AN ELECTRON DIFFRACTION STUDY OF THE Ag-Sb SYSTEM IN THIN FILMS

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INTRODUCTION

The structures of Ag - Sb films in the concentration range of Sb from 0 to 50% have been studied. In agreement with x-ray results, the existence of an α-phase, a disordered hexagonal ϵ -phase and an ordered orthorhombic ϵ' -phase with lattice constants close to those of the orthohexagonal cell of the ϵ-phase have been established.

In papers on the Ag-Sb system, published in the literature [1-4], the structural characteristics of the following phases are given (Fig. 1):

1) The α solid solution of Sb in silver exists in the range up to 6% (at). Sb and has a lattice constant a = 4.076 – 4.109 A.

2) The ϵ -phase in the limits from 11 to 17.7% (at.) Sb, has a disordered structure based on hexagonal close packing with the lattice constants a= 2.92 – 2.96 and c= 4.77 – 4.78 A; c/a = 1.63.

3) The ϵ' -phase in the limits from 22 to 27.3% (at.) Sb, has an ordered orthorhombic structure with the lattice constants: a = 4.80 – 4.83, b= 2.98 – 3.00 and c= 5.19 – 5.23 A. At the limiting concentration of 27.3% (at.) Sb, the ϵ' - phase corresponds to the compound Ag_3Sb.

According to [5], the structure of the ϵ' -phase is described by the space group C_{2v}^{1} -- Pmm with the Ag and Sb atoms on twofold axes: Ag: $0\frac{1}{2}z_1$, $z_1 = \frac{1}{2}$; $\frac{1}{2}\ 0z_2$; $z_2 = 0.65$ and $\frac{1}{2}\ \frac{1}{2}\ z_3$; $z_3 = 0.17$. Sb: $00z_4$, $z_4 = 0$ (Fig. 2). As will be readily appreciated, the structure of the ϵ' - phase corresponds to an ordered distribution of the Sb atoms in the ϵ -phase and is pseudohexagonal. Actually, the constants of the orthorhombic cell are connected by the following relationships: $c = b\sqrt{3}$, $a/b = 1.61$.

In the planes perpendicular to the X-axis, the atoms form almost exactly a hexagonal pattern (Fig. 3). Thus, the ϵ'-phase represents an ordered arrangement of the Sb atoms (in a hexagonal close-packed structure) at the corners of the orthohexagonal cell. We have here an interesting example of an ordering process occurring in parallel with an increase in the Sb content of the alloy from 11 - 17.7 % for the disordered ϵ-phase, up to 22-27.3 % for the ϵ'-phase. A feature of this process is the quite insignificant change in the coordinates of the atoms at the $\epsilon \rightarrow \epsilon'$ transition, and the sharp change in symmetry on ordering. It is interesting to compare this with the structure of the ϵ-phase, where the Sb and Ag atoms are arranged statistically.

There is a reference in the literature [6] regarding a phase which is possibly a product of a further ordering of the structure of the ϵ'-phase. The author does not, however, provide any concrete data. Finally, in [7] the supposition is made that the ϵ'-phase may have a structure of the Cu_3Ti type [8], which would lead to a twofold increase in the above-mentioned unit cell.

The specimens for the electron diffraction study in the present work were obtained by sublimation of the components in a high vacuum from two evaporators onto a fresh cleavage face of rock salt. An excess of Sb was ensured in the sublimation. Subsequent annealing of the films at 100 - 200°C for 10-60 min led to the formation of two-phase specimens (ϵ'-phase + Sb), or to ϵ' -phase films without Sb. The crystallites of Sb were arranged with their basal faces parallel to the substrate without azimuthal orientation, while the crystallites of the ϵ'-phase were completely unoriented.

Such films were further subjected to additional annealing at 200-300°C for 1-5 hours, as a result of which their structure was altered. Electron diffraction analysis showed the presence of either a polycrystalline ϵ-phase or a mixture of ϵ + α-phase.

