PHYSICAL REVIEW B VOLUME 15, NUMBER 2 15 JANUARY 1977

Temperature dependence of the photoconductivity and photoluminescence spectra of AgCl†

R. H. Stulen and G. Ascarelli
Physics Department, Purdue University, West Lafayette, Indiana 47907
(Received 13 May 1976)

The intrinsic photoluminescence and photoconductivity spectra of AgCl have been measured over a temperature range from 6.8 to 80°K. The luminescence observed is that characteristic of the self-trapped exciton. A calculation of the first and second moments of the photoluminescence spectra indicates that they are comprised of at least two components each of which has its own characteristic temperature dependence. The thermal quenching of the luminescence has been investigated in both zone-refined and non-zone-refined samples. The photoconductivity spectrum shows a strong dependence on previous exposure. In addition, it confirms recent experimental evidence for the existence of a subsidiary valence-band maximum at Δ which is nearly degenerate with the principal maximum at L.

INTRODUCTION

Although there have been many experimental studies of the optical properties of the silver halides, some of the results, particularly in the case of fluorescence and photoconductivity, are still not completely understood. Part of the difficulty lies in the fact that impurities play a dominant role in determining the lifetime and decay mechanisms of both free carriers and free excitons, and therefore in many instances mask the intrinsic properties which one desires to determine. In AgCl, the situation is further complicated by the existence of metastable "intrinsic" impurities such as Frenkel defects and photoproduced self-trapped holes.[1-5] In general, unwanted defects pose a much larger problem in the cases of fluorescence and photoconductivity studies than in the case of optical-absorption measurements. As an aid in the interpretation of the results it is therefore desirable to be able to correlate the fluorescence and photoconductivity data with the optical-absorption data.

In this paper, we present experimental results of the temperature dependence of the fluorescence and photoconductivity of silver chloride. These measurements have been performed using low-intensity optical excitation on samples of both zone-refined and non-zone-refined material, and include the temperature dependence ($4.2 \leq T \leq 80$ °K) of the fluorescence spectrum, the temperature dependence of the total fluorescent yield, and the temperature dependence of the photoconductivity.

Most of the results presented here agree favorably with those of earlier studies.[3,6-14] However, several new and unexpected features have been observed both in the fluorescence and the photoconductivity. The temperature dependence of the fluorescence spectrum shows the existence of at least two separate states associated with the self-trapped exciton, one of which is stable below approximately 40 °K, and the other which is stable at higher temperatures. The photoconductivity data confirm recent experimental evidence[15] concerning the existence of a valence-band maximum at Δ along the $\langle 100 \rangle$ direction. The photoconductivity spectrum depends markedly on previous exposure, providing an indication that a very small number of photoproduced defects can appreciably alter the experimental results.

In the following section we present a brief discussion of the experimental techniques used and then proceed to present our results and their interpretation.

EXPERIMENTAL

Samples were obtained from either an ingot of zone-refined AgCl kindly provided by Dr. F. Moser of the Eastman Kodak Co., or from an ingot grown by the Bridgman technique. Each sample was etched in reagent-grade HCl and washed repeatedly in triply distilled water in order to eliminate surface contaminants prior to annealing. After annealing on a quartz plate at 400 °C in a He atmosphere for 24 h, they were cooled slowly to room temperature over a period of at least 48 h. The annealed sample was then polished with a KCN solution, mounted in a cryostat, and cooled slowly to 77 °K. Samples were exposed only to red light ($\lambda \gtrsim 6000$ Å) while their temperatures exceeded ~ 100 °K.

In the fluorescence study two monochromators were employed; one, in conjunction with a high-pressure Xe arc, was used as the monochromatic source of ultraviolet excitation radiation incident on the sample. The second monochromator, in conjunction with an EMI 9635 photomultiplier, was

