References and Notes

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Superconducting Gallium Antimonide

Abstract. *A metallic phase of gallium antimonide, obtained by quenching at approximately 120 kilobars to 77°K and then releasing pressure, is a superconductor. The transition temperature depends on the annealing conditions; for samples annealed at 250°C under pressure before quenching, it is 4.24° ± 0.10°K, and H_{c2} (the critical field) equals 2640 gauss at 3.50°K. This temperature is higher than the 2.1°K reported for metallic indium antimonide.*

Gallium antimonide transforms from a semiconducting to a metallic state at approximately 70 kb at 25°C (*1*). X-ray powder photographs taken at high pressures show that the metallic phase has a structure similar to that of white tin (*2*). Recently the high-pressure phase has been retained by quenching the sample to 77°K before releasing pressure (*3, 4*). X-ray powder photographs taken at 77°K and 1 bar confirm the "white tin" structure and indicate that the high-pressure phase has been retained (*3*). Because the metallic phase of indium antimonide is superconducting at 2.1°K (*5*), we have determined the superconducting properties of metallic gallium antimonide in order to compare them with those of InSb.

Three different sources of gallium antimonide were used: (i) single-crystal material from Merck and Co., (ii) single-crystal GaSb doped with about 0.01 percent Te to reduce the possibility of excess gallium (*6*), and (iii) *p*-type polycrystalline material from American Smelting and Refining Co. (Asarco). The samples were compressed between tungsten carbide anvils with 2.4-mm faces to an average pressure of 120 kb and then cooled to 77°K before pressure was released; some were annealed by heating the anvils before quenching. The resulting samples were discs ~ 0.05 mm thick and 2.5 mm in diameter. The samples were transferred at 77°K to a helium cryostat and tested for superconductivity by the alternating-current method (*7*).

Superconducting properties of the quenched gallium antimonide apparently depend on the annealing conditions (Table 1). The transition temperature, T_c, and the hardness (that is, the relative strength of the magnetic field necessary to destroy the superconducting state) vary differently with annealing. Annealing at temperatures above 100°C causes T_c to drop from 5.9° toward 4.2°K; annealing at 50°C appears to make the samples magnetically softer. An annealed and an unannealed sample were reconverted by warming them to room temperature. X-ray powder photographs of the reconverted material showed two broad halos centered around the first few lines of the zinc-blende structure. These samples were tested for superconductivity, and the negative result indicated that the retained phase is responsible for the observed superconductivity. X-ray diffraction patterns taken at 77°K of annealed (200°C) and unannealed samples show the "white tin" structure. The data were not sufficiently accurate to determine whether there was a small systematic variation in lattice parameter with annealing. The samples annealed at 200°C also showed two faint additional lines at 3.3 and 1.65 Å. These lines may be attributable to small amounts of $GaSbO_4$, but when an annealed sample was reconverted by heating for 1 hour at 200°C an x-ray photograph showed only the diffraction lines of the zinc-blende form of GaSb. If the additional lines at 3.3 and 1.65 Å were from $GaSbO_4$ they should have appeared in the film of the reconverted material.

The large change in T_c for GaSb observed on annealing may result from an order–disorder transition or from the relief of strains in the sample. The extra faint lines observed in the annealed samples may be superstructure lines; for example, the 111 and 222 reflections for a cell with the *c*-axis of the "white tin" structure doubled. However, available data do not permit an unambiguous description.

It is also known that strain can substantially change the transition temperature. For example, a difference of > 1°K was observed in annealed and unannealed specimens of Nb containing 10 percent Cr (*8*). There was similar change in samples of InTe quenched from high pressures and tem-

Table 1. Superconductivity of GaSb; eight independent experiments.

Sample	T_c (°K)	H (gauss)	Annealing Temp. (°C)	Annealing Time (min)	Source
2544	4.20–4.28 3.46	0 2640	250	60	Merck
2522	4.24–4.38 3.82 3.50	0 1640 2640	200	90	Te "doped"
2530	4.24–4.38 4.12	0 660	200	15	Merck
2529	4.45–4.90 (4.2 ± 0.5)*	0 (1000)	100	45	Merck
2534	5.85–6.05 (3 ± 1)*	0 (4600)	50	30	Asarco
2519	5.85–6.15 5.44	0 4600			Te doped
2523	5.75–6.05	0			Merck
2507	5.40–6.15	0			Merck

* Obtained by cycling the magnetic field at about constant temperature.