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Metastable structures of liquid-quenched and vapour-quenched antimony films

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Antimony foils/films have been prepared by liquid-quenching and by vapour-quenching. (1) Simple cubic ($a = 3.16$ Å), (2) f c c ($a = 4.61$ Å), (3) tetragonal ($a = 3.01$ Å, $c = 4.96$ Å and $c/a = 1.64$) structures, and (4) a new rhombohedral ($a_H = 4.12$ Å, $c_H = 10.26$ Å and $c_H/a_H = 2.49$) metastable structure have been observed in splat-quenched foils. The metastable rhombohedral phase transforms to the equilibrium rhombohedral phase ($a_H = 4.30$ Å, $c_H = 11.27$ Å and $c_H/a_H = 2.62$) on heating. The simple cubic, f c c and tetragonal phases are converted in to a hexagonal close-packed ($a = 3.33$ Å, $c = 5.23$ Å and $c/a = 1.57$) structure on heating in the electron microscope. The simple cubic and h c p phases correspond to the known high-pressure phases of antimony. The h c p phase does not transform on further heating. Films prepared by vapour deposition on substrates held at room temperature show the same metastable f c c and rhombohedral phases as observed in splat-quenched foils, in addition to the equilibrium rhombohedral phase. On heating, these metastable phases transform in the same way as the splat-quenched specimens. The films deposited at liquid air temperature are amorphous; on electron-beam heating, these crystallize first to an unidentified complicated structure and then to the equilibrium structure.

1. Introduction

Antimony has an equilibrium rhombohedral structure ($a_H = 4.30$ Å, $c_H = 11.27$ Å and $c_H/a_H = 2.62$). It is known to exist in simple cubic ($a = 2.96$ Å) and hexagonal close packed ($a = 3.33$ Å, $c = 5.27$ Å and $c/a = 1.58$) structures at high pressures of 50 and 90 kbar, respectively [1]. An amorphous phase is obtained in pure antimony films deposited by quenching the vapour at room temperature or lower temperatures [2]. However, no metastable crystalline phase has been observed in vapour-quenched or liquid-quenched antimony. It is well known (see, for example [3]) that high-temperature and/or high-pressure phases of a material can be stabilized by rapid quenching of vapour or liquid under controlled conditions. In a search for the simple cubic and h c p structures, we have studied the structure of antimony quenched from its vapour phase in vacuum and also from its liquid phase by using a gun assembly [4]. The various metastable crystalline phases of antimony obtained on liquid-quenching and vapour-quenching are discussed in this paper.

2. Experimental details

About 100 mg antimony (99.999% pure) was quenched from the melt by the gun technique [4] in a vacuum of $\sim 10^{-5}$ Torr. Details of the apparatus are given elsewhere [5]. Antimony was melted in a resistively heated graphite crucible having an orifice of 0.9 mm diameter. The temperature of the crucible was measured by a chromel–alumel thermocouple. A thin (~0.1 mm thick) aluminium foil was used as a diaphragm. A pressure of 8 MN m^{-2} (≈ 1160 psi) was employed to rupture the diaphragm and eject the molten droplet for splat-quenching on a water-cooled copper substrate. To promote good adhesion between the substrate and the foil and to ensure that the substrate was free of oxide, the copper substrate was abraded with fine SiC paper and cleaned prior to each quench. The resulting

TABLE I Summary of the metastable phases identified by transmission electron microscopy in liquid-quenched and vapour-quenched antimony films

Liquid-quenched specimens	Vapour-quenched specimens		Known phases
	Substrate at room temperature	Substrate at liquid air temperature	
sc ($a = 3.16$ Å)			sc ($a = 2.96$ Å)*
fcc ($a = 4.61$ Å)	fcc ($a = 4.61$ Å)		
tetragonal ($a = 3.01$ Å, $c = 4.96$ Å)			
On heating	On heating		
hcp ($a = 3.33$ Å, $c = 5.23$ Å)	hcp ($a = 3.33$ Å, $c = 5.23$ Å)		hcp ($a = 3.33$ Å, $c = 5.27$ Å)†
rhombohedral ($a_H = 4.12$ Å, $c_H = 10.26$ Å)	rhombohedral ($a_H = 4.12$ Å, $c_H = 10.26$ Å)	rhombohedral ($a_H = 4.12$ Å, $c_H = 10.26$ Å)	
		On heating	
On heating	On heating	Unidentified phase	
		On heating	
rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)
		Amorphous	
		On heating	
		Unidentified phase	
		On heating	
	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)	rhombohedral ($a_H = 4.30$ Å, $c_H = 11.27$ Å)

* At 50 kbar.
† At 90 kbar.

foils were irregular and their thickness varied from a fraction of a micron to a few microns. These could be easily stripped from the copper substrate and some regions were suitable for transmission electron microscopy at 80 kV without any further preparation.

