of the hydrogen spin-exchange cross section in hydrogen-hydrogen collisions. This could be done in the hydrogen maser.[14] In that case, since the population inversion is obtained through magnetic selection, the atomic beam would be pulsed. This experiment would be of basic importance because a large amount of theoretical work has been done on spin-exchange interactions between hydrogen atoms and because little experimental data are available.

The author has benefited from several discussions with Dr. R. F. Lacey and Professor R. Novick. The work described above has been funded by the U. S. Electronics Command, Fort Monmouth, New Jersey.

[1]H. Warren Moos and Richard H. Sands, Phys. Rev. 135, A591 (1964).
[2]L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. 133, A607 (1963).
[3]Hyatt Gibbs, thesis, University of California, Lawrance Radiation Laboratory, 1965 (unpublished); H. M. Gibbs and R. J. Hull, Phys. Rev. 153, 132 (1967).
[4]S. M. Jarrett, Phys. Rev. 133, A111 (1964).
[5]P. Franken, R. Sands, and J. Hobart, Phys. Rev. Letters 1, 118 (1959).
[6]R. Novick and H. E. Peters, Phys. Rev. Letters 1, 54 (1958).
[7]Marie Anne Boushat, Etude par Pompage Optique de la Relaxation de Rubidium, Publications Scientifiques et Techniques du Ministere de l'Air, Paris (Service de Documentation et d'Information Technique de l'Aeronautique, Paris, France, 1965).
[8]S. M. Jarrett and P. A. Franken, J. Opt. Soc. Am. 55, 1603 (1965).
[9]Stanley Bloom, J. Appl. Phys. 27, 785 (1956).
[10]P. Davidovits and W. A. Stern, Appl. Phys. Letters 6, 20 (1965).
[11]C. O. Alley, "Investigation of the Effect of Gas Collisions and Optical Pumping on the Breadth of Spectral Lines," Final Report on Optical Detection Phase, Palmer Physical Laboratory, Princeton University, Princeton, New Jersey, 1960 (unpublished).
[12]J. P. Wittke and R. H. Dicke, Phys. Rev. 103, 620 (1956).
[13]M. Arditi and T. R. Carver, Phys. Rev. 136, A643 (1964).
[14]H. M. Goldenberg, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters 5, 361 (1960).

STRONG-COUPLING SUPERCONDUCTIVITY IN GALLIUM

Roger W. Cohen, B. Abeles, and Gabriel S. Weisbarth
RCA Laboratories, Princeton, New Jersey
(Received 12 January 1967; revised manuscript received 10 February 1967)

Ordinary gallium has a superconducting energy gap $\Delta_0 = 0.16$ mV and is a weak-coupling superconductor ($2\Delta/k_B T_C = 3.5$). We have prepared Ga films which exhibit three distinct energy gaps: $\Delta_1 = 1.03$ mV, $\Delta_2 = 1.38$ mV, and $\Delta_3 = 1.53$ mV. The corresponding values of $2\Delta/k_B T_C$ are substantially larger than the BCS value[1] 3.5, indicating strong-coupling superconductivity. We believe that the three energy gaps are those of three high-T_C modifications of Ga present in the films. The high Δ's can be accounted for by an increase in N, the density of electronic states at the Fermi surface, above that of ordinary gallium, which has the lowest value of N of all superconductive elements.[2]

The Ga films were evaporated from an alumina-coated tungsten filament at the rate of 70 Å/sec onto a microscope slide at room temperature. An oxygen pressure of 10^{-4} mm Hg was maintained during the evaporation. The oxygen provides nucleation centers for the film to grow in the form of extremely small particles.[3] The small particle size is favorable for the formation of high-T_C phases of gallium.[4] The T_C of the films did not change significantly upon storing at room temperature for several days. Emission spectroscopy of the films showed a metallic impurity content of less than 0.1%.

The energy gaps were determined by means of tunneling measurements using Al-Al_xO_y-Ga, Sn-Sn_xO_y-Ga, and Ga-Ga_xO_y-Pb junctions. The junctions were made of crossed strips of the two metals; the width of the Ga and Al strips was 1 mm, while that of the Pb or Sn strips was 0.5 mm. The Ga-Pb junctions were made by first evaporating a 500-Å-thick Ga film, letting it oxidize in air for 2 h, and then evaporating a 1500-Å-thick Pb film on top of the Ga. If the Ga film was evaporated on top of the Pb, the resulting junctions always had elec-

trical shorts. In the case of the Al-Ga and Sn-Ga junctions, the Al and Sn were evaporated first. The Ga which was evaporated on top of these metals was 2000 Å thick. The resistive transitions of the gallium films were very broad, extending from about 5 to about 8°K. The temperature coefficient of the normal resistivity was negative; at 8°K the resistivities were about 1×10^{-3} Ω cm and this value decreased by a factor of 2 upon warming to room temperature. The aluminum films had an enhanced[3] $T_c = 2.3$°K and an energy gap $\Delta_{Al} = 0.31$ mV.

