Results are presented of the Kapitza resistance of lead specimens between 1 and 2 K. The specimens underwent surface treatments which included annealing, electropolishing, argon ion bombardment, and finally surface preparation by guillotining under liquid helium. The difference in Kapitza resistance between normal and superconducting states is seen to be compatible with the presence of a bulk thermal resistance due to mechanical strain which is operative in the superconducting state only. A preliminary result on a Pb—20% at In alloy is also given.

Some experimental investigations of the Kapitza resistance of lead

J. D. N. Cheeke

There have been a large number of measurements of the Kapitza conductance of lead during the last ten years.[1-9] This is partly due to the fact that the Kapitza conductance of all solids with He^4 is still an unresolved problem; a general review of the subject was recently given by Pollack.[10] However interest in lead was mainly stimulated by Challis' observation [1] that at the superconducting-to-normal state transition in lead at 1·3 K, $h_N/h_S \sim 3$, where $h_i = 1/R_i = \dot{Q}/A\Delta T$ in $W\,cm^{-2}\,K^{-1}$ and N, S refer to normal and superconducting states respectively. This observation was taken as evidence of the participation of the conduction electrons in the heat transfer process in the normal state, as predicted by Little [11] who used standard perturbation techniques to calculate the interaction between the surface wave set up in the solid by the incident liquid phonons and the conduction electrons of a free electron metal.[12] This calculated value of the electronic conductance (h_{el}) was however orders of magnitude less than the effect observed by Challis.

Challis further observed [2] that h_N/h_S and h_N, h_S decreased as a function of the time for which the specimen was kept at room temperature. This he attributed to progressive oxidation of the surface. The magnitude of the field effects found in [1,2] was confirmed by Gittleman and Bozowski [3] and by Barnes and Dillinger,[4] the former showing that h_N/h_S was only of the order of a few % for Sn and In. Further results on lead were reported by Kuang Wey-Yen.[5] In a series of experiments in which the superconducting lead surfaces were scraped under liquid helium II, he showed directly the important role of surface strain by reducing the conductance of a strained surface by a factor of ten compared to that of the annealed surface. This evidence was supported by the work of Challis and Cheeke [6] who annealed, electropolished, and ion-bombarded lead surfaces in an attempt to eliminate the effects of strain and oxide and so obtain reproducible and representative results for lead. However the value of h_N/h_S observed ranged from 1·3 to 2·0.

Andreev [13] reconsidered the electronic contribution, using a semi-classical calculation based on the Boltzmann equation solution of the electron distribution in the same sound field considered by Little. Assuming $\omega\tau \ll 1$ and $ql \gg 1$, he found h_{el} to be of the same order as the conductance h_ϕ due to phonon transmission calculated by Khalatnikov.[14] Assuming the superconducting and normal state conductances to be determined by these two mechanisms, this gave qualitative agreement of h_N/h_S with the experimental observations, but a quantitative discrepancy with Little's calculation remained. This difficulty was resolved in the work of Challis and Cheeke [15] who showed that Little's and Andreev's calculation correspond to different limits of the same problem ($\omega\tau \gg 1$ and $\omega\tau \ll 1$, $ql \gg 1$ respectively). By extending Andreev's model to the limit $\omega\tau \gg 1$, they obtained essential agreement with Little's result. Moreover it was found [15] that the Little limit should hold for $T \gtrsim 10^{-2}$ K for a free electron model. On the experimental side recent work by Cheeke [8] and preliminary work by Challis and Sherlock [9] showed that the values of $h_N/h_S > 1$ previously observed could well be quite satisfactorily explained by the presence of surface strain.

Thus the present situation seems to be that there have been no unambiguous observations of h_{el} in lead, or indeed in other superconductors where the observed h_N/h_S are much smaller. Further, present evidence suggests that h_{el} is negligible for a reasonably free electron metal at 1 K. Any experimental observation of h_{el} is complicated by the high sensitivity of the measurements (especially of h_S) to the physical and chemical state of the surface. In the present

The author is with the Centre de Recherches sur les Très Basses Temperatures, CNRS Cedex 166, 38 Grenoble-Gare, France.
Received 1 July 1970.

paper we give a full treatment of the preliminary results reported in references 6 and 8. Particular attention is placed on the preparation of the specimen surfaces, and a more critical assessment of the data is presented, taking this into account. We stress especially the effect of strained surface layers, which seem to play a much more important role than oxide for apparently clean and well-defined surfaces. Preliminary results are also given for a lead–indium alloy.