Thin films of antimony were also prepared by vapour deposition in a high vacuum of $\sim 10^{-6}$ Torr onto carbon-coated grids and NaCl crystal substrates, held at temperatures ranging from room temperature down to liquid air temperature.

3. Results and discussion

Table I shows the various metastable phases of antimony obtained on liquid-quenching and vapour-quenching along with the known equilibrium and high-pressure phases. The transformation behaviour of these metastable structures is schematically shown in Fig. 1.

3.1. Liquid-quenched specimens

Owing to varying thickness of the foil and hence different quenching rates for different regions of the foil, the liquid-quenched specimens yielded a number of metastable phases. Analysis of the diffraction patterns of different regions showed the existence of simple cubic (sc), fcc, tetragonal structures and a new rhombohedral metastable structure. The calculated d-spacings, indices of reflection ($h\,k\,l$) and visually observed intensities for various metastable phases are given in Table II.

The diffraction pattern of the simple cubic structure shown in Fig. 2a has a lattic parameter $a = 3.16$ Å. This phase must correspond to the high-pressure (50 kbar) phase of antimony ($a = 2.96$ Å). A change of 6.75% in lattice parameter is observed, which means ~20% change in density.

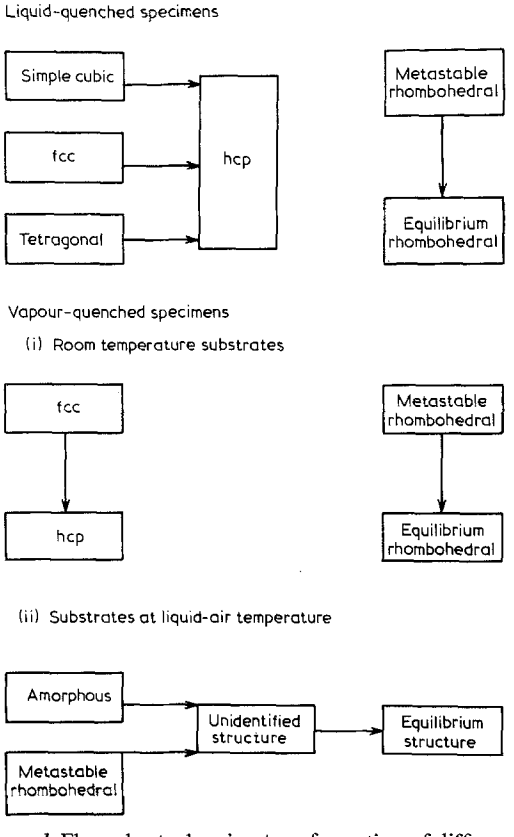


Figure 1 Flow chart, showing transformation of different metastable phases obtained on liquid-quenching and vapour-quenching of pure antimony.

TABLE II Observed d-spacings and indices of reflection ($h\,k\,l$) for different structures observed in liquid-quenched and vapour-quenched antimony films (VW = very weak, W = weak, M = medium, S = strong, VS = very strong)

Structure	d(Å) (observed)	Intensity (visually observed)	$h\,k\,l$
sc	3.16	S	1 0 0
	2.23	M	1 1 0
	1.83	W	1 1 1
	1.57	VW	2 0 0
	1.41	W	2 1 0
	1.28	M	2 1 1
fcc	2.66	VS	1 1 1
	2.30	S	2 0 0
	1.62	S	3 1 1
	1.39	S	3 1 1
	1.15	M	4 0 0
	0.93	W	4 2 2
Tetragonal	4.96	VW	0 0 1
	3.00	S	1 0 0
	2.58	VS	1 0 1
	2.13	S	1 1 0
	1.65	M	0 0 3
	1.51	S	2 0 0
Metastable rhombohedral	3.39	S	1 0 1
	2.06	S	1 1 0
	1.76	S	0 2 1
	1.69	VW	2 0 2
	1.46	W	0 2 4
	1.33	M	1 1 6
	1.19	M	3 0 0
hcp	2.89	S	1 0 0
	2.54	VS	1 0 1
	1.95	S	1 0 2
	1.65	S	1 1 0
	1.50	S	1 0 3
	1.41	S	1 1 2
	1.11	W	2 0 3
	1.06	W	2 1 1
	1.00	W	2 1 2
	0.94	W	3 0 1

