Properties of Cold Condensed Metal Chloride and of Cocondensed Metal/Metal Chloride Films
II. Raman Spectra

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Z. Naturforsch. **43a,** 481–484 (1988); received January 28, 1988

We report on Raman spectroscopic investigations with cold condensed films of silver chloride, thallium chloride, and sodium chloride in the absence and in the presence of cocondensed metal. With films of 1000 nm – 2000 nm thickness, Raman signals only can be seen if small silver particles are present. These are either cocondensed particles or they are formed by photolysis of silver chloride. At low temperatures, noncrystalline films can absorb light from the exciting laser, while at room temperature also crystalline silver chloride can be photolyzed by the argon ion laser.

The signals are interpreted as surface enhanced Raman transitions of a chloride – silver vibration. No indications for the presence of silver chloride or thallium chloride molecules can be found from the spectra.

1. Introduction

Already some decades ago, the structure of cold condensed metal halide films was of considerable interest for solid state physicists. 1956 Rühl investigated the x-ray diffraction properties of halide films, condensed onto substrates which were cooled by liquid helium [1, 2]. He found, that alkali halide films gave rise to diffraction patterns typical for more or less non-ideal crystals. Films from the less ionic substances CuI, AgI, and TlCl, on the other hand, were x-ray amorphous.

1954 Fischer reported UV/VIS spectra of cold condensed metal halide films [3]. Alkali halides give rise to spectra which resemble those of normally grown crystals, they contain exciton bands and sharp absorption edges. The edges are red shifted and the exciton bands slightly broadened. In contrast, comparison of the UV spectra of amorphous thallium chloride with those of crystalline material displays marked differences: the amorphous TlCl film showed a blue shifted absorption, the lowest energy exciton absorption is absolutely absent and the short wavelength exciton bands are strongly broadened.

In two recent papers [4, 5] we reported on UV/VIS spectroscopic investigations of cold condensed halide films with and without cocondensed metal. From the spectra we came to the conclusion that silver-, copper-, and thallium halide films can be condensed as noncrystalline solids. Cocondensed metal is not atomically dispersed but forms only small, colloidal particles in the glassy matrix. Upon annealing of the films above a critical temperature the glass crystallizes and the colloidal metal particles form larger aggregates.

The present study is aimed at finding by Raman spectroscopy, whether molecular species are present in the cold condensed films. While the previous results indicate an ionic state of the glassy solid, the presence of undissociated molecules could not yet be satisfactorily be ruled out.

2. Experimental

The experimental set-up is described in detail in [4]. A Raman spectrometer LRT 800 from Coderg was used. Raman signals were excited by the 514.5 nm emission from an argon ion laser (Spectra Physics) with a maximum power of 0.6 Watt. In order to suppress plasma bands from the laser emission, a double monochromator from Burleigh Instruments was placed between laser and specimen.

The preparation of films suitable for Raman investigations posed a non-trivial problem: In order to obtain non-crystalline films, the evaporation rate has to be kept below about 1 nm/min [4]. For sensitivity rea-

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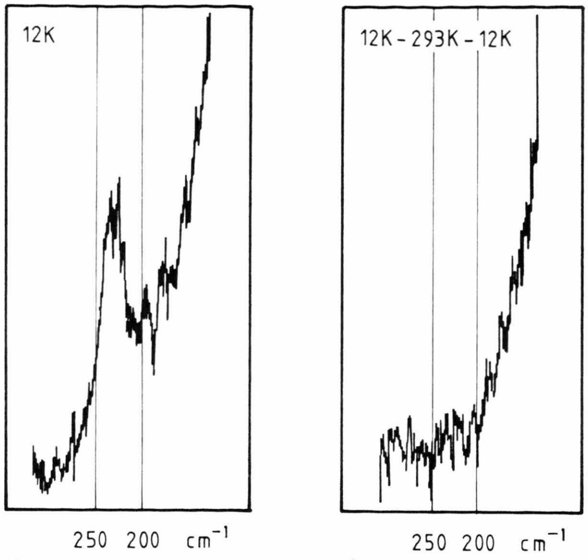
sons, on the other hand, thicknesses above 2000 nm are desirable. Hence the evaporation conditions had to be stable for periods of more than 30 hours. Even when this condition was satisfied, in most cases the films became very inhomogeneous and parts of them flaked off. As a compromise we worked with films the thickness of which never exceeded 2000 nm. In order to compensate for the low sensitivities in these cases, the entrance slit of the spectrometer had to be adjusted at ≈ 800 µm. This led to a relatively poor resolution. The films were condensed on LiF windows, the evaporation angle was 45°.