Ion bombardment

An attempt was made [6] to obtain clean strain free surfaces in order to make a quantitative comparison with theory. While the present interpretation suggests that this goal was not fully achieved, application of these procedures should still be extremely useful in obtaining more reliable results than can be obtained by measuring untreated surfaces. Apart from annealing in vacuo and electro-polishing, the main cleaning treatment chosen was that of argon ion bombardment. This was the standard cleaning treatment available which could be most simply adapted to an *in situ* cleaning prior to the experiment. While some surface damage is known to be produced [16,23] the specimen was at ambient temperature for about 2 hours before cooling, which should anneal out a considerable part of this damage. The results suggest in fact that it produced a negligible effect compared to that from other origins. A real disadvantage however is the possibility of depositing argon atom layers on the surface. Before considering the ion bombardment in detail, we outline the mounting of the specimen and the preliminary cleaning procedures.

Design and mounting of specimens. The specimens were prepared from lead rods (5 N spectroscopic purity), supplied by Johnson and Matthey, London. The geometry chosen was similar to that used by Challis [2] with some modifications. The final arrangement and the cryostat into which it was inserted are shown in Figure 1. The specimen was machined over-size; the upper portion being made at least 5 mm longer than necessary. The final position of the surface was set by machining a small hub around the specimen approximately 0·5 mm wide and protruding about 1 mm. For some of the experiments the specimen was then annealed in vacuum for about 15 hours at 270 C. A 0·1 mm thick German silver disc was used as a mounting plate for the specimen. A hole considerably less than the specimen diameter was cut in the disc centre and this was then pushed out so as to fit closely around the specimen (6 mm diameter). The lip thus formed was then machined off until it projected 1 mm or less from the plane of the disc. The disc was then soldered in place with bismuth–cadmium solder. This low melting point solder, which is not superconducting above 0·50 K (Carruthers et al [17]) was used to avoid distortion of magnetic fields parallel to the surface caused by the presence of a superconducting ring around the specimen.

The excess solder on the upper surface of the disc was then turned off in a lathe and the disc surface covered with a layer of Araldite. In the final assembly, the function of the Araldite was to protect the bismuth in the solder from electrolytic attack during electropolishing. The upper surface was then turned back until the Araldite layer was about 0·1 mm thick, and the specimen rod protruded 0·1 mm above it (again to facilitate electropolishing). Finally, a mica ring was placed over the German silver and Araldite to shield these from the discharge during ion bombardment.

Copper wires for use as thermometer contacts were then soldered to the specimen, the hub around the specimen forming a convenient means of accurately locating the thermometer closest to the interface (~ 1 mm from the surface). The German silver disc was secured into the cryostat by means of a gold O-ring, being pressed against the gold by a hardened BeCu baseplate screwed with six BeCu bolts at slightly more than hand tightness. A Kapitza conductance experiment could then be performed using standard techniques.

Preliminary surface treatment. The surface was electropolished immediately before the specimen was fitted into the cryostat. Polishing was done by means of an Ellopol tampon probe [18] using an electrolyte consisting of 909 ml acetic anhydride mixed slowly with 79 ml perchloric acid