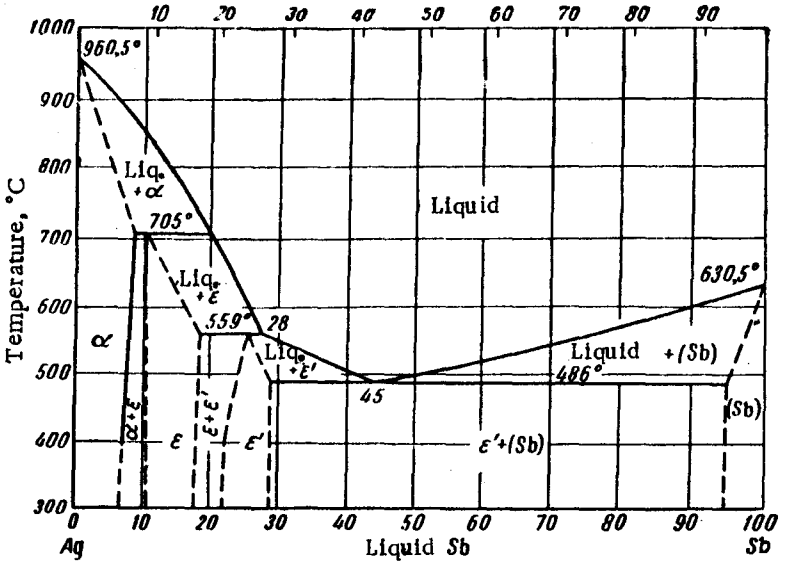

Fig. 1. Phase diagram of the Ag-Sb system

Evidently, the above-mentioned additional annealing was accompanied by partial decomposition of the ϵ'-phase and evaporation of Sb, and corresponded to a displacement on the phase diagram towards a reduction in the Sb concentration. In none of these experiments were we able to observe the formation of the Ag_2Sb phase,

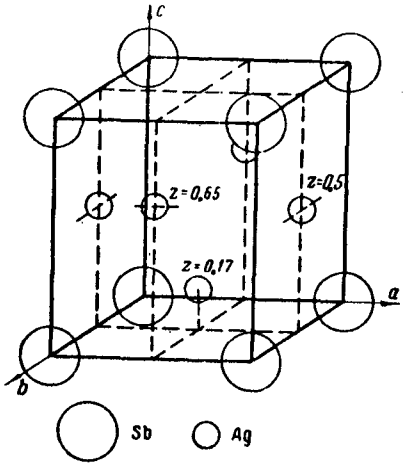

Fig. 2. Structure of the ϵ'-phase

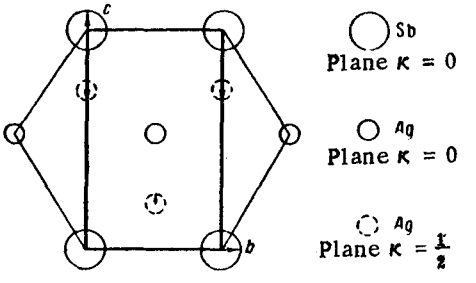

Fig. 3. Projection of the structure of the ϵ'-phase on the (yz) plane. The arrows indicate the directions of displacement of the Ag atoms in the ordering process.

not shown on the phase diagram, but existing in nature [9]. Thus, the results of our investigation are entirely in quantitative agreement with the generally accepted phase diagram of the Ag - Sb system.

The electron diffraction patterns of the ϵ'- and ϵ-phases are distinguished by a characteristic splitting of a number of lines in agreement with the pseudohexagonal nature of the structure of the ϵ'-phase. To permit reliable identification of the phases studied, steps are taken to obtain sufficiently sharp electron diffraction photographs of the ϵ-phase and to utilize the resolving power of the apparatus to the fullest extent.

Films of the ϵ'-phase were prepared by successive sublimation of the components (first Sb and then Ag) on a crystal heated to 150°C, followed by annealing at 200°C for 60 min. Portions of two electron diffraction patterns of the ϵ- and ϵ'-phases are shown in Fig. 4.

