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The Change of the Absorption Spectrum of Copper Chloride Containing an Excess of Copper Under the Action of Water Vapor

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When water vapor acts on copper chloride films sublimed in vacuum and containing an excess of copper their color vanishes. In the absorption spectrum the sharp maxima due to the excess copper at 3725 A° and 3780 A° are replaced by a broad maximum at 3900 A°. Near 2800 A° a new maximum appears and disappears with time. It is shown that the absorption of the excess copper particles in the surface layers differs from the absorption of the copper particles in the interior layers of the crystal.

COLOR of a yellow or brown tint of copper chloride films sublimed in vacuum quickly fades when the films contact moist air. Carefully dried air in no way affects the color of the films. In the present work the influence of water vapor on the absorption spectrum of copper chloride films sublimed in vacuum and containing an excess of copper has been investigated. Use is made of the gradual change of the absorption spectrum upon the adsorption of water vapor by the films to obtain a separation of the absorption spectrum of the excess copper in the surface layers and the absorption spectrum of the excess copper in the inner layers of the crystal.

The films of copper chloride containing an excess of copper were obtained by sublimation in a vacuum. The compounds used were either cuprous chloride or anhydrous cupric chloride. All experiments were carried out at constant temperature. In Fig. 1 the change in the spectrum of one of the samples is shown in the region of the absorption band due to a stoichiometric excess of copper. Curve 1 is the absorption of the film before the admission of water vapor. In the curve are the sharp maxima characteristic of the excess copper 3720 A (unresolved doublet) and 3810 A. The film is yellow. Curve 2 is the absorption 10 minutes after the admission of the water vapor. The film has faded. Curve 3 was obtained after the water vapor had acted 3 hours on the film, while curve 4 was obtained after the water vapor had acted 50 hours on the film. From the figure we see that the sharp maxima due to the excess copper gradually disappear and are replaced by a broad diffuse maximum from 3880 to 3900 A. Upon removing the adsorbed water, by heating and pumping, the film again becomes yellow (dotted Curve 5). However the original absorption spectrum of the film is not reestablished. Upon proceeding still further, the broad maximum increases and is shifted toward the short wavelength side. The appearance of this broad maximum indicates a transition of the particles of excess copper to new energy states. This transition does not correspond to the transition of excess copper in the colloidal state because the absorption maximum of colloidal particles of copper is found in the visible region.

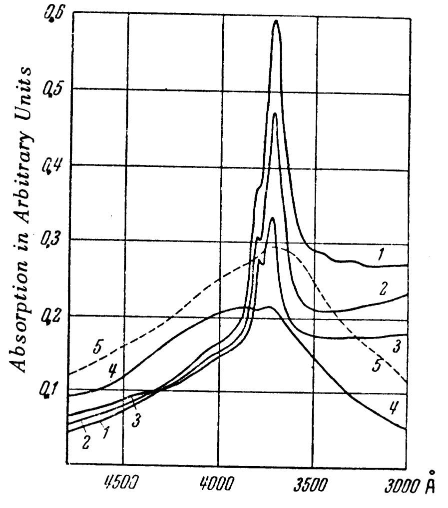

FIG. 1

The time for the complete disappearance of the characteristic absorption band of the excess copper particles under the action of water vapor on the film of copper chloride depends upon the structure and thickness of the film.

In addition to the change of the characteristic band in the absorption spectrum of the film which is acted upon by water vapor, a new strong absorption maximum appears from 2750 to 2800 A. In Fig. 2 is shown the absorption of one of the samples before the admission of water vapor (Curve 1) and 10 minutes after the admission of water vapor into the reaction chamber (Curve 2). Upon the admission of water vapor the sharp intense maximum at 3730 A weakens, and there is a new maximum at 2800A. Curve 3 is the absorption spectrum 5 hours after the admission of the water vapor. Not only has the

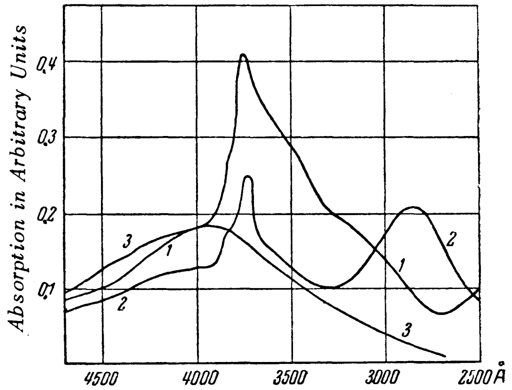

FIG.2

absorption band of the excess copper disappeared but also the new maximum. The final absorption spectrum, as has already been noted above, consists of one diffuse band with a maximum at 3900 A . The water adsorbed by the surface layers is bound very loosely. A film whitened by the adsorption of water vapor becomes yellow again upon heating it up to 36 to 40°C. If the water which was separated by heating is not withdrawn upon cooling the film to room temperature, the film again whitens as a result of the interaction with water vapor. The experiment can be repeated many times with similar changes in color of the film.