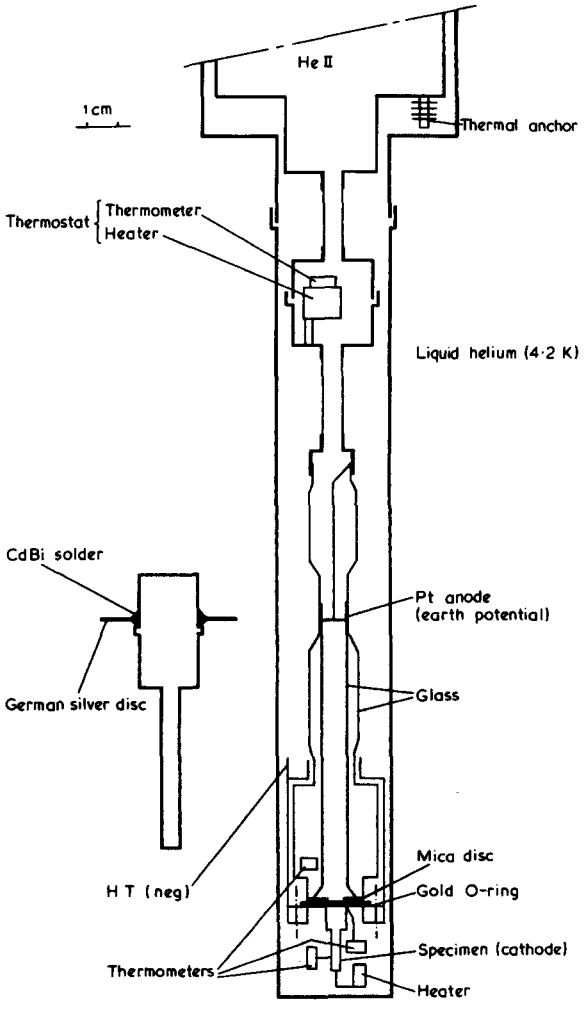


Figure 1. Ion bombardment and Kapitza conductance cryostat; the specimen is shown at left on an expanded scale, before machining of the upper portion

and 12 ml distilled water. In all cases the surface was polished until it was level with or below the Araldite layer, that is, at least 100 microns of lead were removed. The final appearance of the surface was shiny and wavy, sometimes hollowed in the centre where the polishing had been intensive. In some cases stains developed on the surface after polishing but these were apparently removed by subsequent ion bombardment.

Ion bombardment techniques. The technique of argon ion bombardment was used in an attempt to remove unwanted surface deposits, for example, oxides and chemical stains. A detailed discussion of the method is given by Holland.[16] The general principles outlined there were followed, and the empirical determination of known important parameters such as gas temperature and pressure, cathode fall and current density, cathode material, etc were determined by preliminary experiments in a 'mock-up' cryostat.

In the final experiments the bombardment was carried out *in situ* in the cryostat using the arrangement shown in Figure 1. The cathode (specimen holder) and anode (~ 5 mm^2 platinum foil) were separated by two concentric glass tubes, the inner one defining the discharge path. Pure argon gas (99·995%) was admitted to the system at a pressure of 100–200 microns (13–26 N m^{-2}) through a cold trap after the system had twice been flushed with argon. A 0–3 kV HT power supply was used to put typically 2 kV across the electrodes through a 600 kΩ series resistor. A tesla coil was used to initiate the discharge when necessary. The use of reasonably low currents ($< 0{\cdot}3$ mA), while at the same time preventing the discharge from leaking outside the inner tube, was attained by putting a constriction between the two tubes. The inner tube was flared at the bottom so that the whole surface was sputtered evenly. The pressure was typically 100μ (13 N m^{-2}), giving a dark space of several centimetres.

Following the principles outlined in Holland,[16] several precautionary measures were taken to reduce surface contamination: protection of the German silver, solder, and Araldite by a mica disc, pre-pumping of the system at least overnight, use of silicon fluid 702 and a liquid nitrogen trap to reduce oil contamination, use of pre-cold trapped argon gas, etc. Also, as the external system volume was much bigger than that of the cryostat, the ordinary diffusion process should remove many of the contaminant gases.

No attempt was made to measure the actual amount of material sputtered; formation of shiny lead layers on the tube indicated that considerable quantities of bulk lead were removed. Examination of pre-annealed surfaces after sputtering revealed the existence of clearly defined grains which had not been previously observable, thus indicating the superior etching qualities of the process. Also extended sputtering (½–1 hour) gave rise to an apparently heavily damaged surface. The sputtering time was thus limited so that score marks due to gross mechanical damage were scarcely visible under a laboratory microscope (magnification $\sim$ x 100). As defined in Table 1 light sputtering thus corresponds to ~ 7 minutes and heavy to about 20 minutes under the stated operating conditions.

