 0.063$ eV, $B = 2.63\times10^{-8}$ eV cm, $m_\perp = 0.108m_0$. These are in good agreement with the results obtained by other authors from cyclotron resonance, interband magneto-optics, and the Shubnikov–de Haas effect. Equation (1) describes a saddle point at $k = 0$ and a "camelback" shape along the k_z direction, with two maxima at $\pm k_z^m = \pm 1.98\times10^6$ cm^{-1}. The longitudinal mass at the maxima is $m_\parallel(\pm k_z^m) = 0.22m_0$. The zero of energy is chosen at the band maxima and $\Delta = A - C = -2.18$ meV represents the energy of the saddle point. Our purpose is to find the optical response of free holes induced by the electric component of a monochromatic incident beam polarized along the z direction: $E_z(t) = E_0\sin\omega t$. In the region of low losses, $\omega\tau \gg 1$, and long wavelengths, $\hbar\omega \ll \epsilon_g$, the equation of motion, $d(\hbar k_z)/dt = eE_0\times\sin\omega t$, has the solution

$$k_z(t) = -K\cos\omega t + k_{z0}, \quad (2)$$

where $K = eE_0/\hbar\omega$ represents the amplitude of oscillations and k_{z0} the initial value. The usual expansion of nonlinear current in powers of electric field corresponds to an expansion of velocity in powers of K, which is in turn equivalent to the perturbation approach in quantum mechanics. In the case of tellurium, however, one can reach values of K comparable to A/B and k_z^m, for which the above expansion is no longer valid, and one must calculate the current to all orders of K.

The current induced in one band by a low-frequency electric field of any magnitude (Butcher and McLean,[11] cf. also Genkin and Mednis[12]) is given by

$$\vec{j}(t) = e\sum_{\vec{k}_0}\vec{v}(t, \vec{k}_0)f(\vec{k}_0), \quad (3)$$

where $f(\vec{k}_0)$ is the unperturbed distribution function. A small term due to distortion of the Bloch bands by the electromagnetic field has been neglected. The velocity is

$$v_z(\vec{k}) = \frac{1}{\hbar}\frac{\partial\epsilon}{\partial k_z} = -\frac{2\alpha}{\hbar}k_z + \frac{B^2}{\hbar}\frac{k_z}{(A^2 + B^2k_z^2)^{1/2}} \quad (4)$$

and upon using Eq. (2) one obtains $v_z(t, K, \vec{k}_0)$. The first term in Eq. (4) does not contribute to the nonlinear current, while the second has a form similar to that in InSb and InAs.[13] However, in III-V compounds the initial $\vec{k}_0$ values occur around $k = 0$, whereas in tellurium the holes are initially located in two pockets around $\vec{k} = (\pm k_z^m; k_\perp = 0)$. When integrating over the initial values, the velocity $v(t, K, \vec{k}_0)$ is expanded around the points $\pm k_z^m$ to the quadratic terms in $\delta k_z = k_{z0} - k_z^m$. For hole concentrations $p < 2\times10^{16}$ cm^{-3} the Fermi energy is small compared to Δ and one can use ellipsoidal and parabolic $\epsilon(\delta\vec{k})$ dependence in the vicinity of the maxima. Finally, in order to find exactly the linear and nonlinear responses, the current is expanded in the Fourier series

$$j_z(t, K) = j_1(K)\cos\omega t + j_3(K)\cos3\omega t + \ldots, \quad (5)$$

which is *not equivalent* to the expansion in powers of K. For a strongly degenerate hole gas one obtains

$$j_1(K) = (4B/\hbar)pR_1 + (4\alpha/\hbar)pK, \quad (6)$$

$$j_n(K) = (4B/\hbar)pR_n \quad (n = 3, 5, \ldots), \quad (7)$$

where

$$R_n(K) = -\left[I_n - \frac{3}{10}\left(\frac{3\pi^2}{2}\right)\frac{m_\parallel}{m_{ds}}\frac{B^2}{A^2}p^{2/3}J_n\right] \quad (8)$$

for $n = 1, 3, 5, \ldots$ with $m_{ds} = (m_\parallel m_\perp^2)^{1/3}$, while I_n and J_n denote the Fourier coefficients

$$I_n(K) = \frac{1}{\pi}\int_0^\pi \frac{(k_z'^m + K'\cos x)\cos nx\,dx}{[1 + (k_z'^m + K'\cos x)^2]^{1/2}}, \quad (9)$$

$$J_n(K) = \frac{1}{\pi}\int_0^\pi \frac{(k_z'^m + K'\cos x)\cos nx\,dx}{[1 + (k_z'^m + K'\cos x)^2]^{5/2}}, \quad (10)$$

with $k_z'^m = (B/A)k_z^m$ and $K' = (B/A)K$. The integrals (9) and (10) can be expressed by the elliptic integrals of the first and second kind, but the final expressions become cumbersome and we chose to calculate them numerically.