In Fig. 1 are shown the dI/dV-vs-V characteristics of an Al-Ga and a Ga-Pb junction taken at 1.4°K. The complex structure of the Al-Ga junction can be consistently interpreted by assuming the existence of three distinct Ga gaps: $\Delta_1 = 1.03$ mV, $\Delta_2 = 1.38$ mV, and $\Delta_3 = 1.53$ mV. The criteria for establishing the values of the various gaps are as follows: (a) The values of $(\Delta_2-\Delta_1)$ and $(\Delta_3-\Delta_2)$ are given by the voltage differences between the three main conductance peaks, (b) the values of $(\Delta_{1,2}-\Delta_{Al})$ are given by the position of the conductance maxima due to thermally excited quasiparticles, and (c) the point $(\Delta_1+\Delta_{Al})$ is established according to the criterion of Douglass and Meservey,[5] i.e.,

$$dI/dV\,|_{V=\Delta_1+\Delta_{Al}} = dI/dV\,|_{V=\Delta_1-\Delta_{Al}}.$$

The peak at $(\Delta_3-\Delta_{Al})$ was not resolved; we have, in any case, indicated where it is expected to occur. In the Ga-Pb junction the peaks due to thermally excited quasiparticle tunneling are not discernable at this temperature. The peak at $V=0$ is believed to be due to a Josephson current. The lead energy gap $\Delta_{Pb} = 1.37$ mV was determined from an extrapolation of measurements at higher temperatures (where peaks due to thermally excited quasiparticles were discernable). Using this value of Δ_{Pb}, the values of the Ga gaps so obtained agree with Δ_1 and Δ_2 obtained from the Al-Ga junction. The gap Δ_3, absent in the Ga-Pb junction in Fig. 1, was observed only in Al-Ga junctions. Measurements on a total of nine junctions yielded the same values of Δ_1 and Δ_2 to within 3%.

The temperature dependence of the Ga energy gaps $\Delta_1(T)$ and $\Delta_2(T)$, measured on the Ga-Pb junction, is shown in Fig. 2 by the open circles. The solid lines represent the BCS temperature dependence of the energy gap $\Delta(T)$ for the indicated T_c's and $\Delta(0)$'s. In both cases, the fit between the theoretical and the experimental points is very good for $T \lesssim 5$°K; for $T \gtrsim 5$°K, the measured values fall below the theoretical curve. Similar departures were also seen in the temperature dependence of the Pb energy gap. The effect is believed to result from the fact that the Ga strip became resistive at $T \sim 5$°K. In that case, the voltage mea-

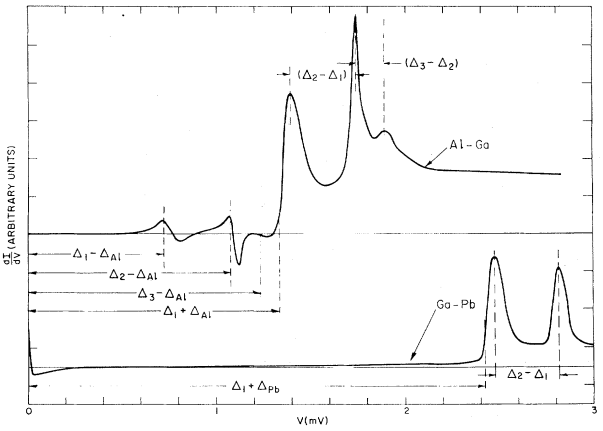

FIG. 1. dI/dV-vs-V characteristics of Al-Ga and Ga-Pb junctions measured at 1.4°K. The voltages at which the various peaks occur are expressed in terms of the Al gap Δ_{Al}, the Pb gap Δ_{Pb}, and the gaps $\Delta_{1,2,3}$ of the three modifications of Ga. The normal resistances of the junctions were about 10 Ω.