Table 1. Surface treatment and conductances (reference 6) in watt units

Specimen	Surface treatment	Removed by polishing microns	Sputtering time min	T = 1·6 K h_N	h_S	h_N/h_S	1·3 → 2·2 K h_N	h_S
1A	As machined	–	–	0·9	0·5	1·8	$0{\cdot}25\,T^{2\cdot5}$	$0{\cdot}1\,T^{3\cdot25}$
1B	6 days air – 2 days O_2 at 300 K	–	–	0·9	0·5	1·8	$0{\cdot}25\,T^{2\cdot5}$	$0{\cdot}1\,T^{3\cdot25}$
1C	1 day He 300 K	–	~ 7	1	0·5	2	$0{\cdot}2\,T^{3\cdot5}$	$0{\cdot}1\,T^{3\cdot5}$
1D	1 day He 300 K	~ 500	$\sim$ 20–25	1·3	0·7	1·9	$0{\cdot}25\,T^{3\cdot5}$	$0{\cdot}13\,T^{3\cdot5}$
1E	1 day He 300 K	~ 800	–	1·3	0·9	1·4	$0{\cdot}25\,T^{3\cdot5}$	$0{\cdot}17\,T^{3\cdot5}$
2	Annealed 15 hrs in vacuo at 270 C	$\gtrsim 100$	$\sim$ 20–25	1·7	1·3	1·3	$0{\cdot}3\,T^{3\cdot7}$	$0{\cdot}25\,T^{3\cdot5}$
3	As specimen 2	$\gtrsim 100$	~ 30	1·7	0·9	1·9	$0{\cdot}37\,T^{3\cdot2}$	$0{\cdot}2\,T^{3\cdot2}$

Theoretical values — *Reference*

S State Khalatnikov: $h_\phi = 1{\cdot}8 \times 10^{-2}\,T^3$ 14

Khalatnikov + dense layer: $h_\phi = 4{\cdot}5 \times 10^{-2}\,T^{4\cdot2}$ 7,25

PbO (Khalatnikov + dense layer): $h_\phi = 3 \times 10^{-2}\,T^{4\cdot2}$ 7

N State $h_N = h_S$ 15

All conductances are in W cm^{-2} K^{-1}

All specimens are numbered 1, 2, and 3 and letters A, B etc refer to treatments on the same specimen. For specimen 1 the 300 K annealing time given in each row is to be added to the total of the preceding entries to give the total annealing time at each stage.

Upon completion of ion bombardment with the specimen *in situ* the argon was pumped out and the measuring leads and auxiliary vacuum jackets etc installed as quickly as possible. The specimen surface region and bombardment space could thus be filled with liquid helium in about two hours. This delay between sputtering and cooling to helium temperatures should have allowed some annealing of any surface damage caused by sputtering while keeping subsequent oxidation etc at a minimum. However, it is almost certain that at least a few monolayers of oxide or absorbed gas formed on the surface in the background cryostat pressure of about 10^{-5} cm ($1{\cdot}3 \times 10^{-2}$ N m^{-2}).

Results. The essential experimental results have already been reported [6] and are included here for reference, in tabular form, together with details of the treatment given to each specimen, in Table 1. We note that the reproducibility of the fully treated specimens is at best qualitative. Even though a comparison of absolute values is difficult due to unknown differences in surface area etc, there is a large variation in the h_N/h_S ratios, for which these uncertainties are eliminated. Thus even though the conductances are much higher than those previously observed for lead [1,4] and the reproducibility is much greater, we must conclude that the surfaces obtained are not yet 'ideal'. A more detailed discussion of these results appears later.