3. Results and Discussion

No Raman scattering could be observed from freshly prepared, cold condensed silver chloride films. After some time of irradiation with the laser light, a Raman signal appeared at 240 cm^{-1}. Figure 1 gives a typical example of this signal. The same signal can be observed when a cold condensed film is annealed and afterwards investigated at 293 K. It also appears when a film, which was prepared at room temperature is irradiated at room temperature. No signals appear when crystalline films are irradiated at 12 K. Figure 2 demonstrates that the signal from crystalline films, investigated at room temperature is relatively strong; even the anti-Stokes-scattering can be detected at the same spot of the film.

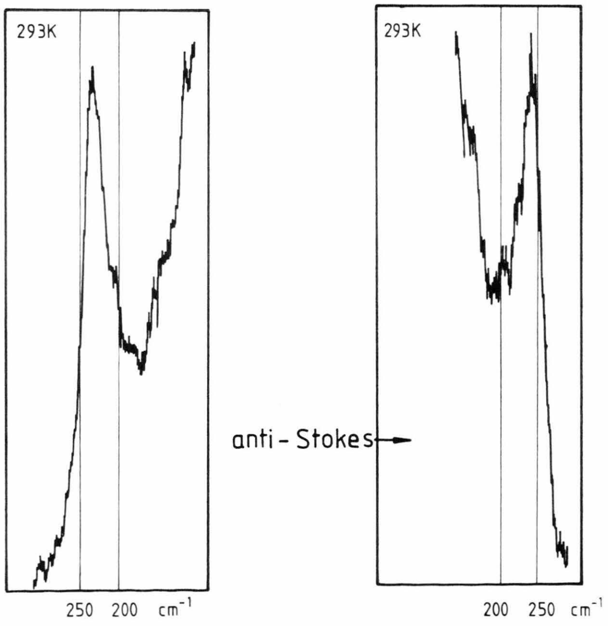
Non-crystalline films at low temperatures and crystalline films at room temperature both have their UV absorption bands extending into the visible regime. Laser light can therefore be absorbed, and it seems possible that small silver particles are formed photolytically. Then the observed signal can be interpreted as the surface enhanced Raman scattering of Cl-ions, adsorbed on the particles. Macomber and Furtak [6] and Barz et al. [7] observed the same signal on electrochemically roughened silver electrodes. Visual inspection of the films for which Raman activity was observed, clearly shows that dark spots were formed at the locations where the laser beam was passing the films.

When silver chloride is cocondensed with silver, a Raman signal can be observed immediately. It is relatively broad and is centered around 195 cm^{-1}, see Figure 3. It also appears when silver is cocondensed with sodium halide and when thallium is cocondensed with silver chloride. All results are summarized in



a) b)

Fig. 1. a) Raman signal from a silver chloride film, prepared and investigated at 12 K. This signal appears after some minutes of irradiation with the green light of an argon ion laser. b) Same part of the spectrum with a film which was annealed at 293 K prior to the Raman experiments.



a) b)

Fig. 2. a) Raman signal from a crystalline silver chloride film. The signal appears after some seconds of irradiation of the film at 293 K. b) Anti-Stokes signal of the same band. To obtain the anti-Stokes signal, the sensitivity of the spectrometer was increased by a factor of 6.

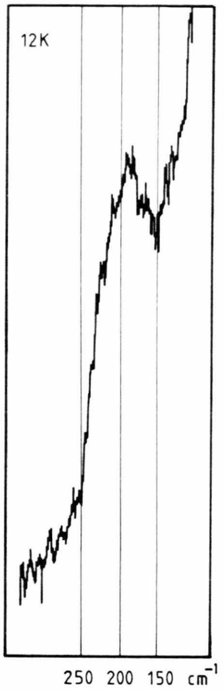
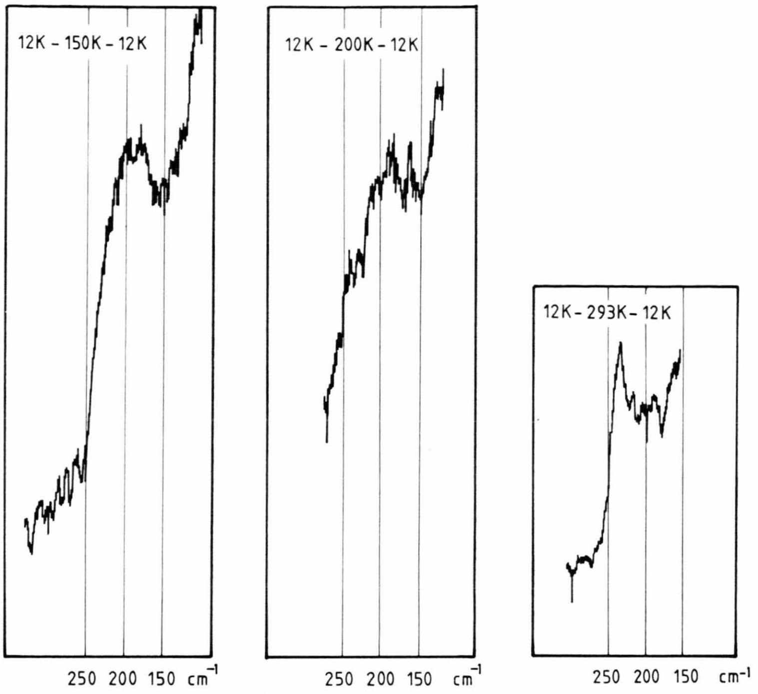


