

FIG. 1. Heat capacity of niobium below 6°K.

A C_v/T vs T^2 plot of the experimental data for the superconducting phase at the lowest temperatures is shown in Fig. 1 (open circles). The solid line through the origin gives the best fit for a T^3 specific heat dependence with no linear term, i.e., $C_s = 464(T/\theta_s)^3$, with $\theta_s = 161^\circ$. (Superconducting data at higher temperatures are shown in Fig. 2.) It will be noted that below 4.5°K the data lie below the solid line, the departure being definitely greater than the estimated experimental error. It thus appears that for niobium the superconducting specific heat below 4.5°K falls off more rapidly than a T^3 law would allow. It would be of considerable theoretical interest to know whether a departure of this kind is a general property of the superconducting phase at very low temperatures or whether this behavior is peculiar to niobium, or to take a more pessimistic point of view, only to the present specimen. There is not enough information on low temperature heat capacities to choose among these possibilities. In the published papers on low temperature heat capacities this effect either has not been noticed or the data have too much scatter to determine if it is present.

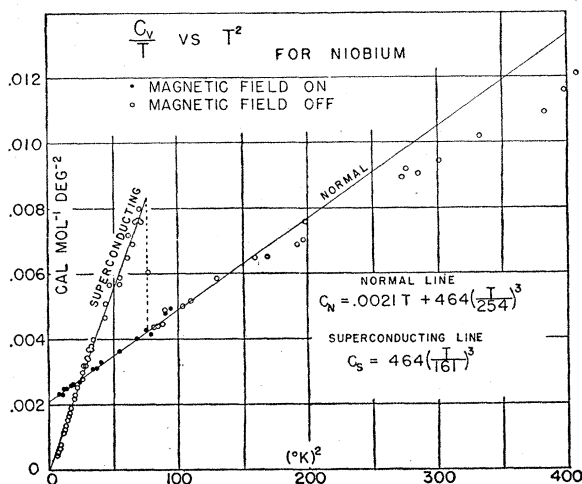


FIG. 2. Heat capacity of niobium below 20°K.

In contrast with the behavior of the specific heat in the superconducting phase, the specific heat in the normal phase follows the usual relation $C_n = \gamma T + 464(T/\theta_n)^3$, where in this case the constants θ_n and γ are 254° and 21.0×10^{-4} cal/mol-deg 2 . The specific heat expressed in this way fits the data from the lowest measured temperature to about 12°K, above which the experimental points fall below those predicted by the equation (see Fig. 2). This is interpreted as indicating that the Debye characteristic temperature changes, a value of 268° being appropriate to 20°K. This behavior was expected since earlier determinations of the specific heat made in this laboratory at liquid nitrogen temperatures gave a value for θ_n of about 280° .

If we assume an ideal case for which the superconductor follows the parabolic relation, $H = H_0(1 - T^2/T_0^2)$, between the critical magnetic field, H , and the absolute temperature, and also for which the superconductor has thermodynamically reversible transitions between the normal and superconducting phases, then a number of well-known relations⁵ hold among the following quantities, H_0 , $(dH/dT)T = T_0$, γ , T_0 , $T C_n = C_s$, $(\Delta C)T = T_0$. (The last four of these were determined independently in this experiment.) With the aid of these relations, any pair of experimental values, except the pair T_0 and $T C_n = C_s$, serves to determine all the other quantities. When H_0 is chosen to be 1960 gauss (a value considerably lower than any previously reported), complete consistency was found between the theoretical relations and the experimental data. In other words, the heat capacity data reported here correspond to the behavior of a sample of niobium which undergoes reversible transitions and which follows the parabolic relation with the constants $H_0 = 1960$ gauss, $T_0 = 8.7^\circ$ K.

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‡ Assisted by the ONR and Linde Air Products Company.

§ J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

¶ Cook, Zemansky, and Boorse, Phys. Rev. **80**, 737 (1950).

‡ L. C. Jackson and H. Preston-Thomas, Phil. Mag. **41**, 1284 (1950).

§ Brown, Zemansky, and Boorse, Phys. Rev. **84**, 1050 (1951).

¶ M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1951), third edition, p. 369.