Under the action of water vapor on the film of copper chloride the first change in the absorption spectrum is the disappearance of the absorption of the excess copper particles found in the surface layers and not in the interior of the crystal. In the first stages of this process the absorption band of the excess copper is observed merely to decrease in absorption. The newly formed maximum near 3900 A appears only after the water vaporhas acted upon the film for a long time. The disappearance of the absorbing light centers in the surface layers of the salt crystals is caused by the penetration of the water molecules into the crystal and is not accompanied by the formation of new surfaces, since the copper particles distributed within the crystal do not occupy levels characteristic of the surface layers. By making use of this situationit is possible to obtain separately spectra of the absorbing particles of excess copper (atoms or ions) located in the surface layers and the spectrum of the absorbing particles found in the interior of the crystal. If the absorption curve obtained a short time after water vapor is admitted to the apparatus is subtracted from the initial absorption curve of a given sample, the resulting difference will give the absorption spectrum of the copper particles of the surfaces. If differences between the absorption curves obtained after more or less extended times of action of the water vapor on the film are taken they will be characteristic of the absorption spectrum of the particles of excess copper within the crystal. In Fig. 3 is an example of two difference curves pertaining to the sample whose absorption was given in Fig. 1. Curve 1 in Fig. 3 is the difference between Curve 1 in Fig. 1 corresponding to the initial absorption of the sample and Curve 2 of the same sample which was obtained 10 minutes after the admission of the water vapor. The curve is a wide band with a diffuse shape on the short wavelength side and a maximum at 3620 to 3630 A . On the long wavelenth side of this band is an adjoining weak band at 3720 A . In the case of other samples the difference curves have a similar form. In the difference curves of certain samples the band at 3725 A is even less apparent than in Fig. 3. The position of the maximum of the wide band varies for different samples and lies between 3580 and 3630 A. The dotted Curve 2 of Fig. 3 was obtained by subtracting Curve 3 in Fig. 1, which corresponds to the absorption after the water vapor has acted on the film for 3 hours, from Curve 2 in this same figure. This curve is due to the absorption of the particles of excess copper found in the interior of the salt crystal and has the form of a narrow symmetric band. Judging by the form of similar difference bands we can conclude that the particles of excess copper (atoms or ions) located inside the crystal give a sharp narrow band in the absorption spectrum and particles located in the surface layers of the crystal give a wide band which is diffuse on the short wavelength side. It is interesting that in general the absorption spectra of vacuum sublimed films of the halogen series of salts with a stoichiometric excess of metal often have the form of either a

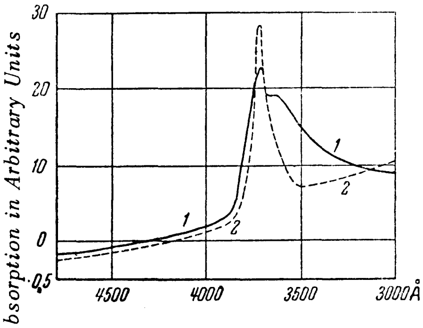

FIG.3

single band that is diffuse on the short wavelength side or the form of a continuous absorption with a sharp long wavelength cutoff, the position of the long wave length band depends upon the excess metal.[1] This indicates that the surface layers play a significant role in the total absorption of sublimed films of salt.

With regard to the strong absorption maximum at 2800 A upon the adsorption of water, we can definitely say only that is is connected with the presence of particles of excess copper in the surface layers of the salt crystal. This maximum is usually as intense as the intensity of the diffuse absorption on the short wavelength of the band of the excess copper at 3725 A in the original spectrum of the sample as is due to the copper particles located in the surface layers of the crystal. The disappearane of the maximum at 2800 A after a lengthy action of water vapor is connected with a general change in the structure of the film which also brings about the replacement of the clear maximum of the excess copper at 3790 and 3725 A by a diffuse maximum at 3900 A . If a small amount of water vapor is admitted to the reaction apparatus and the vapor inlet then closed, a maximum at 2800 A which appears remains longer. It is possible to believe that this maximum is connected with complex bonds of the copper. The tendency of the cations of heavymetals to associate with different anions is known.

Because of the incomplete thermal dissociation upon heating, the sublimed films of copper chloride contain the impurity cupric chloride. Upon the adsorption of water vapor on these films the transformation to chlorine ions from hhe solution of cuprous chloride impurity is possible. The chlorine can transform to polyhalide complexes of various compounds with CuCl, $CuCl_2$ or ions of excess copper.

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[1] P. N. Kokhanenko, J. Exper. Theoret. Phys. USSR 26, 120(1954).

Translated by F. P. Dickey
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