

Absorption Spectrum of Excess Silver in the Low Temperature and High Temperature Modifications of Silver Iodide

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(Submitted to JETP editor July 8, 1954)

J. Exper. Theoret. Phys. USSR **29**, 676-679 (November, 1955)

It is demonstrated that maxima at 4290 and 3340 Å in the absorption spectrum of AgI, which are due to atoms or ions of excess silver, disappear when the AgI is transformed into the high temperature modification, and reappear during the reverse transformation into the low temperature modification. The presence of excess silver increases the transition temperature of one modification of AgI into the other by 5-15° C.

THE connection between the absorption spectra of atoms or ions of excess metals distributed in sublimated films of the haloid salts and the type of lattice typical of the salt has been previously demonstrated^{1,2}. It was thought interesting to determine how the absorption of the excess metal in any particular polymorphous substance would change when the substance was transformed from one modification to another. In this instance, the change in the lattice structure of the basic substance will take place under conditions of unvarying concentration and distribution of the diffused particles of excess metal.

A convenient object for investigation is silver iodide with a stoichiometric excess of silver. The excess silver (atoms or ions) in the absorption spectrum of sublimated AgI films produces sharp and strong maxima at 4290 and 3340 Å. The transformation of the low temperature modification of AgI into the high temperature modification takes place at a relatively low temperature, i.e., at 145.8° C. These modifications, as is well known, are enantiotropic, and when cooled to less than 145.8° C the high temperature modification re-transforms into the low temperature modification. The low temperature modification of AgI has a lattice of the wurtzite type. In the high temperature modification only the iodine lattice remains solid (cubic volume-centered), while the ions of silver distribute themselves statistically among all the positions possible to them, moving freely within the iodine lattice.

Sublimated AgI films with an adequate content of excess silver were obtained by the Shalimova³

method of vacuum sublimation. The quartz test-glass with flat walls, on one of which the salt film was deposited, was placed in a special oven, and the absorption spectra were photographed at various film temperatures, using transmitted light. A hydrogen gas tube was used as the light source. The temperature of that portion of the wall of the test glass on which the illuminated portion of the salt film was located was measured with the aid of a thermocouple. The absorption spectra were recorded at intervals of 15-20° C while the films were being heated from room temperature to 170-180° C, and while they were being re-cooled to room temperature. Before each recording, the required temperature of the film was determined, and the film was maintained at this temperature for thirty minutes. The spectra were photographed by means of a quartz spectrograph having low dispersion. In all, 11 sublimated AgI films were prepared and investigated. In the spectra of several of the films, the excess silver maximum at 3340 Å was poorly delineated, and the spectra of such films were investigated photometrically only in the region of the intensive maximum at 4290 Å. For this reason the data given below refer only to that portion of the spectrum in which the maximum at 4290 Å occurs, which was intensive in the spectra of all the investigated films. In those cases in which the maximum at 3340 Å was clearly defined, as measurements demonstrated, its behavior with change in temperature of the film and transformation of one modification into the other differs in no way from the behavior of the maximum at 4290 Å.

Upon increasing the temperature of the AgI films, the change in the absorption spectrum proceeds in two directions. On the one hand, the excess silver absorption maximum is continuously displaced in the direction of the long waves, becomes broader, and the height of the maximum is reduced. On the other hand, the general level of absorption is at first reduced, and beginning at 120-130° C, again becomes stronger. The excess

¹ K. V. Shalimova, *Photoluminescence of sublimated phosphors*, Avtoreferat, Inst. of Phys., Acad. Sci., Moscow, 1952.

² P. N. Kokhanenko and V. D. Gol'tsov, *Dokl. Akad. Nauk SSSR* **85**, 543 (1952); P. N. Kokhanenko, *J. Exper. Theoret. Phys. USSR* **26**, 120 (1954).

³ K. V. Shalimova and A. V. Byelkina, *J. Exper. Theoret. Phys. USSR* **21**, 326 (1951).

silver absorption band, despite a certain amount of indefiniteness, remains adequately intensive and clear up to the point of transition of the AgI from the low temperature to the high temperature modification. Upon transformation of the AgI into the high temperature modification, the excess silver absorption band disappears and no other new bands appear in the investigated portion of the spectrum. The transition temperature, judging from the spectra, is different for different samples, and lies between 150 and 160° C, i.e., is 5-15° C higher than the transition temperature of one modification into the other in the case of the pure AgI salt (145.8° C). The disappearance of the band itself takes place over a temperature interval of 10-15° C. When the films are cooled below the transition temperature, the excess silver absorption band reappears at the same point and with the same intensity. The selective reflection from the short wave side of the band is somewhat intensified. Figure 1 presents the absorption curves for one of the AgI samples. The broken curve 1 shows the absorption at room temperature before heating of the film; curve 2 is the lowermost absorption curve, corresponding to 127° C. To assure clarity of the sketch, not all of the intermediate curves are drawn. Upon further heating, the general level of absorption again increases and the absorption curves rise above curve 2. Curve 3 is the absorption curve at 146° C; the excess silver absorption maximum is clearly defined on the curve. Curve 4 is recorded at a 10° higher level, at 156°; the maximum has disappeared and only an insignificant bulge is noticeable in its place. Curve 5 shows the absorption at 170°; there is not a trace of a maximum on the curve. Curve 6 shows the absorption at room temperature after solidification of the film; an intense excess silver maximum has again appeared on the curve, which is somewhat less symmetrical as a result of the intensification of the selective reflection from the short wave end of the band.