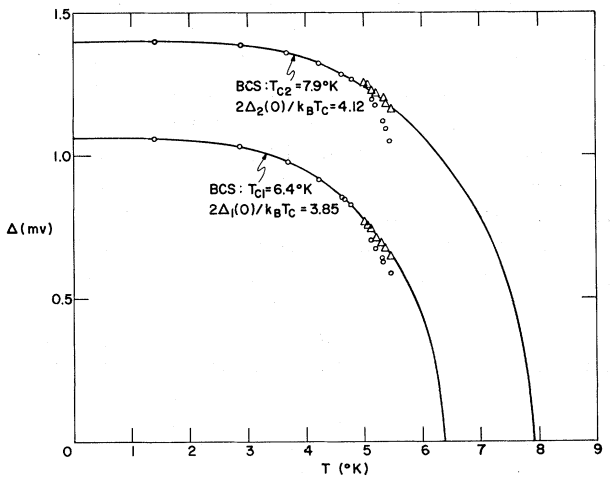

FIG. 2. The temperature dependence of the Ga energy gaps Δ_1 and Δ_2. The solid lines represent the BCS temperature dependence for the indicated values of T_c and $2\Delta(0)/k_BT_c$. The open circles represent uncorrected data points, while the triangles are points which were corrected to take account of the voltage drop in the Ga film (for clarity, the open circles were omitted in those cases where they overlapped with the triangles).

sured between the ends of the crossed strips is given by[6] $V_{meas} = \alpha I R_t$, where $\alpha = (R_S/R_t)^{1/2}/\sinh[(R_S/R_t)^{1/2}]$, I is the tunneling current, R_t is the tunneling resistance, and R_S is the resistance of the part of the Ga strip covered by the lead. The true energy gaps Δ are then given by $\Delta = \alpha^{-1}\Delta_{meas}$. The coefficient α was determined at each temperature by using the measured lead gap and assuming that the true lead gap follows the BCS temperature dependence. These values of α were then used to obtain the corrected Ga gaps indicated by the triangles in Fig. 2.

We were unable to determine the temperature dependence of Δ_3 because the temperature range over which Al is superconducting is not sufficiently large (it is necessary for the Al to be superconducting in order to resolve the structure in the Ga density of states). X-ray and electron diffraction patterns and electron micrographs of the Ga were of such poor quality that we could not determine the crystal structure of the films.

The observation of three energy gaps suggests that the films consist of a mixture of three modifications of gallium. Well-defined energy gaps are measured since the tunneling current is made up of independent contributions from particles within essentially a mean free path of the oxide interface. In view of the short electronic mean free path, it is unlikely that the structure in the dI/dV characteristics of the tunnel junctions results from gap anisotropy. The extremely high normal resistivity of the Ga films and its negative temperature coefficient indicate that the conduction mechanism is tunneling through oxide barriers between adjacent gallium particles (to be distinguished from tunneling from Ga to Al, Pb, and Sn films). The internal junction resistances vanish because of the onset of Josephson tunneling (or weak links). The resistive transitions of the films are broad because of spatial inhomogeneities in the junction resistances. The absence of the gap Δ_3 in junctions in which the Ga films were evaporated first (the Ga-Pb junctions) suggests that the relative concentration of the phase associated with Δ_3 decreases as the film is deposited.

High-T_C modifications of Ga observed by other workers are amorphous gallium,[4] $T_C = 8.4°K$; γ gallium,[7,8] $T_C = 7.6°K$; β gallium,[9,10] $T_C = 6.2°K$. From the temperature dependence of $\Delta_1(T)$ and $\Delta_2(T)$ shown in Fig. 2, we determined $T_{C1} = 6.4°K$ and $T_{C2} = 7.9°K$. These values are very close to the values listed for β and γ gallium. The gallium modification with the gap Δ_3 probably corresponds to the amorphous modification with $T_C = 8.4°K$. The values of Δ, T_C, and $2\Delta/k_B T_C$ for the three high-T_C modifications, along with ordinary gallium, are given in Table I.

The values of $2\Delta/k_B T_C$ for the high-T_C modifications of Ga are substantially larger than the BCS value of 3.5. Thus, these modifications are strong-coupling superconductors. One is thus led to ascribe the increase in T_C to a rise in the BCS coupling constant[1] NV, rather than to an increase in the average phonon energy $\langle\hbar\omega\rangle$. To determine the coupling constants NV for each of the gallium modifications, we employ the equation for the energy gap at absolute zero[1]:

$$\Delta = 2\langle\hbar\omega\rangle \exp(-1/NV). \quad (1)$$

Taking[11] $\langle\hbar\omega\rangle/k_B = \frac{1}{2}\theta_D = 160°K$ (θ_D is the Debye temperature) for ordinary Ga and the three high-T_C modifications, we obtain the values of NV given in Table I. Values of N are also given in the table for ordinary Ga and modification 1. In order to obtain N for modification 1, we have made use of the expression for the

Table I. Parameters of superconducting modifications of gallium.