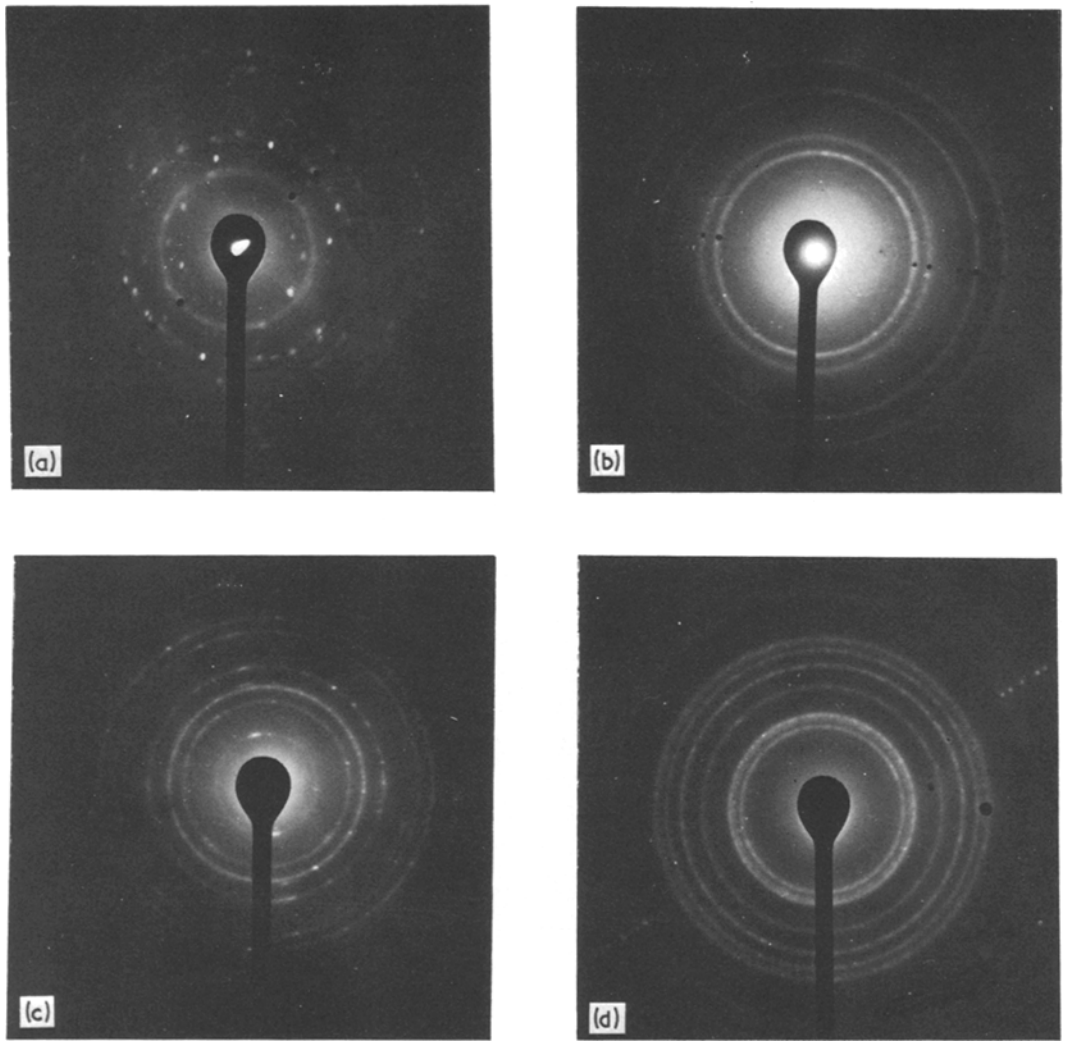


Figure 2 Electron diffraction patterns of (a) simple cubic, (b) f c c, and (c) tetragonal metastable phases, (d) Diffraction pattern of h c p phase obtained on heating (a), (b) or (c).