Total Collision Cross Sections of Negative Atomic Iodine Ions in Nitrogen and Argon

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(Received February 14, 1952)

THE total collision cross sections of positive ions in gases have been measured for several cases,¹ but no previous measurements have been reported for negative ions. A convenient instrument for measuring these cross sections is a Bennett radio-frequency mass spectrometer.²

The source of negative atomic iodine ions was an oxide-coated cathode that had been previously exposed to iodine fumes. The iodine poisoned the cathode so that it emitted negative iodine ions but no electrons when heated. These ions were accelerated and passed through the mass spectrometer, and a fraction of them was detected at the plate of the spectrometer. If I_0 is the current due to the iodine ions at the plate of the spectrometer with a high vacuum in the spectrometer tube, the ion current I , when gas at a pressure p is introduced in the path of the ions, is

$$I = I_0 e^{-\sigma p L / kT},$$

where σ is the cross section for collisions between the ions and gas molecules which prevent the ions from reaching the plate, L is the distance the ions travel in the gas, k is Boltzmann's constant, and T is the temperature of the gas. The value of σ can be calculated from the slope of the straight line obtained by plotting $\ln I$ against p . Some typical curves are shown in Fig. 1.

The Bennett mass spectrometer does not require that the ions be formed in a narrow beam, so a measurable ion current is more easily obtained than in a magnetic type of spectrometer. Measurements were made at pressures from 10^{-5} to 6×10^{-4} mm of Hg.

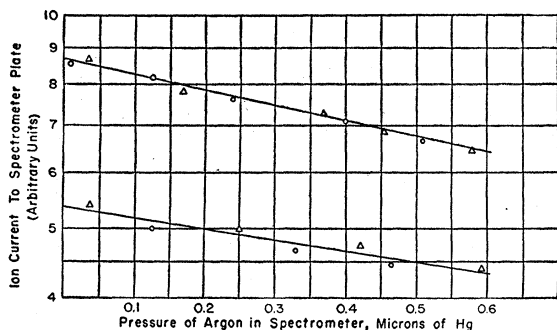


FIG. 1. Typical curves used to calculate the total cross section of ions of 400-volts energy in argon. The readings indicated by triangles were taken as the pressure was increased, and then the readings indicated by circles were taken as the pressure was reduced.

These pressures were measured on an ionization gauge calibrated for each gas. A weak magnetic field applied across the ion beam swept out stray electrons.

Considerable scattering of the measured cross sections was observed, which was partially a result of variations in emission from the cathode during a particular run. This variation can be seen in Fig. 2. The gases used should not react chemically with the cathode and did not appear to affect the ion yield. The temperature of the cathode was measured by means of a thermocouple but was found not to vary appreciably with the gas pressure or variations in the heater current. Therefore the variation in emission was not mainly caused by variation in the temperature of the cathode or gas pressure.

The types of collisions that are expected are elastic collisions, de-ionization of the iodine ion by a neutral molecule, and inelastic collisions. Charge transfer is not possible, as the gases used do not form negative ions. De-ionization of a negative ion produces a neutral atom which will not be detected. The energy selection of the spectrometer prevents all ions slowed down by more than one volt from reaching the plate. Therefore, all ionizing and nearly all inelastic collisions are included in the measured cross section. Elastic collisions prevent the ions from reaching the plate if the decrease in the velocity along the axis of the tube corresponds to more than one volt. For ions of 20 volts energy this corresponds to scattering of more than 6° and for ions of 400 volts, more than 1.4° from conservation of energy and momentum.

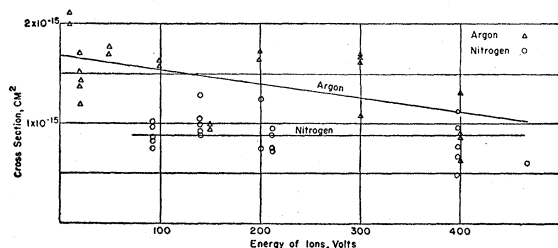


FIG. 2. The measured cross sections for collisions of negative iodine ions in argon and nitrogen.

The average value of the measured cross section in nitrogen was 9×10^{-16} cm². The measured cross section was constant within the accuracy of the measurements from 100 to 400 volts. The average value of the measured cross section in argon was 14×10^{-16} cm². The measured cross section appeared to decrease slightly from 10 to 400 volts, and the decrease was on the borderline of experimental error. The accuracy of both averages is estimated to be $\pm 3 \times 10^{-16}$ cm².

¹ For example, R. B. Kennard, Phys. Rev. 31, 423 (1928); A. J. Dempster, Phil. Mag. 3, 115 (1927); G. P. Thomson, Phil. Mag. 2, 1076 (1926); C. Ramsauer and O. Beek, Ann. Physik 87, 1 (1928); J. S. Thompson, Phys. Rev. 35, 1196 (1930).

² W. H. Bennett, J. Appl. Phys. 21, 143 (1950).