Fig. 3. Raman signal from a cocondensed silver/silver chloride film. $n_{Ag}/n_{AgCl} = 1/4$. The film was prepared and investigated at 12 K.



a) b) c)

Fig. 4. Raman signal from a cocondensed silver/silver chloride film. $n_{Ag}/n_{AgCl} = 1/4$. The films were prepared and investigated at 12 K. Annealing temperature: a) 150 K, b) 200 K, c) 293 K.

Table 1. Collection of Raman signals.

T_p /T_a /T_R	AgCl	TlCl	Ag/AgCl	Ag/ NaCl	Tl/ AgCl	Tl/ NaCl
12/ 12/ 12	$\underline{240}$	ns	195	195	195	ns
12/200/ 12	ns	ns	195 (240)	195	195	ns
12/293/ 12	ns	ns	240	240	240	ns
12/150/150			240			
12/293/293	$\underline{240}$		240	240	240	ns
293/ / 12	ns		240	ns		
293/ /293	$\underline{240}$		240	ns		

T_p temperature of film preparation.
T_a annealing temperature.
T_R temperature at which the signal was measured.
Temperatures are given in K and band positions in cm^{-1}; the signal given in brackets was very weak.

Table 1. Underlined wave numbers indicate signals which appear only after some time of irradiation, while the other bands can be seen without an induction period. ns indicates that no signal was found; no entry at all means that no experiments were made under the respective conditions.

From the fact that the band at 195 cm^{-1} appears when silver is cocondensed with either AgCl or NaCl we draw the conclusion that the presence of colloidal silver is a necessary prerequisite for its appearance. Its presence in the case of thallium cocondensed with silver chloride supports the assumption that during the growth of the film colloidal silver is formed by the reaction

$$\mathrm{Tl} + \mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{TlCl},$$

as was proposed in [5]. The signal at 195 cm^{-1} is only present when the films are prepared at low temperatures, and it transforms into the well known signal at 240 cm^{-1} at annealing temperatures >150 K. The series of Figs. 4a–4c shows that this transformation occurs gradually. The broadness of the 195 cm^{-1} signal indicates, that several different vibrations contribute to this signal. If one assumes that for very small silver particles the wavelength of the vibration of chemisorbed chloride ions depends on the particle size, a simple interpretation offers itself: At low temperatures, very small particles with a broad size distribution are formed. Above 150 K large particles can grow at the expense of the smaller ones. Therefore the Raman scattering at 240 cm^{-1}, the high wavenumber limit of the broad signal, increases, while the intensity at the band center around 195 cm^{-1} decreases. Nevertheless, one should clearly state that this interpretation is only tentative and should be verified independently.

Conclusions

The absence of Raman signals from freshly prepared silver chloride and thallium chloride films clearly demonstrates that these films do not consist of undissociated molecules. The partial or complete absence of exciton bands in the UV spectra of the cold condensed halides, on the other hand, indicates a non-crystalline structure of these films. The assumption, mentioned in [5], that these films are ionic glasses, is therefore corroborated by the Raman experiments.

In accord with other reports [6], we find that green laser light (514.5 nm) can photolyze silver chloride. This happens when and only when the light can be absorbed by the halide. This is the case for crystalline silver chloride at room temperature and for non-crystalline silver chloride at temperatures below the transition temperature ionic glass/crystal.

Silver particles in halide matrices are able to enhance Raman scattering. They possess this property when they are formed photolytically or by cocondensation of the metal. Our experiments give strong evidence for a size dependence of the frequency of the vibration of chemisorbed chloride ions.

Acknowledgements

This work was sponsored by the Deutsche Forschungsgemeinschaft. Further thanks are due to the Fonds der Chemischen Industrie for financial assistance and to Prof. Alarich Weiss, who placed the Raman spectrometer at our disposal. The Vereinigung von Freunden der Technischen Hochschule Darmstadt generously donated the monochromator used in this study.

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