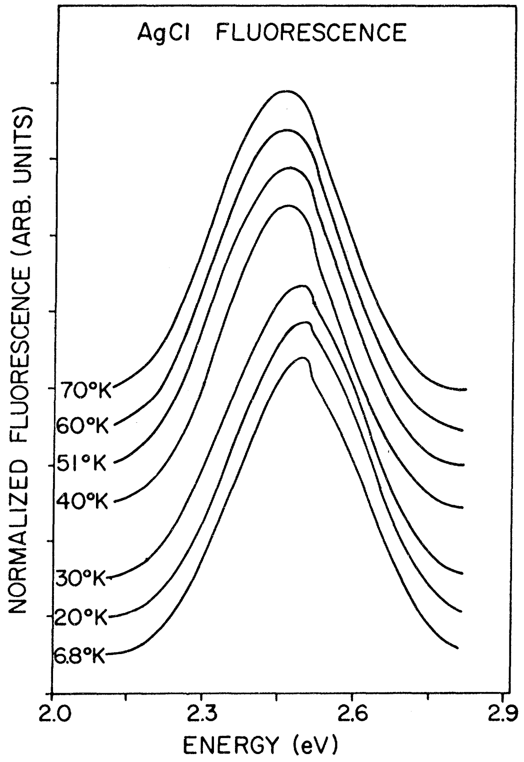

FIG. 1. Photoluminescence spectrum of zone-refined AgCl at various temperatures. Excitation at $\lambda = 3785$ Å. See text for details.

used to analyze the emitted fluorescence. In the measurements of the temperature dependence of the spectral distribution of the fluorescence, the "source" monochromator was a Spex "mini-mate" (dispersion, 40 Å/mm) while the analyzing monochromator was a Spex model 1700 (dispersion, 10 Å/mm). The roles of these two monochromators were then interchanged in the measurements of the temperature dependence of the total fluorescence yield. In this latter case, the function of the "mini-mate" monochromator was essentially that of a narrow bandpass filter, which allowed all of the fluorescent radiation to be detected simultaneously while at the same time blocking any of the exciting radiation.

The photoconductivity results were obtained by means of an ac capacitance technique in which the sample (approximately $5 \times 5 \times 15$ mm^3) formed the dielectric between the plates of a parallel-plate capacitor. Light emerging from the exit slit of the Spex 1700 monochromator was chopped (225 Hz) and then focused onto the sample. The creation of free carriers was then detected by observing changes in the loss tangent associated with the sample capacitor. These changes were measured using standard three-terminal measurement techniques with the aid of a General Radio model 1615-A capacitance bridge. The output of the bridge was adjusted to a null for energies of the incident light less than the indirect gap energy. Changes about this null were then phase sensitively detected as the wavelength of the light incident on the sample was scanned from short wavelengths where it is absorbed to longer wavelengths where the sample is transparent.

RESULTS AND DISCUSSIONS

Photoluminescence

Early studies of the photoluminescence in AgCl showed the existence of a broad blue-green luminescence band centered at approximately 2.5 eV.[13] This has been assigned to the recombination of self-trapped excitons.[3] The large Stokes shift (approximately 0.75 eV) between absorption and emission reflects the lattice relaxation associated with the self-trapping of the hole. In our measurements we have examined both the temperature dependence of the fluorescence spectrum, and the total fluorescent yield as a function of temperature in an effort to determine activation energies associated with its thermal quenching. The temperature dependence of the fluorescence spectrum for the zone-refined sample is shown in Fig. 1. The spectrum at each temperature represents an average of many runs. The curves have been drawn displaced on top of one another and, in addition, each has been normalized to the same peak value. The results for the non-zone-refined samples are similar. At each temperature, the sample was irradiated at $\lambda = 3785$ Å. The spectrum at 6.8 °K agrees qualitatively with the results presented in previous papers. From our results it is seen that around 35 °K the fluorescence maximum shifts towards lower energy. In order to investigate this shift, we have calculated both the first and second moments of the spectra at each temperature. These are plotted in Fig. 2 along with similar results for the non-zone-refined material. The results from both types of material show the same behavior except that the changes in the case of the non-zone-refined material are not as large.

The first moment, which gives the center of gravity of each curve, is clearly seen to shift towards lower energy between 30 and 40 °K. At the same time, the second moment, which reflects the width of the spectrum, is also seen to decrease. This change in the moments indicates that the entire spectrum does not simply undergo a rigid shift with temperature, but instead that the fluorescence spectrum is composed of at least two components each associated with a given type of self-trapped exciton (STE). Two Gaussian curves with the same half-width and intensities in the ratio 1 : 5 dis-

