

Superconductivity of rapidly condensed films

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With InSb as an example, it was demonstrated that it is possible to produce and stabilize films of crystalline metastable superconducting phases having the structure of high-pressure phases, by rapid condensation on cooled substrates, followed by heat treatment.

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A large number of potential superconductors are phases produced at high pressures (>10 kbar).^[1] The feasibility in principle of obtaining such phases in films at condensation rates exceeding the phase-transition rates was indicated in^[2]. In this case the crystallization goes through intermediate crystalline metastable modification. However, the short lifetime of the metastable phases under the conditions of^[2] (tenth of a second) did not make it possible to investigate their properties. The aim of the present study was to produce and stabilize intermediate phases in InSb films, to determine their nature, and to observe superconductivity.

To study the structural transformations and the superconducting transitions, the films were condensed in an ER-100 electronograph or in a helium cryostat. Films of thickness $L=200$ to 2000 Å were deposited in a vacuum $\sim 10^{-6}$ Torr at a rate ~ 1 $\mu\text{m}/\text{sec}$ simultaneously on Al or C foils in order to investigate the structure in transmission and on glass substrates for electric measurements.^[3] The substrate temperature T_s was varied in the range from 80 to 400 K.

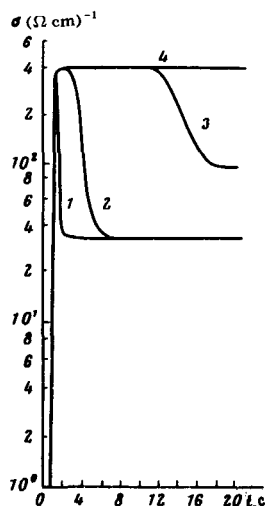


FIG. 1. Oscillograms of $\sigma(t)$ obtained in the course of condensation of films ($L=1300$ Å) at $T_s=263$ K (1), 243 K (2), 233 K (3), and 213 K (4). The time is reckoned from the instant when the evaporator is turned on. The condensation ends prior to the appearance of the conductivity peak.

TABLE I.

T, K	Structure type	a , Å	b , Å	c , Å	ρ , g cm ⁻³
200 - 240	InSb IV	3.035	5.79	3.084	7.25
	InSb II (β -Sn)	5.982	—	3.181	6.92
	NaCl	6.120	—	—	6.85
> 240	Wurtzite	4.553	—	7.543	5.80
	Sphalerite	6.478	—	—	5.78

In the investigated intervals of T_s and L , condensation results in an amorphous phase with low conductance σ (on Fig. 1—up to the conductivity peak). At $T_s > 200$ K, a smooth increase of the radii of the coordination spheres takes place in the amorphous phase, followed by spontaneous crystallization accompanied by a sharp increase of σ (see Fig. 1), and the film is transformed into a polycrystalline mixture of metastable phases analogous in structure to the high-pressure metallic phases.^[4,5] In the course of time, beyond the conductivity peak, the metastable phases go over into a mixture of stable polycrystalline sphalerite and wurtzite phases with semiconductor conductivity σ . As seen from Fig. 1, lowering T_s increases the lifetime of the metastable phases. Whereas the lifetime for $T_s \approx 260$ K is 0.15 sec, at $T_s \approx 230$ K it is 12 sec.

The films remain amorphous at $T_s < 200$ K (Fig. 2, region I). Heating these films has made it possible to determine the temperatures of the phase transitions. Near 200 K, the amorphous phase goes over into metastable phases that

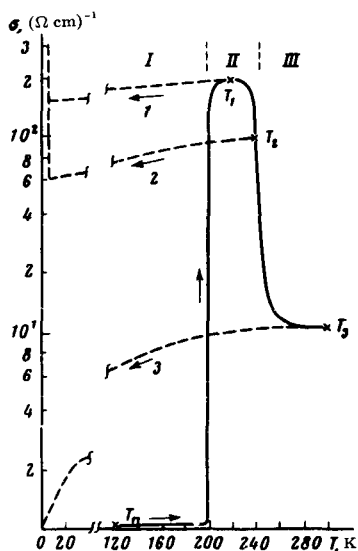


FIG. 2. Effect of heat treatment on σ of films condensed at $T_s < 200$ K.

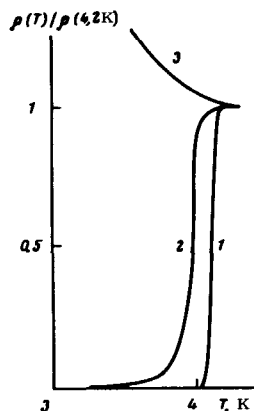


FIG. 3. Relative resistivity of films ($L = 300 \text{ \AA}$) vs T after different heat-treatment cycles. The numbering of the curves corresponds to the heat-treatment cycles shown in Fig. 2.

are preserved up to 240 K (region II), and above 240 we get a stable mixture of sphalerite and wurtzite (region III). Table I lists the structure types, the calculated lattice parameters, and the densities of the crystalline phases observed when amorphous films are heated in different temperature regions. The number of simultaneously present metastable phases depends on the type of substrate. In films condensed on aluminum foils, the preferred phase is InSb II, whereas on a carbon foil a mixture of all phases is observed as a rule. On going to the final state, the phases that is preserved the longest is the one with the NaCl lattice, having the lowest density of all the high-pressure phases.

The metastable phases obtained when amorphous films are heated to 200–240 K are “frozen” by subsequent cooling and go over in the region of helium temperatures into the superconducting state. Figure 2 shows the heat-treatment cycles (dashed lines 1, 2, and 3) of films condensed at $T_s = 120 \text{ K}$, and then heated to T_1 , T_2 , or T_3 and cooled to helium temperature. The behavior of the film resistivity at helium temperatures after the indicated cycles is shown in Fig. 3. The metastable-phase films obtained via cycle 1 have an abrupt superconducting transition near 4.1 K. The sphalerite-wurtzite mixture (cycle 3) has no superconductivity down to 1.5 K. The superconducting transition of films with a mixture of metastable and final phases (cycle 3) becomes smeared out and the critical temperature is decreased.

It has thus been observed that under conditions of fast condensation, a crystallization mechanism is realized via intermediate metastable high-pressure phases that are superconducting. The obtained regularity is apparently general in character. This is corroborated by experiments with Sb and Bi films, which assumed a highly conducting metastable state in the intervals 115–245 and 90–270 K, respectively. The results uncover in principle new ways of obtaining and stabilizing superconducting metastable phases.

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