Modification	Δ (mV)	T_C (°K)	$2\Delta/k_B T_C$	H_C (G)	N (10^{33} erg^{-1} cm^{-3})	NV
Ordinary	0.16[a]	1.08	3.5	59.2[b]	4.1[c]	0.19[d]
1	1.03[e]	6.4±0.1	3.8	560[f]	8.2[a]	0.31[d]
2	1.38[e]	7.9±0.1	4.1	...	...	0.33[d]
3	1.53[e]	8.4±0.1[g]	4.2	...	...	0.35[d]

[a]Calculated from Eq. (2).
[b]N. E. Phillips, Phys. Rev. 134, A385 (1964).
[c]Calculated from specific-heat coefficient given in Ref. 2.
[d]Calculated from Eq. (1)
[e]This work
[f]Ref. 9.
[g]Ref. 4.

ground-state energy at absolute zero,[1]

$$H_c^2/8\pi = \tfrac{1}{2}N\Delta^2, \quad (2)$$

with $\Delta = \Delta_1$. Since our films behaved as dirty type-II superconductors, we were unable to measure H_c. Instead we have assumed $H_c = 560$ G, the value for β gallium.[9] Examination of the table shows that the increase in N accounts for the increase in NV to within 20%. The T_c's of modifications 2 and 3 are probably due to further increases in N. It should be remarked that the values of NV given in the table for the high-T_c modifications are somewhat small, in view of the large values of $2\Delta/k_B T_c$. Larger values of NV would be obtained if the average phonon energy $\langle\hbar\omega\rangle/k_B$ were smaller than the value 160°K used above.

The authors would like to thank Dr. G. D. Cody for many fruitful discussions and helpful suggestions and Dr. M. S. Abrahams for electron microscopy.

[1]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[2]A list of the specific-heat coefficients γ of the superconductive elements can be found in the Handbook of Chemistry and Physics, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, Ohio, 1965), 46th ed., p. E-67.

[3]B. Abeles, Roger W. Cohen, and G. W. Cullen, Phys. Rev. Letters 17, 632 (1966).

[4]W. Buckel and R. Hilsch, Z. Physik 138, 118 (1954).

[5]D. H. Douglass, Jr., and R. Meservey, Phys. Rev. 135, A19 (1964).

[6]This expression was obtained by treating the junction as a distributed resistive network and solving the resulting differential equation for the voltage. It was assumed that R_t can be regarded as essentially independent of I. Because of thermal smearing the error introduced by this assumption is not serious at temperatures above 5°K.

[7]J. Feder, S. R. Kiser, F. Rothwarf, J. P. Burger, and C. Valette, Solid State Commun. 4, 611 (1966).

[8]In addition to γ gallium, there exists a high-pressure modification of Ga with $T_c = 7.5$°K [W. Buckel and W. Gey, Z. Physik 176, 336 (1963)]. Our films may contain a mixture of both these phases.

[9]Louis Bosio, André Defrain, John Keyston, and Jean-Claude Vallier, Compt. Rend. 261, 5431 (1965).

[10]$T_c = 6.2 \pm 0.1$°K is the value for β gallium given by Feder et al. (Ref. 7), Bosio et al. (see Ref. 9) give the value $T_c = 6.0 \pm 0.1$°K, and Buckel and Hilsch (Ref. 4) find for their crystalline modification $T_c = 6.3$°K.

[11]D. Pines, Phys. Rev. 109, 280 (1958).

NEW MEASUREMENTS OF THE ELECTROMAGNETIC ABSORPTION SPECTRUM OF SUPERCONDUCTING LEAD

Scott L. Norman* and David H. Douglass, Jr.†
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
(Received 23 January 1967)

The absorption below the main edge in superconducting lead previously reported was found to have been instrumental in origin, and does not appear in more recent data.

We previously reported observation of a "precursor" absorption in superconducting Pb,[1] which appeared as a doubly peaked structure lying below the energy gap. Further work with the apparatus described in the previous Letter has led us to conclude that this structure was, in fact, spurious, and due to the unsuspected presence of higher order radiation in the beam of our monochromator. With this difficulty corrected, we obtain the data shown in Fig. 1, showing no sign of any precursor. We have obtained similar results for three other films of thickness 1400, 6000, and approximately 54 000 Å. In each case, the Pb absorption signal appears to remain at 0 below the main edge; maximum error bars extend only to 2-3% absorption. Note also that the absorption edge seems fairly smooth, with no clear evidence for additional absorption edges arising from critical gaps.[2] It therefore seems likely that the excess absorption above the main edge previously reported by us was also due to the presence of higher order radiation.

We believe that in our earlier work, higher order radiation diffracted out of the monochromator beam by a transmission filter grating was nevertheless able to reach the sample, presumably after undergoing a reflection not allowed for in our original design of the optical path. The presence of such radiation would