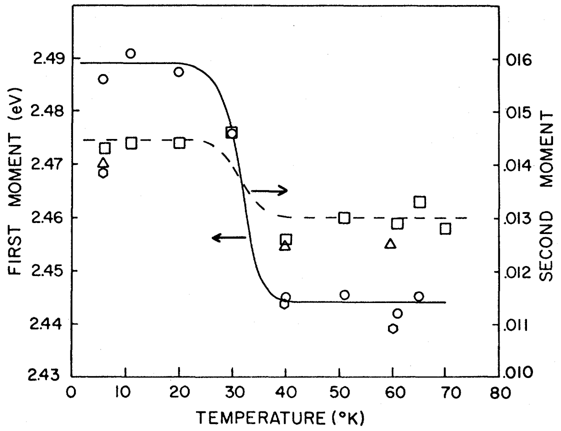

FIG. 2. Change in both the first and second moments associated with the photoluminescence spectra of Fig. 1. For the case of zone-refined AgCl the first moments are plotted as circles while the second moments are plotted as squares. Similar results for the non-zone-refined material are plotted as hexagons (first moment) and triangles (second moment).

placed ~250 meV from each other are a good representation of the observed spectrum. Above 40 °K, the higher-energy, and less intense, band is bleached giving rise to a change in the moments of the total fluorescence spectrum. We speculate that the high-energy portion of the spectrum reflects the recombination associated with the isolated STE of the perfect lattice, while the low-energy portion of the spectrum reflects the recombination of a STE near a defect. Possible candidates for the latter are isolated self-trapped holes, silver vacancies, silver interstitials that could remain from relatively high temperatures, and polyvalent metal-ion impurities.

The assignment of the low-energy fluorescence to a STE near a defect is consistent with the results of Marquardt *et al.*,[3] which show that the fluorescence spectrum depends on the mode of excitation. Their results have shown that the fluorescence spectrum excited by either 50-kV x-rays or 500-keV electrons, exhibits a maximum at a lower energy than the case in which the sample is excited with ultraviolet light. Both x-ray and electron-beam excitation produce a larger local concentration of self-trapped holes and possibly Frenkel defects than does excitation with ultraviolet light. The kinetic energy of electron-hole pairs created by x rays or 500-keV electrons is also much larger than for those obtained with band-gap radiation. The intensity of the fluorescence associated with self-trapped excitons near defects is expected to be enhanced in this case and would give a fluorescent maximum at a lower energy than in the case of ultraviolet excitation.

The temperature dependence of the total fluorescence yield was investigated for both zoned-refined and non-zone-refined material. In the zone-refined samples the total fluorescence intensity was found to be approximately five times larger than the non-zone-refined samples. In both cases the quenching of the fluorescence begins at approximately 50 °K. We have measured an activation energy of 50± 5 meV associated with the quenching process in the non-zone-refined samples. This is in agreement with Wiegand's[6] results on similar material. However, our results are not conclusive for the zone-refined samples where the decay of the fluorescence appears to depend on sample history. The spectral shape of the fluorescence is well defined over the temperature range investigated even though the temperature dependence of the quenching of the fluorescence seems to vary with previous exposure and temperature cycling.

Photoconductivity

In principle, both free electrons and free holes can contribute to the conductivity, although in AgCl, on account of the difference in mobility, the electronic contribution dominates. Changes in the conductivity can also occur for incident photon energies less than that associated with the band gap owing to either the ionization of excitons or to ionization of electrons bound to impurities.

In AgCl, the intrinsic optical absorption is characteristic of an indirect process involving both a photon and a phonon. At low temperature, the threshold for optical absorption represents the minimum energy required for exciton formation in which the electronic transition originates from the valence-band maximum at L and a TA phonon is emitted to conserve momentum. Unless ionized, these excitons do not cause a change in the conductivity and are therefore not detected in the photoconductivity measurements.

Recent optical measurements[15] indicate that in addition to the principal valence-band maximum at L, there is a nearly degenerate subsidiary valence-band maximum at Δ (along the $\langle 100 \rangle$ direction). The absorption of light in the vicinity of the absorption edge can therefore result in the formation of two types of excitons: those associated with L and those associated with Δ. Both have been detected in the present photoconductivity study.

