

A New Type of Spinel from Cuprous Chloride

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During evaporation of γ -cuprous chloride in vacuo a new compound ($a_0=8.265\text{\AA}$) having a spinel structure was formed. The theoretical intensities for different hkl reflections with the change of ' u ' values of anions were calculated and compared with experimental values. The discrepancy in the intensities of 400 reflections and the possible mechanism of the spinel formation are discussed.

Introduction

Cuprous halides generally have either zinc blende or wurtzite type of structure, though a third modification¹⁾ (α) has been reported for CuI and CuBr. During electron diffraction studies of evaporated films of cuprous chloride we have occasionally observed another cubic form having the intensities of hkl reflections similar to those of spinel compounds. In the following an investigation has been made on the structure of the above mentioned deposits.

Experimental

Cuprous chloride prepared in the laboratory was evaporated from a filament in vacuo and deposited on rocksalt or mica at about 230°C and the deposits were examined both by reflection and transmission in an electron diffraction camera (Finch type). The intensities of the hkl reflections of polycrystalline and unorientated samples were measured by a non-recording microphotometer and integrated intensities were evaluated by the method of Karle and Karle²⁾. The linearity relationship between optical density of the plate and the electron beam energy was established by the multiexposure method and found to be valid within the region 0.2 to 0.9 for Ilford special rapid plates and the working range was between 0.3 to 0.8.

Results & discussion

The deposits were mostly polycrystalline in nature and their lattice constant ($a_0=8.265\text{\AA}$) was evaluated using graphite standard. The reflections (Fig. 1) consisted only of all odd or even indices and 311 had the maximum intensity. Other important reflections of decreasing intensity were 220, 440, 511+333 and 400; 111 and 200 being practi-

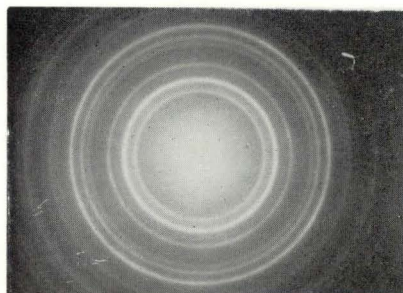


Fig. 1. Spinel.

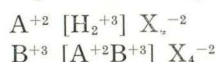
cally absent. These features together with higher lattice constant suggested that the deposits had the spinel type of structure, where 311, 440 and 400 are characteristic reflections in decreasing order of intensity.

Spinel has AB_2X_4 type of composition where A and B are di- and trivalent (similar or dissimilar) metal atoms and X is anion viz., oxygen or sulphur³. Structurally they belong to the space group $\text{O}_h\text{-Fd}3\text{m}$, having 56 atoms in the unit cell, where anions form the lattice frame work and metal ions occupy the tetrahedral or octahedral holes created by the anions. There are eight molecules in a unit cell in which A atoms occupy 8 of the 64 tetrahedral sites and B atoms 16 of the 32 octahedral sites.

The atomic positions in spinel structure are as follows:

- | | |
|---------------|--|
| 8 A atoms in | $0, 0, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4} + \text{F.C.}$ |
| 16 B atoms in | $5/8, 5/8, 5/8; 5/8, 7/8, 7/8;$
$7/8, 5/8, 7/8; 7/8, 7/8, 5/8;$
$+ \text{F.C.}$ |
| 32 X atoms in | $uuu, \bar{u}\bar{u}\bar{u}; \frac{1}{4}-u, \frac{1}{4}-u, \frac{1}{4}-u;$
$\frac{1}{4}-u, \frac{1}{4}+u, \frac{1}{4}+u$
$\bar{u}\bar{u}\bar{u}; \bar{u}\bar{u}\bar{u}; \frac{1}{4}+u, \frac{1}{4}-u,$
$\frac{1}{4}+u; \frac{1}{4}+u, \frac{1}{4}+u, \frac{1}{4}-u;$
$+ \text{F.C.}$ |

The value of u for ideal case is 0.375 (3/8) but it may vary slightly depending on the nature of the spinel. In the case of inverse spinel 8 B^{+3} ions occupy the tetrahedral sites and 8 A^{+2} ions and 8 B^{+3} ions occupy the octahedral sites. The normal and the inverse spinels can be represented respectively as



Assuming spinelization of cuprous chloride for the present, the intensity contribution from different reflections was calculated from relation $I \propto F^2 d^2 p$, where $F = \sum f_{el} \cos 2\pi(hx + ky + lz) + i \sum f_{el} \sin 2\pi(hx + ky + lz)$ for different values of ' u ' and compared with the observed values (Table, Fig. 2). f_{el} was obtained from the values of Ibers and Vainshtein⁴.