Figure 1 shows the dimensionless nonlinear responses R_3 and R_5 calculated with the above band parameters for different free-hole densities. It can be seen that the standard expansion in powers of K breaks down completely for $K > 1\times10^6$ cm^{-1}, the third-harmonic current having a maximum and changing sign. Expanding j_3 in powers of K (for sufficiently small K values), one obtains at low concentrations $j_3 \sim pK^3[(B/A)^2 - 4(k_z^m)^2]$. Thus the initial sign of j_3 in Te is negative because $4(k_z^m)^2 > (B/A)^2$, while in InSb it is positive because there $k_z^m = 0$. In other words, the differ-

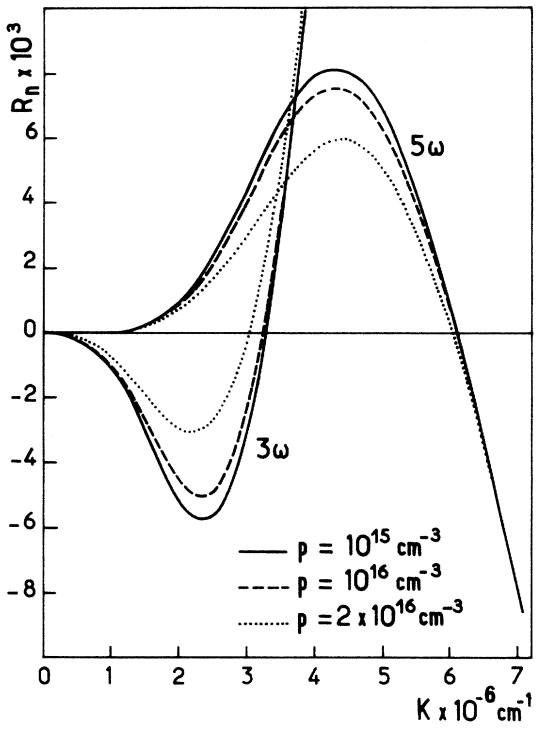

FIG. 1. Nonlinear optical response of free holes in Te at third- and fifth-harmonic frequencies versus $K = eE_0/\hbar\omega$, for different free-hole densities.

ence comes from the fact that in each case the free carriers are differently located in $\vec{k}$ space. With increasing K the initial location is less and less important and the nonlinear behavior becomes similar to that in III-V compounds, which corresponds to the change of sign. For similar reasons the negative anomaly decreases with increasing hole concentration. One can predict that for concentrations $p > 6 \times 10^{16}$ cm^{-3} the response R_3 will be positive at all K values [this region has not been described since the parabolic $\epsilon(\delta\vec{k})$ dependence ceases to be valid]. Thus, at small K values the sign of j_3 should change with increasing hole concentration.

It has been demonstrated by Anzin *et al.*[14] that hydrostatic pressure strongly affects the form of the upper valence band of tellurium. The local energy maxima become smaller, they occur at lower k_z^m values, and finally, at $P \approx 14$ kbar, the camelback shape disappears. On the other hand, the hole density is almost pressure independent. Using the pressure coefficients determined in Ref. 14, the nonlinear optical response at 3ω has been calculated for the low hole density of $p = 10^{15}$ cm^{-3} [which allows us to neglect the second term in Eq. (8)]. The results for R_3 at different pressures are shown in Fig. 2. It can be seen that the standard K^3 dependence breaks down at smaller and smaller K values as the pressure increases, having a particularly unusual K dependence for $P = 6$ kbar. At higher pressures R_3 is positive for all K values, so that at small K the nonlinear current j_3 changes sign as a function of pressure. Finally, Fig. 3 shows the optical response at the driving frequency ω as a function of K, calculated on the basis of Eq. (6) for different pressures. The linear K dependence is observed only at low K values. At the pressure for which the saddle point disappears, the quadratic k_z terms in Eq.

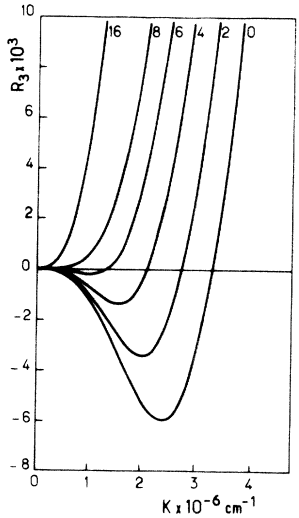

FIG. 2. Nonlinear optical response of free holes ($p = 10^{15}$ cm^{-3}) in Te at third-harmonic frequency versus $K = eE_0/\hbar\omega$, for different hydrostatic pressures (in kilobars).

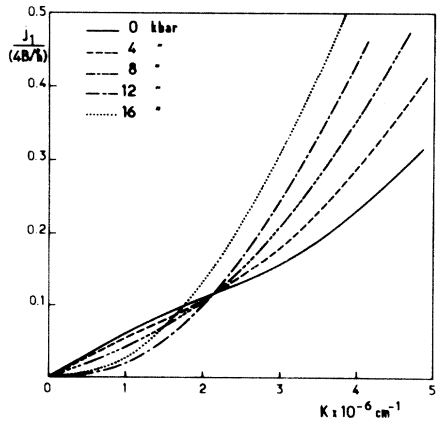

FIG. 3. Linear optical response of free holes ($p = 10^{15}$ cm^{-3}) in Te versus $K = eE_0/\hbar\omega$, for different hydrostatic pressures.

(1) cancel out and one deals with an $\epsilon(k_z)$ relation beginning with k_z^4. In this situation, the linear current is close to zero for small K and one deals with a medium in which the nonlinear response is almost comparable to the linear one. The curve for $P = 14$ kbar has not been calculated, since in the flat band the initial k_{z0} values of holes are not well located. At higher K values, the linear response is highly nonlinear in K, which should result in strong self-focusing properties.

The HCN laser should provide an adequate source to test the above predictions. In pure Te samples relaxation times $\tau \approx 5\times10^{-12}$ sec can be reached, which for $\lambda = 337$ μm gives $\omega\tau \approx 30$. To achieve $K = 2\times10^6$ cm^{-1} one needs an electric field of the wave $E_0 = 7\times10^3$ V/cm. The required power of 650 W/mm^2 can be obtained with a focused beam in the pulse regime.

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