The photoconductivity results are shown in Fig. 3(a). The curve labeled scan 1 is the response during the first scan of the incident light with subsequent scans shown plotted above. The delay between successive scans is of the order of 10 min. It is evident that the response changes dramatically as the exposure to band-gap light increases. The peak labeled Δ exciton grows rapidly and irreversi-

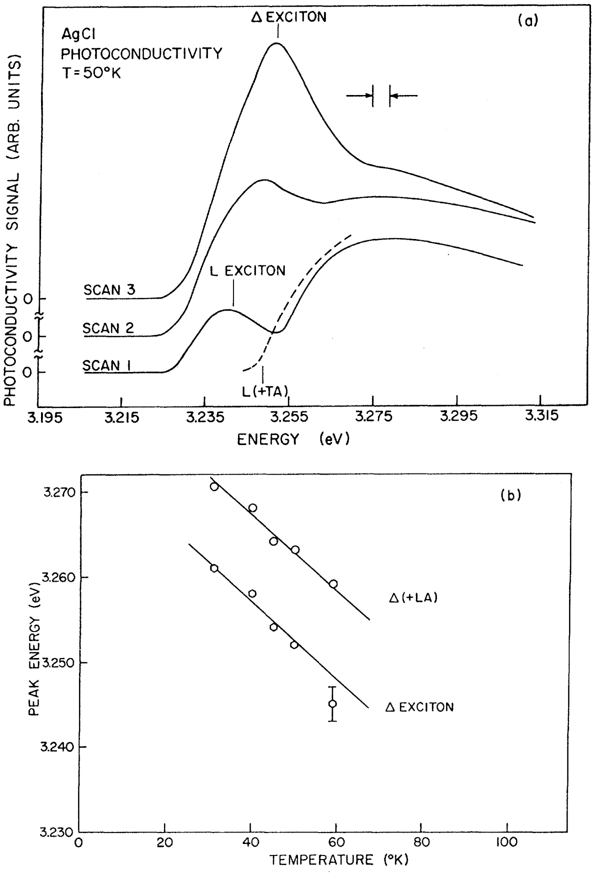

FIG. 3. (a) Photoconductivity spectrum at 50 °K for zone-refined material. The decrease of the photoconductivity signal for $E > 3.275$ eV is due to a filter that was inserted to decrease stray light. See text for details. (b) Temperature dependence of both the photoconductivity peak Δ exciton [Fig. 3(a)] and the wavelength-modulation peak Δ(+ LA) of Ref. 15.

bly until it completely dominates the spectrum. After many scans the photoconductivity response is essentially identical to that measured by Brown and co-workers.[10] Their results, however, did not show any dependence on previous exposure and were subsequently left unexplained.

The Δ-exciton peak was observed in all of the photoconductivity spectra ranging from approximately 30°K to liquid-nitrogen temperature. Owing to both the low excitation intensity and to the small probability of ionization of an exciton at low temperature, no photoconductivity signal was observed at temperatures less than approximately 30 °K. The initial response shown in scan 1 can be restored by annealing the sample in the dark at 150 °K. Upon recooling, the photoconductivity shows exactly the same behavior as for the virgin sample [scan 1 of Fig. 3(a)].

From the results of the wavelength-modulation study,[15] we are able to make the following observations: (i) the peaks labeled Δ exciton and L exciton fall at energies associated with the exciton gaps at Δ and L, respectively. (ii) The position labeled $L(+\mathrm{TA})$ corresponds to the threshold for exciton formation in which the transition originates from the valence-band maximum at L and a TA phonon is emitted. The dashed line is the predicted photoconductivity which would result from the ionization of the $L(+\mathrm{TA})$ exciton. This line shape reflects the energy dependence of the absorption coefficient associated with the indirect absorption threshold. For the case of a simple parabolic exciton band, this absorption coefficient is given by[15]

$$\alpha \propto [(E-E_0)^2+\delta^2]^{1/4}\cos\tfrac{1}{2}\theta,$$

where

$$\theta=\begin{cases}\tan^{-1}\dfrac{\delta}{E-E_0} & \text{for } E \geqslant E_0, \qquad (1)\\[2ex] \dfrac{\pi}{2}+\quad {}^{1}\dfrac{E_0-E}{\delta} & \text{for } E < E_0. \qquad (2)\end{cases}$$

In the above expressions, E is the energy of the incident light, E_0 is the threshold for optical absorption, and δ is a parameter representing both lifetime and instrumental broadening. The absorption at L can also occur with the absorption of an LA phonon, but this component has been found to be small as compared to the TA component and is therefore not observed in our data.