Analogous results were also obtained with other specimens. A somewhat different course of change in absorption was observed in only one of the samples, the absorption curves of which are presented in Fig. 2. The intermediate curves are not shown, in order to preserve the clarity of the figure. The broken curve 1 represents the absorption at room temperature prior to heating the film. In addition to the excess silver absorption maximum, there is a broad, vague maximum at 5000 Å, attributable, probably, to colloidal particles of excess silver. Curve 2 is the lower-

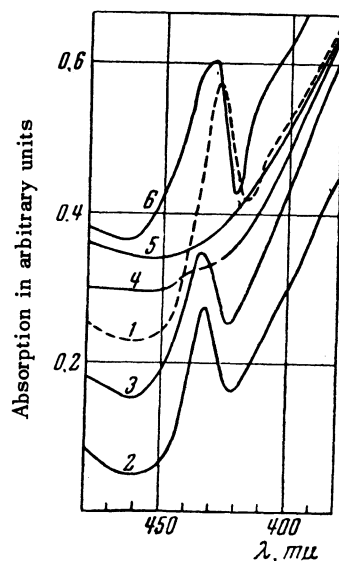


FIG. 1

most absorption curve, corresponding to 131° C. Curve 3 represents the absorption at 140° C; the excess silver absorption maximum on this curve is sufficiently intensive and sharply delineated. The next curve 4 was obtained at 153° C. Increasing the temperature by 13° resulted in the complete disappearance of the maximum. Moreover, in contrast to the other specimens, the absorption in the region of the colloid particle absorption maximum was sharply intensified and the absorption in the ultraviolet portion of the spectrum was weakened (short wave portions of the absorption curves are not shown in the figure). Apparently, during the transformation of the specimen in question, which already contains colloidal silver, from the low temperature to the high temperature modification, a portion of the ions (or atoms) of excess silver diffused in the lattice are forced out, and transformed into colloidal particles. Upon further increase in temperature, the intensification of absorption in the long wave region and decrease of absorption in the ultraviolet region of the spectrum continues, as may be seen from curve 5, recorded at 160°. Upon cooling the film to room temperature, the initial absorption spectrum was not re-established (curve 6). The intensive absorption maximum of the colloidal particles was retained, but instead of the absorption band at 4290 Å, a faint reflection band appeared. The appearance in the absorption spectra, recorded with transmitted light, of selective reflection bands of excess metals only, had already been noted by us for the chemically related substance CuI^2 .

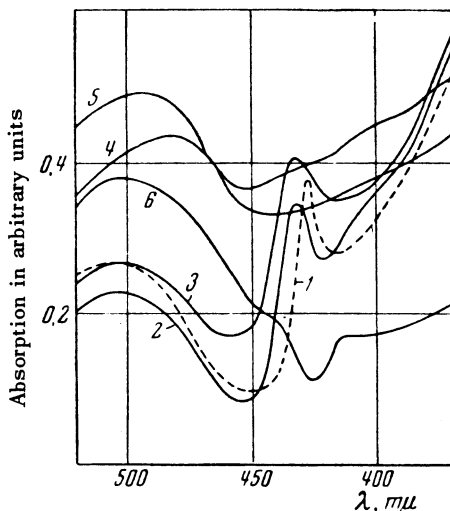


FIG. 2

The results obtained make it possible to draw the following conclusions.

1. During the transformation of the low temperature modification of AgI into the high temperature modification, the absorption bands of excess silver (atoms or ions) disappear, and during the reverse transformation they again reappear. The fact that the excess atoms or ions of silver do not produce any maxima at all in the absorption spectrum of the high temperature modification in the investigated region can be explained by the fact that this modification of AgI has only one fixed lattice---the iodine lattice. Since the silver lattice melts apart and the silver ions intermingle freely, then there is no reason to suppose that the ions (or atoms) of excess silver can occupy any sort of definite, regular position in the crystal, and therefore there is no reason, either, to expect structural absorption of light.

The very fact of the disappearance of the excess silver absorption maxima during the transformation of AgI into the high temperature modification, which does not possess a silver lattice, testifies that the particles of excess metal must dispose themselves in the lattice of the basic substance according to some definite order in order to produce individual maxima in the absorption spectrum.

2. Judging on the basis of the absorption spectra, the presence of excess silver increases the transition temperature for the transformation of the low temperature modification of AgI into the high temperature modification by 5-15° C. A certain disparity in the transition temperatures of the various specimens is apparently connected with a difference in the concentration of the excess silver. Upon transformation of AgI into the high temperature modification, a reduction in volume of approximately 10% takes place⁴. One is led to believe that the presence of a large excess of silver distributed throughout the lattice in the form of atoms or ions interferes with this reduction and delays the reconstruction of the lattice. The fact that the disappearance of the excess silver absorption band in the spectrum of each individual specimen does not take place at a strictly defined temperature, but over an interval of 10-15°, is apparently connected with the complicated structure of the sublimated films. Small, individual crystals of AgI contain a different excess of silver and undergo structural transformation at different temperatures.

⁴ V. D. Kuznyetsov, *Crystals and crystallization*, Moscow, 1953, p. 280.