Thermoreflectance in Ammonium Halides

E. Rieflin, G. Stühmer, and E. Schwab
Fakultät für Physik der Universität Freiburg i. Br., Germany

(Z. Naturforsch. **31 a**, 1333 – 1335 [1976]; received August 16, 1976)

Thermoreflectance spectra of NH_4I at 240 K, NH_4Br at 93 K and NH_4Cl at 160 K are measured. By a Kramers-Kronig analysis the differential optical dielectric constants are calculated to determine band energies and their differential temperature behaviour. The spectra are compared with the excitonic spectra of the alkali halides, and the bands in NH_4I are tentatively interpreted by analogy.

The ultraviolet absorption and reflection spectra of the ammonium halides closely resemble those of the alkali halides and are similarly interpreted [1–3]. Transitions from the spin-orbit split p-like valence band to s-like and d-like conduction bands are found in the energy region up to 10 eV and are related to the Γ, X and L points of the Brillouin zone in the case of NaCl structure. In the case of CsCl structure the d-like conduction band is strongly split and the transitions are related to Γ, X and M points. The low energy region of the spectra is sharply structured by the occurrence of strong exciton bands below the direct band gap at the Γ point.

The large temperature shift of these exciton bands is fundamental for the thermoreflectance measurements in alkali halides [4] and for the measurements given here for ammonium halides. Because dominant line broadening effects were not observed, our spectra can be correlated piece-wise with the energy derivation of the spectra obtained from reflectivity. This seems especially useful for the calculated spectra of the differential complex optical dielectric constant. These spectra, as transformed by the thermoreflectance through Kramers-Kronig analysis, are presented together with the thermoreflectance in Figures 2 – 4. Moreover, in Fig. 1, we compare the imaginary part of the optical dielectric constant with its corresponding temperature derivation integrated over the energy. Such a comparison, too, is reasonable only for dominating line shift phenomena.

The apparatus is similar to that described by Nosenzo et al. [4]; details are given elsewhere [5]. The above mentioned Kramers-Kronig analysis of a thermoreflectance spectrum needs the Kramers-Kronig transformation of the corresponding reflection spectrum, which was measured immediatly before and after the thermoreflectance measurement under the same conditions.

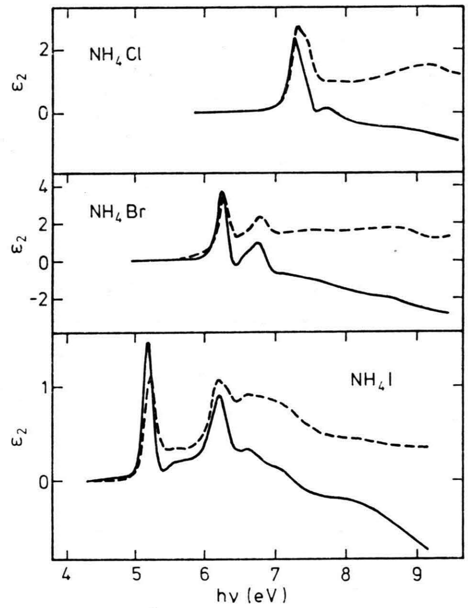

Fig. 1. Imaginary part of the optical dielectric constant (broken curve) and the corresponding integrated differential dielectric constant (full curve) as calculated from the data of Figures 2 – 4.

The strong temperature dependence of the band gap energy isolates the exciton doublet together with the following step-like structures from the background, as is shown in the synoptical Figure 1. In NH_4I, as measured in the NaCl structure at 240 K, the exciton bands have a very symmetrical shape in the full curve. In NH_4Br however, as measured at 93 K in phase III originating from a CsCl structure, the second component of the exciton doublet exhibits a shoulder very similar to NaBr, where such

Reprint requests to Dr. G. Stühmer, Hofmatt-Str. 13, *D-7800 Freiburg-Opfingen.*

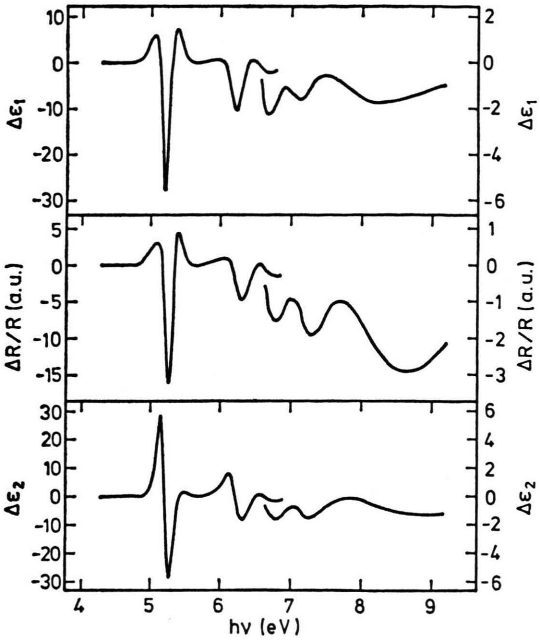

Fig. 2. Thermoreflectance of NH_4I at 240 K and the real and imaginary part of the differential optical dielectric constant.