The temperature dependence of the Δ-exciton peak shown in Fig. 3(b) is a further indication that it is indeed associated with the valence-band maximum at Δ. The photoconductivity peak and the wavelength-modulation peak Δ(+ LA) shift rigidly together as a function of temperature with a constant separation of approximately 10 meV (the LA phonon energy at Δ). The Δ(+ LA) wavelength-modulation peak represents the threshold for exciton formation associated with the valence-band maximum at Δ in which the optical transition takes place with the emission of an LA phonon.

These results suggest that the photoconductivity peaks Δ exciton and L exciton can be ascribed to the thermal ionization of Δ and L excitons which are created by a zero-phonon process. Such a process is allowed provided the translational symmetry of the crystal is broken (e.g., by an impurity or crystal defect).

The number of photons absorbed per scan is not larger than approximately 10^{13} cm^{-3}. The growth of the Δ-exciton peak then reflects the production of photocreated defects as a result of the band gap radiation. The fact that such a small number of photocreated defects strongly influences the photoconductivity spectrum indicates that their effective radius is large. The most likely defect we can imagine is a charged center: either a self-trapped hole or a photoelectron at a deep trap. Such deep traps cannot be charged point defects otherwise they would contribute to the phononless transition during the first scan. Possible traps could be dislocations, voids, photoproduced interstitial silver, or Ag aggregates. Annealing at 150 °K presumably either frees the electron that can then seek a self-trapped hole with which to recombine or it frees the self-trapped hole which then migrates to the trapped electron and recombines.

The symmetry properties of the band structure can be used to explain qualitatively the relative magnitudes of the zero-phonon transitions associated with the Δ and L excitons. At the point Δ of the Brillouin zone, the hole wave function has Δ_1 (C_{4v}) symmetry, whereas at the point L the valence band has L_3^- (D_{3d}) symmetry. From group-theoretical arguments,[16-18] it can be shown that the s-like exciton wave function composed of Δ_1 hole states and Γ_1^+ electron states transforms as $(\Gamma_1^+ + \Gamma_3^+ + \Gamma_4^-)$ of $\bar{O}_h$. The basis function of the Γ_1^+ $(\bar{O}_h)$ representation has a nonzero amplitude at the origin of coordinates (i.e., at the defect). In contrast, the s-like exciton wave function comprised of L_3^- hole states and Γ_1^+ electron states, transforms as $(\Gamma_3^- + \Gamma_4 + \Gamma_5^-)$ of $\bar{O}_h$. Each of these three representations has basis functions which have zero amplitude at the origin. On this basis alone, we expect a larger interaction between defects and Δ excitons, than between defects and L excitons, thus the zero-phonon line associated with Δ should be more intense than that associated with L.

We have assigned the shoulder which begins to appear near the position labeled $L(+\mathrm{TA})$ in scan 1 to the thermal ionization of the L exciton which is produced with the emission of a TA phonon. This assignment is supported by the shape of the shoulder, as discussed earlier, as well as its position.

A decrease in the photoconductivity signal was observed when the sample was irradiated simultaneously with infrared $(1 < \lambda < 2.5\,\mu\mathrm{m})$ and band-gap radiation. On account of the experimental setup this decrease may reflect an increase of the decay time of the photoconductivity without a corresponding decrease in the total number of carriers. If this decay time becomes very large, as compared to the chopping period associated with the incident band-gap radiation, then the observed change in the conductivity will be decreased. This was verified by the observation of a decrease in the photoconductivity when the chopping frequency was increased from 80 to 225 Hz. The direct change of the dc conductivity was too small to be detected. A possible mechanism could be the ionization of deeply trapped electrons whose lifetime is of the order of 10 msec.