Preparation of lead surfaces in liquid helium

This experiment was stimulated by Bloch's suggestion [19] that there may exist another possible mechanism for h_{el} which differs fundamentally from the surface wave model treated by Andreev and Little. Bloch proposed a heat transfer h_{eT} by tunnelling of electrons into the helium and direct energy exchange with the helium phonons. By a standard perturbation theory calculation and substituting reasonable values, he showed that $h_{eT} \sim T^5$, and $h_{eT}/h_{Khal} \sim 10T^2$. Johnson and Little [20] looked for the effect by scraping copper surfaces under liquid He II but found an apparent decrease in conductance, which in the light of reference 8, we suggest may be due to frozen in surface strain. Gittleman and Bozowski [3] also observed a negative result to 1 part in 10^7 in an experiment in which they modulated a strong electric field normal to the surface and looked for an in-phase temperature variation of a platinum surface. Finally the results for Pb surfaces cut in the helium bath [8] also gave a negative result. The h_S results [8] are in remarkably fortuitous agreement with similar earlier measurements made on scraped lead surfaces by Kuang Wey-Yen,[5] the latter being measured in the superconducting state only. We shall see, however, that the results of reference 8 for both states, apart from giving the possibility of testing for a tunnel effect, permit much more definite and convincing conclusions on the origin of the observed temperature jumps in superconductors.

Specimen mounting. The low temperature guillotine is shown in Figure 2. The specimens were formed from 6N purity material supplied by Metals Research Limited Cambridge, England, and were shaped as cylinders 5 mm in

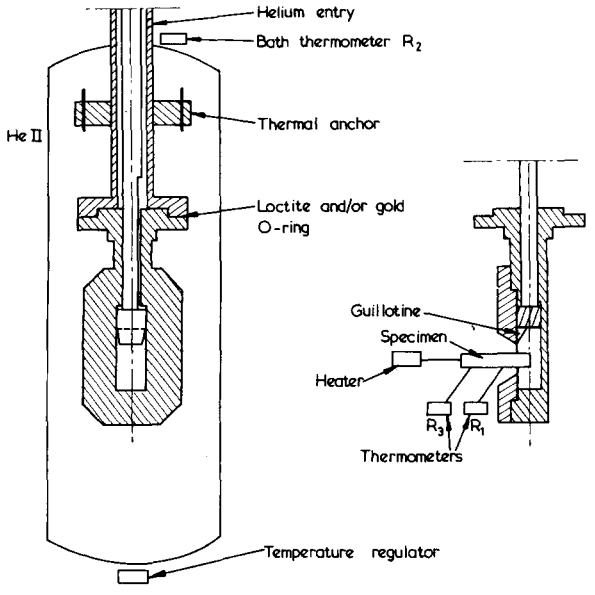


Figure 2. Low temperature guillotine assembly

diameter and about 12 mm long. No systematic measurements were made to determine the actual purity of the specimens after fabrication. However, a resistivity ratio of 1 570 at 7·5 K of lead drawn down from the same source, the sharpness of the superconducting-to-normal transitions observed, and estimates from magneto-thermal resistance measurements indicate that the original purity was largely maintained and in any case was quite sufficient for our purposes. (The residual resistance ratio of this lead was estimated to be greater than 30 000 at 1 K from extrapolations from magneto-resistance measurements.) The specimens were soft soldered into $\frac{1}{10}$mm German silver sheets with several millimetres left protruding into the bath, as shown in the figure. The fabrication details were similar to those described in the previous section except for the following significant differences.

1. The specimen retaining joint was 60–40 PbSn solder rather than BiCd to avoid complications due to the known brittleness of the latter.

2. The 'hub' used to locate the thermometer was made slightly larger than that previously described and it was grooved so as to take a tight fitting $\frac{2}{10}$mm tinned copper wire. It was found that tightly wrapping the wire around the specimen and heating it a short distance from the specimen together with application of flux (for example, Zn Cl) to the groove caused the solder to flow easily around the joint so as to make a perfectly cylindrical symmetric contact of small dimensions (that is, exactly $\frac{2}{10}$mm wide). The success of the method seems to depend strongly on the cleanliness of the groove. The German silver support sheet was glued to the stainless steel holder and to a backing plate on the other side; the latter being bolted into the holder by twelve stainless bolts of 3 mm diameter.

