

References

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Structure of Evaporated Tin Sulphide

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A cubic sulphide ($a_0=5.445\text{\AA}$) having zinc blende type of structure was obtained from stannous sulphide films heated in vacuo to about 425°C .

Sulphide of tin forms two well defined compounds namely stannous sulphide (SnS) having orthorhombic structure¹⁾ and stannic sulphide (SnS_2) with hexagonal structure²⁾. The sesquisulphide of tin (Sn_2S_3), sometimes described in literature, is not well established³⁾. During the evaporation of tin sulphide which is prepared in the laboratory at room temperature under vacuo and further heated to different temperatures, various structures such as h.c.p. along with its cubic form, normal orthorhombic, and a f.c.c. type of structure were observed. In the following an investigation has been made on the last mentioned compound.

Experimental

Stannous sulphide yellowish brown in colour, was prepared by passing H_2S through a solution of stannous chloride (A.R) in 1:1 hydrochloric acid and washing the precipitates with H_2S water finally with distilled water and alcohol, followed by drying in vacuo. This sample was then evaporated also in vacuo from a filament on rock-salt substrate at room or higher temperatures. The deposits were then heated further to about 425°C either in contact with the substrate or after its removal and examined in electron diffraction camera (cold cathode type) by transmission method.

The integrated intensities of different hkl reflections of polycrystalline samples (un-

orientated) were measured by non-recording microphotometer. The characteristics of the plates (Ilford special rapid) regarding its linearity relationship between blackening of the plates and energy of electron beam were established by the multiexposure method⁴⁾.

This relation was found to be valid within the region of 0.2 to 0.9, but the working range was normally between 0.3 to 0.8.

Results & discussion

Various patterns, typical of h.c.p. and its corresponding cubic, orthorhombic or f.c.c. type of structures were obtained from deposits heated to about 200° to 440°C . Deposits formed at about 425°C yielded pattern (Fig. 1) characteristic of a cubic structure having all odd or all even indices present. No mixed indices were observed at all. The pattern was due to unorientated polycrystal-

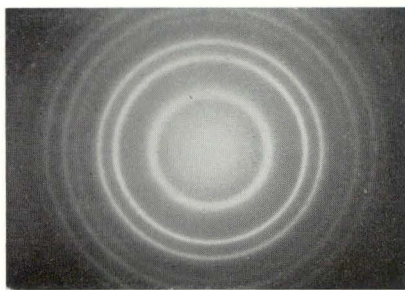


Fig. 1. Tin sulphide.

line deposits alone since no change in intensity of rings or arcing was observed by tilting the specimen around an axis normal to the beam direction. The lattice constant ($a_0=5.445\text{\AA}$) was determined by comparing with graphite rings in usual way. It is seen from the pattern that the intensities of 111, 220 and 311 reflections were in decreasing order and 200 was practically absent. Neither the intensities nor the 'd' values, however, correspond to any of the known sulphide compounds.

To evaluate the general structure of the deposits, the integrated intensities of the different hkl reflections as measured with the microphotometer were compared with the possible f.c.c. type of structures, such as NaCl(O_h^5 -Fm3m), 'ZnS'(T_d^2 -F43m) and CaF_2 (O_h^5 -Fm3m).

Intensities were calculated from the relation $I \propto F^2 d^2 p$ where d and p are the lattice spacings and multiplicity factor for different hkl reflections and $F = \sum f_{el} \cos 2\pi(hx + ky + lz) + i \sum f_{el} \sin 2\pi(hx + ky + lz)$ assuming that the kinematic scattering is valid in the present case. No temperature effect was taken into account. Atomic scattering factors for electron, f_{el} , were taken from the recent values of Ibers and Vainshtein⁵⁾. The relative values of I for the three different structures were compared with the observed values after normalising 220 reflections to 100 (Table). It is seen that the integrated intensities of dif-

ferent rings of tin sulphide having zinc blende type of structure are comparable with the observed values. Further the sulphide with 'NaCl' type of structure would have 200 reflections strongest whereas it is practically absent in the pattern. For 'CaF₂' type of structure also, the agreement is not good enough with the observed one, as 111 and 220 reflections are nearly equal in the former case whereas it is in the ratio of 2:1 in the latter. Similar anomaly can also be noticed in the other reflections of 'NaCl' and 'CaF₂' type of structures. Another probable cubic structure which is sometimes observed in sulphides or oxides having all odd or all even reflections present is of spinel type. Since all spinels have normally high lattice constants ($>7.9\text{\AA}$) and 311 reflections are the strongest and 111 comparatively weak, contrary to our observation, this structure is hence ruled out. It, therefore, appears that the sulphide of tin had its atomic coordinates at positions, Sn (0, 0, 0)+F.C.; S($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)+F.C. similar to that of zinc blende.