CONCLUSION

Several important conclusions can be drawn from the results of this study. In the case of the photoluminescence, we have observed no dependence of the fluorescence on the energy of the excitation radiation implying that the self-trapping and subsequent exciton recombination processes are extremely efficient at low temperature. We have shown that the center of gravity of the fluorescence shifts rather abruptly in the vicinity of 40 °K and that simultaneously the second moment associated with these spectra decreases. This observation implies that the intrinsic fluorescence is composed of at least two components with different activation energies. Recent EPR measurements[19] indicate the existence of two types of excitons: isolated self-trapped excitons localized on a Cl^- ion and electrons trapped in the vicinity of a self-trapped hole localized on a Ag^+ ion. Several types of these impurity-associated excitons exist. Thermal ionization of isolated STE provides electrons that may be trapped by defects that are in the vicinity thus giving rise to an electron trapped near a self-trapped hole. Further evidence for the thermal ionization of excitons is the growth of the photoconductivity signal with temperature, the dependence of the photoconductivity signal with temperature, the dependence of the photoconductivity signal on previous illumination, and the possibility of regeneration of the virgin sample by appropriate annealing near 150 °K in the dark.

The structure observed in the photoconductivity spectrum has been correlated with the optical-absorption spectrum and confirms the identification of a subsidiary valence-band maximum. The most striking feature of the photoconductivity spectra is the rapid growth of the Δ-exciton peak resulting from photoproduced disorder. Both a zero-phonon and a one-phonon component have been identified for the transitions associated with L.

Finally, for the non-zone-refined material we have measured an activation energy of 50 ± 5 meV associated with the quenching of the fluorescence, while for the zone-refined samples this quenching appears to depend in part on previous exposure. Accordingly, we speculate that the decay kinetics of the fluorescence may be determined in part by unfilled deep traps which exist in both types of material. The number of such traps is expected to be at least two orders of magnitude smaller in the zone-refined material than in the non-zone-refined material. Upon illumination a certain portion of these traps are filled and can no longer contribute to the decay kinetics. The number of empty traps that remain will be smaller for the zone-refined material and will strongly depend on previous illumination. Instead, in the non-zone-refined material, many more traps remain unfilled during the experiment with the available light intensity. As a result there is always a large number of empty traps to contribute to the decay kinetics. On this basis we would expect the decay of the fluorescence to depend more strongly on previous history for the zone-refined material than for the non-zone-refined material. Details of the difference of the fluorescence decay for the two types of material are still not completely understood and presently are under further investigation.

The authors are grateful to Dr. C. L. Marquardt for showing us Ref. 19 prior to publication.

---

*Supported in part by NSF Grant No. GH-41524 and MRL Program Grant No. DMR72-02018A03.

[1] F. Moser, R. S. Van Heynigen, and S. Lyu, Solid State Commun. 7, 1609 (1969).

[2] H. Kanzaki and S. Sakuragi, Solid State Commun. 9, 1667 (1971).

[3] C. L. Marquardt, R. T. Williams, and M. N. Kabler, Solid State Commun. 9, 2285 (1971).

[4] W. Ulrici, Phys. Status Solidi 40, 557 (1970).

[5] H. Kanzaki and S. Sakuragi, Technical Report No. 514 (University of Tokyo, Tokyo, Japan, 1972).

[6] D. Wiegand, Phys. Rev. 113, 52 (1958).

[7] R. S. Van Heyningen and F. C. Brown, Phys. Rev. 111, 462 (1958).

[8] G. C. Smith, Phys. Rev. 140, A221 (1965).

[9] R. S. Van Heyningen, Phys. Rev. 128, 2112 (1962).

[10] F. C. Brown, T. Masumi and H. H. Tippins, J. Phys. Chem. Solids 22, 101 (1961).

[11] K. Vacek, R. Levy, A. Bivas, A. Mysyrowicz, and S. Nikitine, Czech. J. Phys. B 19, 771 (1969).

[12] A. M. Gordon, Phys. Rev. 122, 748 (1961).

[13] G. C. Farnell, P. C. Burton, and R. Hallama, Philos. Mag. 41, 157 (1950).

[14] R. B. Laibowitz and H. S. Sack, Phys. Status Solidi. 17, 353 (1966).

[15] R. H. Stulen and G. Ascarelli, Phys. Rev. B 13, 5501 (1976).

[16] A. K. Ramdas, P. M. Lee, and P. Fisher, Phys. Lett. 7, 99 (1963).

[17] G. Ascarelli, Phys. Rev. 179, 797 (1969).

[18] T. N. Morgan, Phys. Rev. Lett. 21, 819 (1968).

[19] K. Murayama, K. Morigaki, S. Sakuragi, and H. Kanzaki, in *Proceedings of the Fifth International Conference on Luminescence*, Tokyo, edited by S. Sugano (North-Holland, Amsterdam, 1976).