Low temperature seals. In some of the earlier measurements the above joints (excepting that retaining the

specimen) and that connecting the cutting assembly to the apparatus were made using indium O-rings. As the success rate was not high and as micro-leaks appeared several hours after cutting in some cases, a more satisfactory solution was sought. It was found that grades BLOCC PRESS (AAV) and 'tube sealant' Loctite joints (Loctite Europa NV Amsterdam) with or without an auxiliary gold O-ring were completely satisfactory, and particularly simple and reliable to use. The AAV while forming a joint apparently less strong than that of tube sealant was more simple to remove, a screw driver placed between the O-ring pieces being sufficient. The tube sealant formed an extremely solid joint for which dismounting generally required heating in a flame.

Two additional glues whose use has not been reported in the literature were found interesting in this work. Loctite weld sealant (as well as AAV) was found useful in plugging suspected leaks in soldered joints. The low viscosity Loctites presumably penetrate relatively easily into the porous sections, and as with other members of the Loctite series, they cure in the absence of air. As a result they were effective in sealing the leaks to superfluid helium. Thus it was found that a simple coating of AAV or weld sealant on the Woods metal calorimeter joint was a simple insurance to avoid any unnecessary leaks.

Another interesting glue was Tecal 44 (Techkits Demarest, NJ, USA). This aluminium epoxy casting resin has a claimed high room temperature thermal conductivity and is also a good electrical insulator. While the low temperature thermal resistance of such joints was not measured directly, Tecal 44 was found to be very convenient and mechanically strong for making thermal anchors which attained a temperature always very close to that of the bath.

A final caution is given concerning the Loctite glues. The recommended application of the catalyst type N mixed 1:20 with trichloroethylene to the joint areas was found to be indispensable as well as a thorough prior cleaning. If a joint did not 'take' it was found to be much safer to dismount it and start again. Finally there have been recent indications that for cryogenic purposes, the self life of either catalyst or the Loctite sealants is limited to about a year, although further evidence is needed on this point.

The guillotine assembly. The guillotine mount consisted of a carbon tungstide blade with a 30° cut held in a brass piece, which was connected to the head of the cryostat by a composite stainless rod–tube passing through an O-ring joint. Several sharp blows with a hammer were sufficient to slice off the end of the specimen, leaving a clean shiny surface with typically ~20% of the area showing signs of gross mechanical damage. The cutting was done at 4 K in the preliminary experiments but at about 2 K in the results reported here, which improved the leak detection sensitivity on guillotining. Several difficulties were experienced with poor quality commercial lead in preliminary experiments due to internal flaws which gave huge leaks upon cutting. No difficulties of this type were experienced with the Metals Research grade material.

Upon completion of cutting, the central rod could be unscrewed and raised from the assembly, leaving the guillotine in the bath at the bottom of the holder. This procedure reduced the heat leak and provided freer access of the liquid to the specimen holder. In some earlier experiments where the rod was not raised, liquid access was assured by the presence of two long flats machined on the side of the control rod.

The thermometer–heater arrangement is shown in Figure 2. The thermometers were 47 Ω, $\frac{1}{10}$W Allen–Bradleys which were easily fitted to the law

$$\frac{A}{\log R} + B\log R + C = \frac{1}{T}$$

in the 1–2 K range with sufficient accuracy for our purposes. The heaters were 600 Ω constantan strain gauges, which were bolted, after the application of Apiezon grease, into copper supports soldered to the end of the specimen. In a typical experiment after cutting at 2 K, measurements were taken in the virgin superconducting state to 1 K then in a field perpendicular to the specimen of 1 000–1 500 Oe supplied by a superconducting solenoid, on warming to 2 K. Measurements were carried out by first stabilizing the resistor R_2 with the bath heater and auxilary thermometer, recording the steady value of R_1, and then noting the change in R_1 when the specimen heater was used to supply a known amount of heat. Heater powers were held below several milliwatts as larger heat currents seemed to give small but systematic variations. The temperature regulation used was type CEA–CNRS[36] which had a stabilization of better than 10^{-4} K at all points measured. The temperature gradient along the specimen was at most only a few % of that at the interface: no correction was made for the thermal resistance between R_1 and the interface, for reasons explained in the discussion of results.