On the ϵ'-phase photographs (Fig. 4,c) it was naturally not possible to separate fully all the reflections, but the resolution of 0.001A obtained was quite effective. Using a comparator, it was possible to measure 106

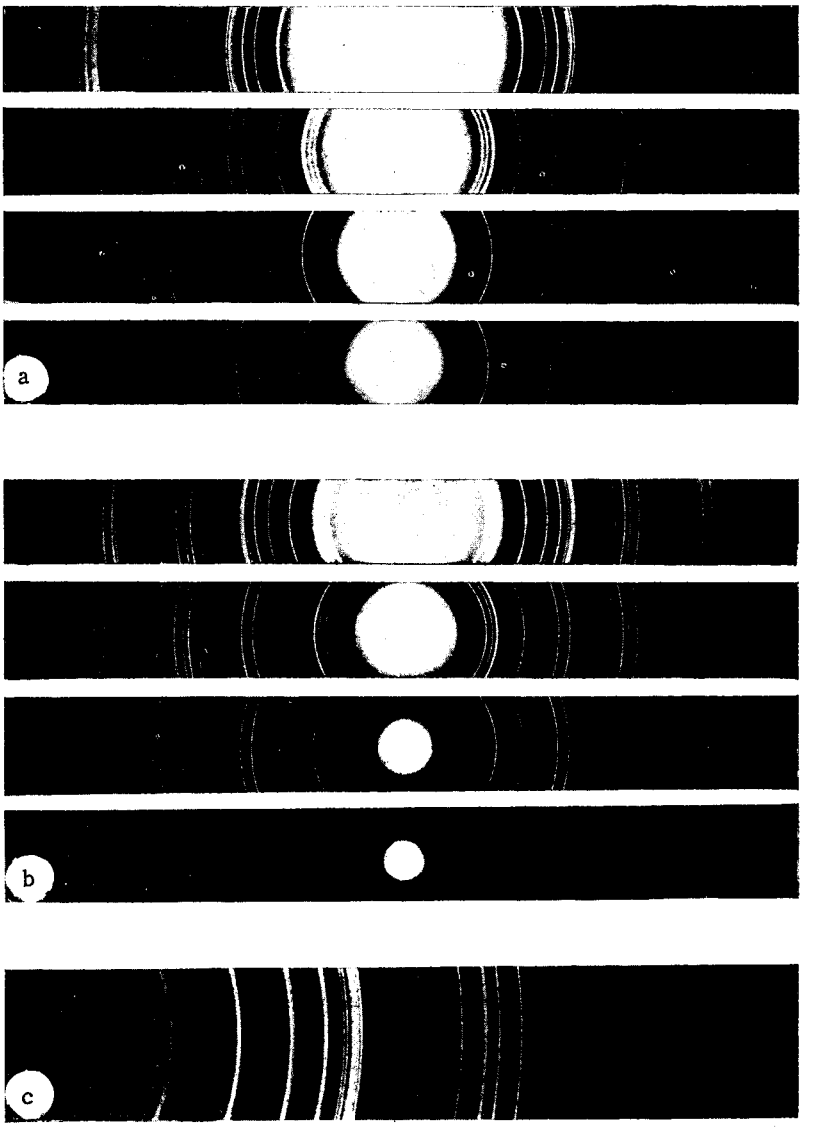

Fig. 4. Comparison of portions of two electron diffraction patterns of ϵ- and ϵ'-phases: a) ϵ-phase, b) ϵ'-phase, c) electron diffraction pattern of the ϵ'-phase magnified 2.6 times.

lines, corresponding to 144 reflections of the ϵ'-phase lattice. On ϵ'-phase electron diffraction patterns with a standard (NH_4Cl), the following values were obtained for the lattice constants: a = 4.813 ± 0.005, b = 2.979 ± 0.003 and c = 5.215 ± 0.005 A, corresponding approximately to the mean point of the concentration range of this phase.

In other experiments, variations in the values of the lattice constants were observed within the following limits: a = 4.812 – 4.820, b = 2.979 – 2.984 and c = 5.204 – 5.217 A. A slight decrease in b compared with the mean value of x-ray determinations is noteworthy.