This large change in density may be attributed to the stabilization of the simple cubic phase from the liquid state under different "equivalent" high-temperature and/or high-pressure conditions. The simple cubic phase transforms to an h c p ($a = 3.33$ Å, $c = 5.23$ Å and $c/a = 1.57$) structure on heating in the electron microscope.

The most prominently observed patterns (Figs. 2b and c) in all films correspond to f c c ($a = 4.61$ Å) and tetragonal ($a = 3.01$ Å, $c = 4.96$ Å and $c/a = 1.64$) lattices. On electron beam heating, these phases transform to the h c p ($a = 3.33$ Å, $c = 5.23$ Å and $c/a = 1.57$) structure as seen by the diffraction pattern shown in Fig. 2d. On further heating the diffraction pattern is unchanged which shows that the h c p structure is stable up to temperatures approaching the melting point of antimony. The h c p phase is the same as the 90 kbar high-pressure phase of antimony, with a larger number of diffraction rings. The formation and high stability of the h c p phase obtained on heating the metastable simple cubic, f c c and tetragonal structures show that the h c p phase is a more stable phase of antimony and it is presumably stabilized in the heating stage by some gaseous impurities.

In very thin regions of the splat-quenched foils, a new metastable rhombohedral phase (different

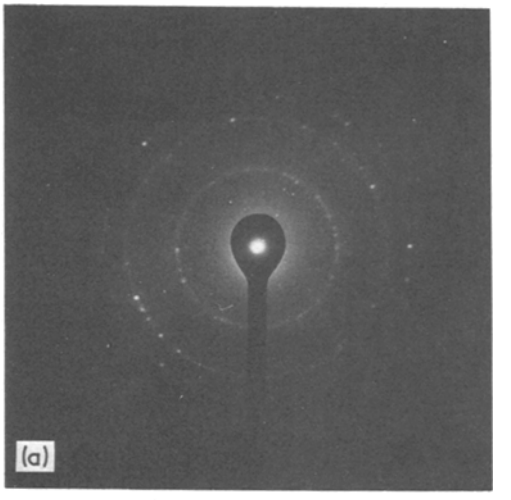
from the equilibrium rhombohedral phase) was observed. The corresponding diffraction pattern is shown in Fig. 3a. The calculated lattice spacings for this phase are: $a_H = 4.12$ Å, $c_H = 10.26$ Å and $c_H/a_H = 2.49$. On electron beam heating, the diffraction pattern becomes very sharp (as shown in Fig. 3c) and is identified as that of the equilibrium rhombohedral phase. The new metastable rhombohedral phase in liquid-quenched foils may by described in terms of the distortion of the normal lattice.

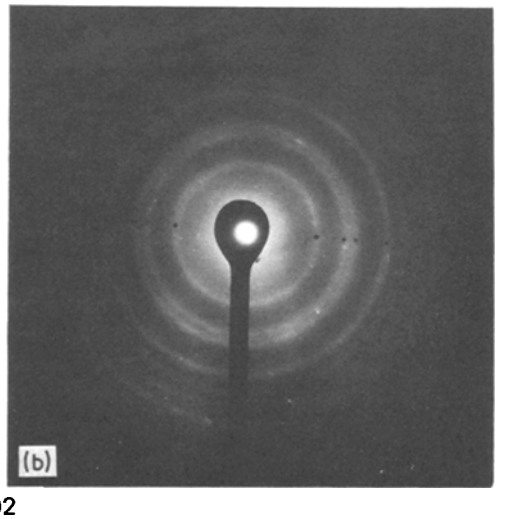
The electron micrographs show black and white contrast due to very fine-grained particles of size varying from 50 to 500 Å, distributed randomly throughout the film. The selected-area diffraction shows that these particles are randomly oriented, having regions of different phases in the foil. A typical electron micrograph of as-quenched foil is shown in Fig. 4a. On electron-beam heating, a uniform network structure (Fig. 4b) was obtained.

3.2. Vapour-quenched films

Films deposited by vapour condensation on substrates held at room temperature showed the equilibrium rhombohedral structure (at thicker portions) and also the metastable fcc and new rhombohedral phases as observed in liquid-quenched specimens. The metastable phases were randomly distributed within any thin area of the film and constituted an appreciable portion of the film. On electron-beam heating, these phases transform in the same way as those observed in liquid-quenched foils. The formation of the metastable fcc and new rhombohedral phases in antimony films deposited at room temperature suggests that the Sb_2 and Sb_4 vapour molecules [6] have a tendency to fit in these lattices.

