

References and Notes

1. C. T. Ewing, J. A. Grand, R. R. Miller, *J. Am. Chem. Soc.* **74**, 11 (1952); *J. Phys. Chem.* **58**, 1086 (1954).
2. C. T. Ewing, J. P. Stone, J. R. Spann, E. W. Steinkuller, D. D. Williams, R. R. Miller, "High Temperature Properties of Sodium and Potassium," *12th Progress Report for U.S. Naval Research Laboratory, NRL Rept. 6094* (Washington, D.C., 9 June 1964).
3. A. W. Lemmon, Jr., H. W. Deem, E. A. Aldridge, E. H. Hall, J. Matolich, Jr., J. F. Walling, "Engineering Properties of Potassium," *NASA CR-54017, BATT-4673-Final* (Battelle Institute, Columbus, Ohio, 1963).
4. I. I. Novikov *et al.*, *J. Nucl. Energy* **4**, 387 (1957).
5. A. V. Grosse, *Science* **140**, 784 (Table 4) (1963).
6. ———, *J. Phys. Chem.* **68**, 3419 (1964).
7. ———, *J. Inorg. Nucl. Chem.* **22**, 23 (1961).
8. E. N. da C. Andrade, *Phil. Mag.* **17**, 698 (1934); both his I and II equations are also fully discussed in ref. 7.
9. M. Sittig, "Sodium, Its Manufacture, Preparation and Uses," *Am. Chem. Soc. Monogr. No. 133* (Reinhold, New York, 1956), pp. 456-461.
10. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 14.
11. L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N.Y., ed. 3, 1960), p. 403.
12. For mercury, the constant is 83×10^{-4} ; thus it may change to some extent in the various families of the periodic system.
13. O. A. Hougen and K. M. Watson, *Chemical Process Principles* (Wiley, New York, 1943), vol. 3, p. 873.
14. A. V. Grosse, *Inorg. Chem.* **1**, 436 (1962).
15. This work was supported by AEC contract AT(30-1)-2082.
16. January 1965

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 $4.24^\circ \pm 0.10^\circ\text{K}$, 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 re-

converted 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 GaSbO₄, 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 GaSbO₄ 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 $> 1^\circ\text{K}$ 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		Source
			Temp. (°C)	Time (min)	
2544	4.20-4.28	0	250	60	Merck
	3.46	2640			
2522	4.24-4.38	0	200	90	Te "doped"
	3.82	1640			
	3.50	2640			
2530	4.24-4.38	0	200	15	Merck
	4.12	660			
2529	4.45-4.90	0	100	45	Merck
	(4.2 $\pm$ 0.5)*	(1000)			
2534	5.85-6.05	0	50	30	Asarco
	(3 $\pm$ 1)*	(4600)			
2519	5.85-6.15	0			Te doped
	5.44	4600			
2523	5.75-6.05	0			Merck
2507	5.40-6.15	0			Merck

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

perature (9). In each case the sharp transition to the superconducting phase in the annealed samples is almost certainly representative of the equilibrium properties of metallic gallium antimonide; it seems reasonable to conclude that the transition temperature is $4.24^\circ \pm 0.10^\circ\text{K}$.

The first change of the detector coil from the normal state on cooling at different magnetic fields can be taken as the definition of H_{c2} . So defined H_{c2} is 2640 gauss at 3.5°K for the annealed samples, and it decreases almost linearly with temperature to the transition.

The transition temperature for GaSb ($4.24^\circ \pm 0.10^\circ\text{K}$) is higher than that for InSb [2.1°K (5)] or Sn (3.7°K) which have similar crystal structures. This trend is similar to that in the superconducting phases of Group IIIB elements—Tl, 2.36°K ; In, 3.396°K ; Ga(II), 7.5°K (10)—but opposite to that of Group VB elements—Bi(III), 7.25°K at 28 kb (11, 12); Bi(II), 3.92°K at 25 kb (12); Sb, $2.6^\circ\text{--}2.7^\circ\text{K}$ (13).

D. B. MCWHAN

G. W. HULL, JR.

Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

T. R. R. McDONALD

E. GREGORY

Central Research Laboratories,
Air Reduction Company, Inc.,
Murray Hill

References and Notes

1. S. Minomura and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 451 (1962); A. Jayaraman, W. Klement, Jr., G. C. Kennedy, *Phys. Rev.* **130**, 540 (1963).
2. J. C. Jamieson, *Science* **139**, 845 (1963).
3. T. R. R. McDonald, R. Sard, E. Gregory, *J. Appl. Phys.*, in press.
4. T. R. R. McDonald, G. S. Barberich, E. Gregory, paper 64-WA/PT-4, meeting of Amer. Soc. Mech. Engineers, New York, December 1964.
5. H. E. Bommel, A. J. Darnell, W. F. Libby, B. R. Tittmann, *Science* **139**, 1301 (1963); S. Geller, D. B. McWhan, G. W. Hull, Jr., *ibid.* **140**, 62 (1963).
6. We thank C. D. Thurmond for discussions on the properties of GaSb and for supplying the tellurium-doped gallium antimonide crystals.
7. A. L. Schawlow and G. E. Devlin, *Phys. Rev.* **113**, 120 (1959).
8. J. K. Hulm and R. D. Blaugher, *ibid.* **123**, 1569 (1961).
9. B. R. Tittmann, A. J. Darnell, H. E. Bommel, W. F. Libby, *ibid.* **135**, 1460A (1964).
10. W. Buckel and W. Gey, *Z. Physik* **176**, 336 (1963).
11. P. F. Chester and G. O. Jones, *Phil. Mag.* **44**, 1281 (1953).
12. N. B. Brandt and N. I. Ginzburg, *Zh. Eksperim. i Teor. Fiz.* **39**, 1554 (1960); English transl., *Sov. Phys. JEPT* **12**, 1082 (1961).
13. T. R. R. McDonald, E. Gregory, G. S. Barberich, D. B. McWhan, T. H. Geballe, G. W. Hull, Jr., *Phys. Letters* **14**, 16 (1965).
14. We thank T. H. Geballe for his interest and for helpful discussions, and G. S. Barberich and V. T. Cunicella for the preparative and x-ray work.