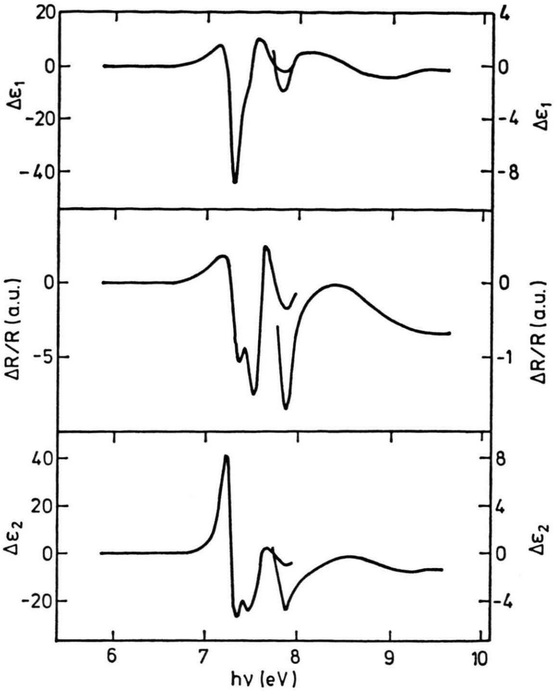

Fig. 4. Thermoreflectance of NH_4Cl at 160 K and the real and imaginary part of the differential optical dielectric constant.

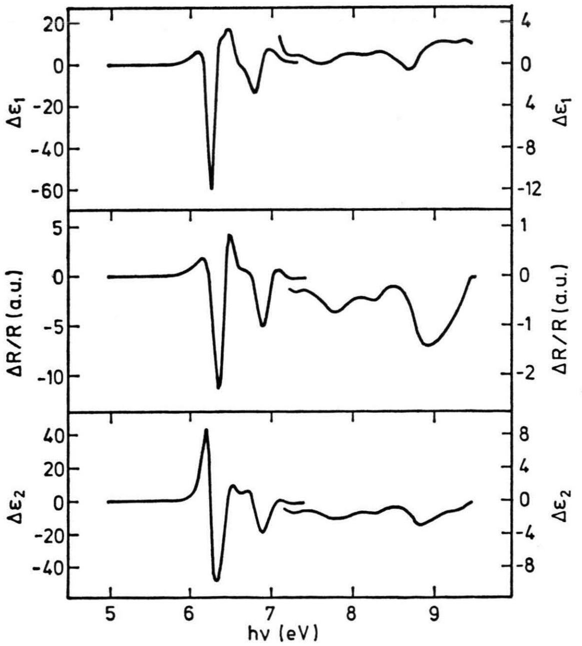

Fig. 3. Thermoreflectance of NH_4Br at 93 K and the real and imaginary part of the differential optical dielectric constant.

a deformation of the exciton bands has been explained by the Fano effect[6]. The step-like structures which follow the exciton bands after about 0.2 eV in NH_4I and NH_4Br are due to a quasicontinuum starting with the $n = 2$ exciton[7]. In NH_4Cl, as measured in the CsCl structure-like phase IV at 160 K, the steps would follow after about 0.3 eV, but this structure at 7.7 eV may also be interpreted as a band and then the distance would be about 0.4 eV. In the high energy part the full curves of Fig. 1 have a drift, which is a consequence of a constant negative contribution to the thermoreflectance in this region. This contribution, which is outside of experimental error, is not understood at present.

The very correspondence of the spectra of ammonium halides to the sodium halides, which seems remarkable because of the structural differences, allows one to interpret most bands of NH_4I on the basis of the results of Kunz[8]. Accordingly the pair of bands at 7.14 eV and 8.24 eV – separated by approximately the spin-orbit splitting energy of the valence band – may be related to X-point transitions, and the band at 6.66 eV to L-point transitions. The temperature shift of their energies has the same sign as that of the gap, in contrast to the band at 7.48 eV, which shifts with the opposite sign. Due to this one cannot interpret it in the same manner. In NH_4Br there are bands at 7.62 eV and 8.72 eV shifting parallely with the gap, and bands at 8.35 eV and 9.38 eV shifting oppositely. The peak at 8.72 eV may tentatively be correlated to X-point transitions. NH_4Cl has a peak at 8.92 eV shifting parallely with the gap.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. The calculations for the Kramers-Kronig analysis were performed in the Rechenzentrum der Universität Freiburg. The plotting work was carried out at the facilities of the Rechenzentrum der Universität Karlsruhe with the aid of Dipl.-Ing. J. Katerbau, whom we gratefully acknowledge.

[1] P. Brauer, N. Aberle, and M. Knothe, Z. Naturforsch. **22 a**, 2059 [1967].

[2] H. Yamashita, J. Phys. Soc. Japan **29**, 1391 [1970].

[3] G. Stühmer and E. Rieflin, J. Phys. **C 6**, L 329 [1973].

[4] L. Nosenzo, E. Regazzoni, and G. Samoggia, Phys. Rev. Lett. **28**, 1388 [1972].

[5] E. Rieflin, G. Stühmer, and E. Schwab, to be published in Opt. Commun.

[6] Y. Onodera, Phys. Rev. **B 4**, 2751 [1971].

[7] D. Fröhlich and B. Staginnus, Phys. Rev. Lett. **19**, 496 [1967].

[8] A. B. Kunz, Phys. Rev. **180**, 934 [1969].