Films deposited on substrates held at liquid air temperature are generally amorphous. On heating with the electron beam, the amorphous regions crystallize to a new structure; this gave rise to a complicated diffraction pattern (Fig. 3b) which we have not been able to index. On further heating, this phase transforms to the equilibrium rhombohedral phase (Fig. 3c). In some films, deposited at low temperatures, traces of the new metastable rhombohedral phase (Fig. 3a) have been observed. On electron-beam heating, the phase first changes to the unidentified structure





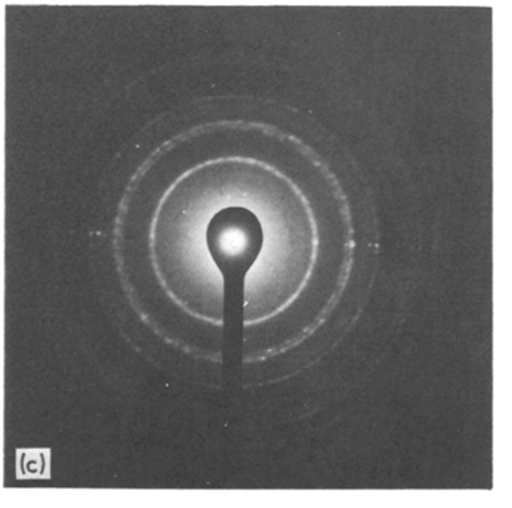


Figure 3 (a) Diffraction pattern of new metastable rhombohedral phase obtained in liquid-quenched and vapour-quenched antimony films. (b) Unidentified structure obtained on heating amorphous phase or (a). (c) Equilibrium rhombohedral phase obtained on heating (a) or (b).

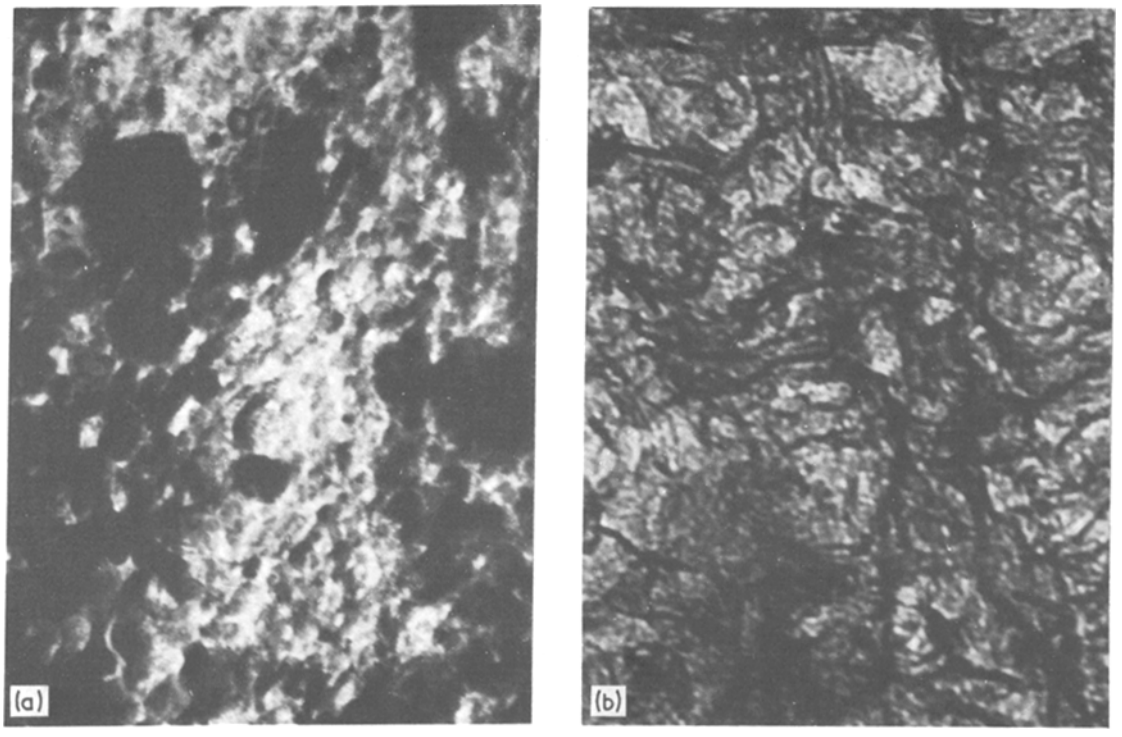


Figure 4 (a) Typical electron micrograph of splat-quenched antimony (× 130 000), (b) Uniform network structure obtained on electron-beam heating of (a) (× 130 000).