Diffusion of Donor and Acceptor Elements into Germanium*

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(Received January 25, 1952)

WHEN donor or acceptor elements diffuse into *p*-type or *n*-type germanium, respectively, *pn* barriers are formed. By determining the distance of these barriers for two specimens of different but known original conductivities, the diffusion constant, *D*, as well as the surface concentration, *C*₀, can be determined from

$$\frac{\sigma_1}{q\mu} = C_0 \operatorname{erfc} \left[\frac{x_1}{2(Dt)^{1/2}} \right], \quad \frac{\sigma_2}{q\mu} = C_0 \operatorname{erfc} \left[\frac{x_2}{2(Dt)^{1/2}} \right], \quad (1)$$

where σ_1, σ_2 are the original conductivities in ohm⁻¹ cm⁻¹; *q*=elementary charge, 1.6×10^{-19} coulombs; μ =carrier mobility, 3600 cm²/volt sec for *n* type, 1700 cm²/volt sec for *p*-type; *erfc*=error function complement,

$$1 - \frac{2}{\sqrt{\pi}} \int_{-x/2(Dt)^{1/2}}^0 \exp(-\beta^2) d\beta;$$

*x*₁, *x*₂=corresponding diffusion distances of barriers in cm; *D*=diffusion constant in cm²/sec; *t*=time in seconds, and *C*₀=the surface concentration in cm⁻³, assumed to be constant and the same for both specimens.

In Eq. (1) the quantity $\sigma/q\mu$ is the concentration of the carriers in the original germanium. This at the boundary is equal to the concentration of diffusing atoms if we assume each atom supplies one electron to the conduction band or one hole to the filled band.

Thus, in a given experiment, Eq. (1) allows *D* to be calculated from the ratio of the conductivities (*p* or *n*) of two specimens exposed to the same surface concentration of donor or acceptor element, respectively, from the relation

$$\operatorname{erfc} \left[\frac{x_1}{2(Dt)^{1/2}} \right] / \operatorname{erfc} \left[\frac{x_2}{2(Dt)^{1/2}} \right] = \frac{\sigma_1}{\sigma_2}. \quad (2)$$

When *D* is known, *C*₀ is obtainable from (1).

Specimens of single crystal *p*-type germanium containing gallium have been subjected to both arsenic and antimony diffusion. Similar specimens of *n*-type germanium have been diffused with indium. The barrier positions were determined by means of a "cold" tungsten probe employing contact rectification as an indicator and by means of a "hot" tungsten probe connected to a galvanometer to measure the sign of the thermoelectric voltage. The hot probe method in most instances gave somewhat lower values for the barrier distances. Values of *D*

TABLE I. Data for antimony and arsenic diffusion into germanium.

<i>T</i> (°C)	(Time) ¹ (sec) ²	$\frac{\sigma_1}{q\mu}$ (ohm ⁻¹ cm ⁻¹)	$\frac{\sigma_2}{q\mu}$ (ohm ⁻¹ cm ⁻¹)	<i>x</i> ₁ (cm)	<i>x</i> ₂ (cm)	<i>D</i> × 10 ¹⁰ cm ² /sec	<i>C</i> ₀ (cm ⁻³)
Antimony							
710	778	14.5	1.12	0.0038	0.0045	0.03	2.0×10^{20}
755	761	11.1	0.50	0.0084	0.0123	0.13	3.2×10^{19}
810	564	32.3	1.08	0.0152	0.0229	0.76	1.8×10^{18}
850	922	52.6	1.25	0.0350	0.0399	0.37	1.0×10^{22}
850	704	52.6	1.25	0.0186	0.0265	0.51	2.9×10^{19}
850	481	13.5	1.30	0.0166	0.0217	0.96	4.4×10^{18}
850	481	13.5	1.30	0.0180	0.0227	0.96	7.0×10^{18}
905	408	32.3	1.08	0.0154	0.0263	2.3	7.2×10^{17}
Arsenic							
710	778	13.5	1.12	0.0064	0.0075	0.01	1.0×10^{20}
750	831	11.1	1.30	0.0127	0.0138	0.05	1.0×10^{20a}
755	761	11.1	0.50	0.0150	0.0164	(0.09) ^a 0.04	1.0×10^{20a}
800	613	16.7	5.6	0.0112	0.0133	0.36	3.0×10^{18}
800	487	16.7	8.3	0.0038	0.0052	0.36	3.0×10^{17}
850	701	76.9	12.5	0.0183	0.0350	1.2	1.5×10^{18}
850	920	76.9	12.5	0.0169	0.0355	0.79	2.2×10^{18}
905	701	14.3	1.08	0.0222	0.0333	1.4	1.0×10^{18}

^a These values of *D* are calculated assuming *C*₀ = 1.0×10^{20} .