At the limit of resolution of the MF-4 microphotometer, we were able to measure photometrically 81 lines out of 106. The experimental intensity was determined from multiple-exposure photomicrographs (Fig. 4 b) and blackening curves. The intensity of the other lines was estimated visually.

In comparing the theoretical and experimental values of d_{hkl}, a correction being introduced for L λ [10], it was necessary to take into account the effect of the coalescence of many reflections in the observed lines.

A comparison was therefore made of the intensities and also the squares of the structure amplitudes calculated by the kinetic approximation

$$\Phi_e^2 = I_e / pd^2. \quad (1)$$

The values of I_e for pairs of coalesced reflections was determined by dividing the total experimental intensity in the ratio I'_t/I''_t. The theoretical structure amplitudes were calculated for the structural model of the ϵ'-phase just described, without a center of symmetry (Pmm), with the above-mentioned values of the parameters. The first comparison of the series of theoretical and experimental values of Φ^2 revealed a sharper drop with increase in $\sin\delta/\lambda$ for I_t, even without the introduction of a temperature factor. After the introduction of a temperature factor with a value of B = 1.0, corrections were calculated for extinction, i.e., dynamic scattering. The method described in [11] was used. A value of $\approx$ 700 A was assumed for the thickness of the crystal H_m. As a result, the value of

$$R = \frac{\Sigma \| \Phi_e^2 | - | \Phi_t^2 \|}{\Sigma | \Phi_T^2 |} \quad (2)$$

for all 144 reflections was found to be 32.4%.

It may thus be considered that, as a first approximation, the x-ray data for the structure of the ϵ'-phase are confirmed by the electron diffraction analysis of thin films. As regards the exact values of the parameters z_i for the atoms of Ag and Sb, these will require further verification.

Flectron diffraction patterns of the type of Fig. 4 a were used for the study of the structure of the ϵ-phase. The corresponding film was made by successive sublimation of the components (first Sb and then Ag) on a crystal heated to 150°C followed by annealing for 4 hours at 230°C. By the use of the microphotometric method described above it was possible to measure the intensities of 51 lines, comprising 65 reflections. The following values were found from photographs with a standard: a = 2.888 $\pm$ 0.003 and c = 4.730 $\pm$ 0.005 A. In other experiments, the following values were observed for the lattice constants: a = 2.888 - 2.947 and c = 4.730 - 4.788 A.

The calculation of the theoretical structure amplitudes was based on the model of a hexagonal close-packed structure of spherical atoms of equal radius with the scattering power

$$f_m = \frac{(n-1) f_{Ag} + f_{Sb}}{n} \quad (3)$$

where n = 10 (Ag – 90 % Sb – 10%). In making the comparison with experiment, a temperature factor of B = 1.0 was introduced into the theoretical intensity and a dynamic correction was introduced into the experimental values. The mean thickness of the crystal H_m was 636 A and the value of R was 20.4%.

It should be mentioned that in some electron diffraction patterns of the ϵ-phase, a number of superfluous lines ($11\bar{2}1$, $30\bar{3}1$, $22\bar{4}1$ and others) were observed. The occurrence of these lines, forbidden by the space group C6/mmc, is easily explained on the assumption of a partial ordering of the Sb atoms, which appears as a preferred arrangement through the film in planes parallel to the base.

In electron diffraction patterns of a mixture of ϵ-phase and α-phase, a spread in the values of the lattice constant of the α-phase within the limits 4.084 – 4.092 A was observed. It may be seen that the lattice period of silver in the α-phase is increased from 4.071 (for pure silver) to 4.092 A. This increase corresponds approximately to the mean concentration range of existence of the α-phase.

The shortest atomic distances in the structure of the ϵ-phase and ϵ'-phase are: in the ϵ'-phase, Ag_1 – Sb = 3.003, Sb – Sb = 2.979 and Ag_2 – Ag_3 = 2.913 A; in the ϵ-phase, 2.98 A. Comparison of these values with the sum of the radii of the atoms of Ag and Sb (1.44 + 1.61 = 3.05 A) shows that the bonds in the ϵ- and ϵ'-phases are mainly covalent.

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