(Fig. 3b) and then changes to the equilibrium rhombohedral phase. It is noteworthy that the new metastable rhombohedral phase is also observed in low-temperature depositions, which suggests that this phase has higher energy compared to the metastable f c c phase.

Except for polonium and possibly a non-equilibrium phase of selenium, a simple cubic structure is not known to exist in pure elements at normal temperature and pressure. By liquid quenching, a few alloys have been reported to solidify in this simple structure [7, 8]. Antimony is known to transform to a simple cubic structure ($a = 2.96$ Å) at 50 kbar pressure [1]. The change in lattice parameter of the simple cubic structure that we have observed may be due to effectively different high-temperature and/or high-pressure conditions. In view of the transformation of simple cubic, f c c, and tetragonal phases to more stable h c p structure on heating, it may be suggested that the metastable f c c and tetragonal phases of antimony might be stabilized at high pressures under optimum conditions.

The occurrence of metastable phases directly from the melt during the quenching process suggests that the nuclei of these phases are present in the liquid at some stage of the splat-quenching process. The stabilization processes are complex and varied. Since no detailed quantitative studies were possible at present, only a phenomenological understanding can be given to explain the occurrence of the metastable structures on the basis of Ostwald's rule. According to this rule, these structures are the high-temperature and/or high-pressure polymorphs of the material. A system undergoing reaction proceeds from a less stable through a series of increasingly more stable intermediate states to reach the final equilibrium state. The formation and high stability of the h c p phase show that this phase seems to be an equilibrium phase of antimony. It is noteworthy that the observed lattice parameters of the h c p structure can be obtained from that of the metastable f c c phase by assuming the same atomic volume for both the f c c and h c p structures. This shows that the metastable f c c phase is a rearrangement of atoms of h c p phase. This is in accordance with the transformation observed in films of Hf, Zr, etc. obtained by sputtering or vapour deposition under different conditions of growth [9].

Clearly, the transformation temperatures, associated heats of transformation and the transformation kinetics of the different metastable crystalline phases need detailed and quantitative investigations in order to throw light on the stability of the different phases. Such work is currently in progress.

4. Conclusions

(1) In addition to the metastable high-pressure simple cubic and h c p phases of Sb, new metastable structures, namely f c c, tetragonal and distorted rhombohedral have been observed.

(2) Transformation studies of the different phases indicate that h c p is a stable phase, possibly stabilized by some gaseous impurities.

(3) Of the simple cubic, f c c and tetragonal phases, f c c and tetragonal seem to be relatively higher energy phases as compared with the simple cubic phase since these phases have not previously been observed. Experiments at high pressures/temperatures may stabilize these phases.

(4) The new rhombohedral phase appears to be a distorted equilibrium phase.

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References

1. S. S. KABALKINA and V. P. MYLOV, *Sov. Phys. Doklady* **8** (1964) 917.
2. T. ICHIKAWA, *Jap. J. Appl. Phys.* **9** (1970) 948.
3. K. L. CHOPRA, "Thin Film Phenomena" (McGraw-Hill, New York, 1969).
4. P. DUWEZ and R. H. WILLENS, *Trans. Met. Soc. AIME* **227** (1963) 362.
5. DILSHAD AKHTAR, V. D. VANKAR, T. C. GOEL and K. L. CHOPRA, *J. Mater. Sci.* **14** (1979) 983.
6. G. M. ROSENBLATT, *J. Chem. Phys.* **45** (1966) 3454.
7. H. L. LUO and W. KLEMENT, Jr., *ibid.* **36** (1962) 1870.
8. B. C. GIESSEN, U. WOLFF and N. J. GRANT, *Trans. Met. Soc. AIME* **242** (1968) 597.
9. K. L. CHOPRA, M. R. RANDLETT and R. H. DUFF, *Appl. Phys. Letters* **9** (1966) 402.

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