It is seen (Fig. 2) that (i) 311 reflection is the strongest for all reasonable values of u ; (ii) 440 and 400 reflections had more or less similar values and vary in the similar way with change of u ; (iii) 440 or 400 had maxima,

Table

hkl	$I_{obs.}$	$I_{cal.}$ $u = .375$
111	10	7
220	58	28
311	100	100
400	26	66
422	18	7
511 + 333	35	20
440	52	67

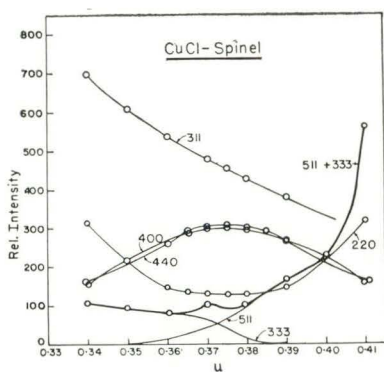


Fig. 2.

but for 220, minimum at $u \simeq .375$, and decreases and increases symmetrically on either side of u ; (iv) (511+333) contributions become very high at higher value of u . One striking discrepancy is of (ii) compared with observed values. In no case I_{400} becomes much less than I_{440} , unless f_{el} for 400 is made less than given by Ibers and Vainshtein. Using corresponding f_{X-ray} atomic scattering factor, the ratio of I_{440}/I_{400} becomes comparable to the observed value.

Comparing the values of I_{220} , I_{440} and $I_{511+333}$, it appears that at $u \simeq .35$ the results agree well with observed values. But then $I_{311}/I_{440} \simeq 3:1$ whereas observed value is $\simeq 2:1$. This discrepancy is not too much large in view of many factors contributing to the inaccuracy of this estimation. These are: (a) uncertainty in the position of metal atoms, occupying the holes, sizes of which are small ($.7-.9\text{\AA}$) compared with anions (1.81\AA) and more so in an unstable film, (b) inaccuracy in atomic scattering factor, f_{el} , (c) possible non-stoichiometric composition of spinel type of compounds, etc. Similar discrepancy in intensities of different reflections are well known in all spinels³. Spinel of this type formed from halides have not been reported so far. Since its formation was occasional, a much more accurate analysis was not, however, possible.

It was not feasible to estimate the composition of cuprous chloride spinel. But from the structural consideration its composition would be Cu_3Cl_4 i.e., $Cu_1^{+2} [Cu_2^{+1}] Cl_4^{-1}$ or $Cu_1^{+1} [Cu_1^{+2} Cu_1^{+1}] Cl_4^{-1}$, which also satisfy the neutrality of charge in the molecule. The mechanism of its formation seems to be $2Cu_2Cl_2 \rightarrow Cu_3Cl_4 + Cu$ rather than $Cu_2Cl_2 + CuCl_2 \rightarrow Cu_3Cl_4$, since we have observed reddish deposits of copper in the filament itself after evaporation and also that the initial sample contained γ -cuprous chloride alone.

From the lattice parameter of this compound, the ionic character of chlorine can roughly be estimated. Since the cell constant of a spinel is not affected by the metal atoms but only by the effective radii of anions, the observed radius is 1.46\AA ($=8.265/4\sqrt{2}$) compared to fully its ionic radius 1.81\AA of chlorine atom. Thus ionic character decreases considerably and tends towards the tetrahedral or neutral atomic state (0.99\AA).

References

- 1 A. S. T. M. Cards No. 6-0623, 6-0310.
- 2 J. Karle and I. I. Karle: *J. Chem. Phys.* **18** (1950) 957.
- 3 R. W. G. Wyckoff: Vol. II, Chapt. VIII (Interscience Publication, 1948).
- 4 J. A. Ibers and B. K. Vainshtein: *Soviet Phys Cryst.* **4** (1960) 601.

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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-

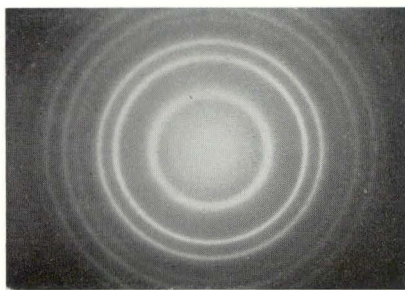


Fig. 1. Tin sulphide.