29 December 1964

Sodium Pump: Its Electrical Effects in Skeletal Muscle

Abstract. *The variations in the membrane potentials of skeletal muscle fibers which follow high rates of sodium extrusion are not due to changes in the ionic concentrations of the fiber; experiments suggest that sodium is extruded by an electrogenic mechanism.*

One of the problems in studying the mechanism by which ionic concentrations in nerve and muscle are maintained in a steady state at rest, in spite of the electrochemical gradient, is that of determining whether the sodium pump is electrically neutral or not.

The possibility of an electroneutral pump moving a potassium ion inward for each sodium ion that passes out was first suggested for red cells by Shaw (1) and by Hodgkin and Keynes (2) for nonmyelinated nerve fibers; a linkage between the fluxes of both ions has also been suggested for skeletal muscle (3). According to the results obtained by Kernan (4), Keynes and Rybova (5), and Mullins and Awad (6), however, the sodium pump is not electroneutral in skeletal muscle; Mullins and Noda (7) hold that if there is a linkage between the sodium and potassium pumps, the coupling ratio cannot be higher than one potassium ion pumped in for each three sodium ions pumped out; this makes the mechanism nonelectroneutral. In this report new evidence is presented in favor of the non-neutrality of the sodium pump in the skeletal muscle of the South American frog.

If there exists in the muscle membrane a potassium pump linked in some way to the sodium extrusion mechanism, the equivalent electric circuit of the membrane (8) may be expanded by adding two direct-current (constant or not) generators, representing the pumps, as shown in Fig. 1.

In such a circuit, the membrane potential difference $V_o - V_i$ may be altered by two mechanisms; (i) by changing the currents $i_{Na,p}$ and $i_{K,p}$ generated by the pumps; (ii) by causing a change in the electromotive forces E_K , E_{Na} and E_{Cl} , which represent, respectively, the equilibrium potential for K^+ , Na^+ , and Cl^- . If the two pumped currents compensate each other (the pump being neutral), the first mechanism by itself will not produce any change in the potential, but a change in the membrane potential will appear as soon as the rate of pumping is changed if the pump is

Table 1. Changes in membrane potential and extrusion of sodium.

Expt.	Extrusion of Na (mmole liter ⁻¹ min ⁻¹)	Membrane potential		Corrected potential (mv)
		At 3°C (mv)	At 25°C (mv)	
A	0.18	79	96	10
B	.50	46	92	42
C	.36	46	76	26
D	.29	63	86	17
E	.23	61	76	9
F	.24	63	77	8
G	.15	61	73	6
H	.11	63	77	8

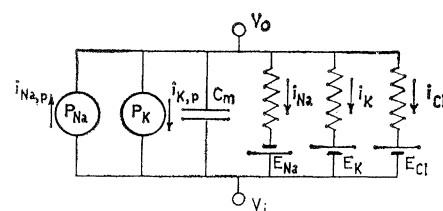


Fig. 1. Equivalent electric circuit of the membrane. E_{Na} , E_K , and E_{Cl} are the equilibrium potentials of Na^+ , K^+ , and Cl^- , respectively; C_m is membrane capacity; i_{Na} , i_K , and i_{Cl} are the passive currents of Na^+ , K^+ , and Cl^- . P_{Na} and P_K are ion permeabilities; $i_{Na,p}$ and $i_{K,p}$ are the currents generated by the Na and K pumps; V_o and V_i are potentials outside and inside the membrane.

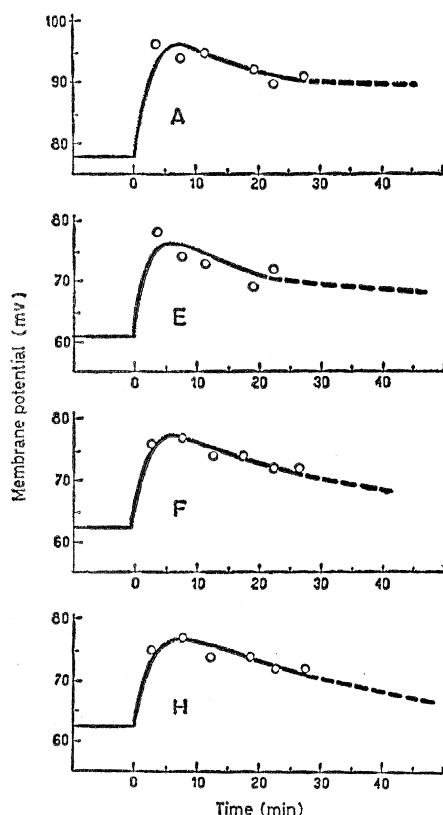


Fig. 2. Membrane potential plotted against time for muscles A, E, F, and H (see Table 1). Each point is a mean of 10 to 12 punctures.