Consideration of atomic radii of tin and sulphur also lends support to the above view. It is known that the ratio of cationic to anionic radii in a cubic close packing system determines the structure of many compounds. Thus r_c/r_a for ZnS, NaCl and CsCl structures are respectively between 0.22 to 0.41, 0.41 to 0.71 and 0.71 to 1.0. The ratio of r_{Sn}/r_S (0.386) also conforms to the above mentioned structure. It may be argued that both lead and tin belonging to the same group should have similar NaCl type structure, but its lower r_c/r_a value compared for PbS(0.456) favours ZnS type of structure.

Table

hkl	Relative Integrated Intensities			
	ZnS type	NaCl type	CaF ₂ type	Observed
111	220	42.5	118	215
200	21	182	10	—
220	100	100	100	100
311	58	14	3	62
222	4	28	1	—
400	11	11	11	15
331	18	4	9	26
420	5	27	—	4
422	18	18	—	19

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DISCUSSION.

S. H. BAUER: Have you considered the possibility of the reaction of the residual

oxygen present in your apparatus, so that the material you studied was an oxychloride? Such an oxy-chloride would more likely assume a spinel structure than would cuprous chloride.

A. GOSWAMI: We have considered the possibilities of the formation of cuprous oxychloride. Known oxychloride does not have a spinel structure. But, as the film was too thin, we are not sure of its composition and it could not be subjected to chemical analysis. We don't even know the composition of the film.

S. OGAWA: Isn't there any possibility that your spinels were caused by oxides? How high was your vacuum?

A. GOSWAMI: Since we took pure cuprous chloride, the oxide was not present in the original compound. But during evaporation it dissociated to Cu_2Cl_2 and Cu, we believe. We are not sure of the formation of oxide, since no chemical analysis could be carried out on the film. Vacuum was $\approx 1 \times 10^{-2}$ mmHg.

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On the Anti-Phase Domain Structures in Ordered Alloys

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Recent studies on the anti-phase domain structures in ordered alloys by electron diffraction and electron microscopy are surveyed.

In the course of the ordering of alloys, domains out of phase with each other in their manner of ordering will arise. Such anti-phase domains will affect the aspect of super-

lattice reflections in diffraction patterns. This diffraction effect was confirmed on a partially ordered Cu_3Au by X-ray diffraction¹⁾, but the electron diffraction work by Raether²⁾ more clearly showed characteristic shapes of superlattice spots caused by the formation of anti-phase domains in this alloy, as shown in Fig. 1. Well oriented evaporated films were used in this case. Such anti-phase domains will increase in size as the ordering proceeds by atomic diffusion and at last domain boundaries will vanish. In fact,

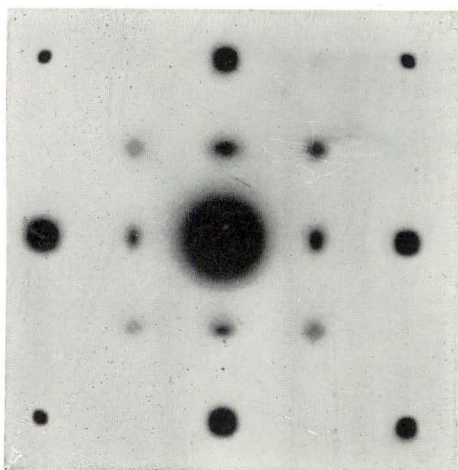


Fig. 1. Electron diffraction pattern of a partially ordered Cu_3Au .

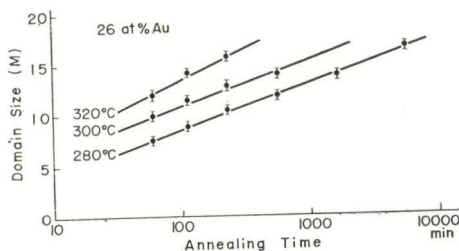


Fig. 2. Isothermal growth of anti-phase domains in Cu_3Au .