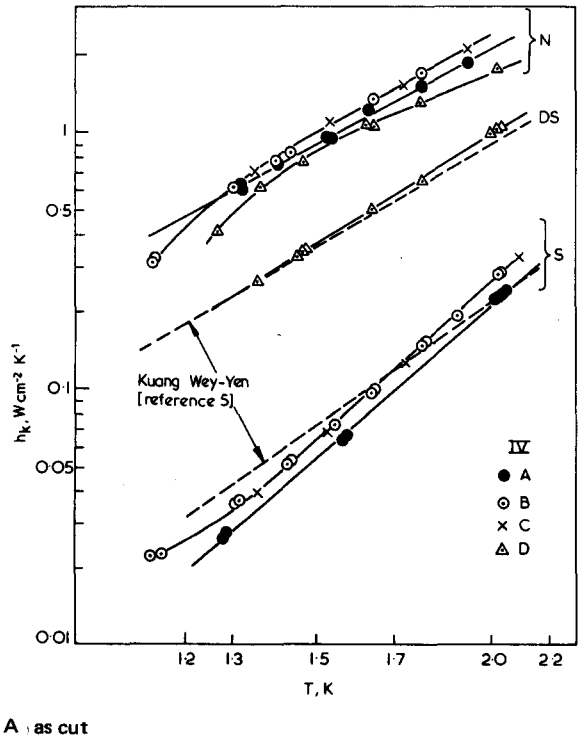
Results. The main results from reference 8 are collected in tabular form in Table 2 and the observed variation in conductance of one specimen for various annealing procedures is shown in Figure 3. The results for the other specimens, as a function of temperature are shown in Figure 4. It is evident that the results for IN are anomalous (especially concerning T dependence). The results on this specimen are preliminary in the sense that they were obtained during the perfecting of experimental procedures. They have been included because subsequent changes in technique cannot readily explain the discrepancy and also IS is not anomalous. It is possible that the detailed nature of the guillotining, the temperature at which it was carried out etc, could explain the discrepancy. We were not able to investigate this as the work had to be temporarily discontinued; in any case the discrepancy does not affect our present conclusions, which are essentially qualitative in nature. (The high accuracy suggested by the tabular values quoted in reference 8 is the result of an oversight; this has been corrected in Table 2 of the present paper).

The essential interpretation of these results which will be given later is based on the behaviour of specimen IV. All of

Table 2. Summary of conductances of cut specimens at 1·6 K

No.	h(1·6 K) Wcm^{-2} K^{-1}	h_N/h_S (1·6 K)	$h = aT^n$ a	n	Pre-annealing
IS	0·1	3·5	0·02	3·5	20 days 300 K
IN	0·4		0·2	1·5	
II S	0·06	—	0·015	3	24 hours in vacuo at 150 C
III S	0·1	—	0·02	3·5	as II
IV AS	0·075	15	0·0075	4·9	as I
IV AN	1·1		0·3	2·6	
IV BS	0·09	15	0·01	4·75	
IV BN	1·25		0·25	3·5	
IV CS	0·09	15	0·01	5	
IV CN	1·25		0·3	3	
IV DS	0·5	2	0·1	3·25	
IV DN	1		0·25	3	
V AS	0·09		0·01	4·5	100 days 300 K
V BN	0·9		0·2	3	
V CN	0·9		0·2	3	

The nomenclature is the same in all tables and figures and is as follows. The various specimens are denoted by I, II etc. Letters A, B etc correspond to various annealing procedures explained in the text and figure captions. Final letters N or S refer to normal and superconducting states respectively.



IV A as cut
IV B as cut + ~ 2 days at 77 K
IV C as cut + ~ 3 days at 77 K
IV D as cut + ~ 3 days at 77 + ~ 5 days at 300 K

Figure 3. The variation of conductance values of specimen IV as a function of temperature following various annealing procedures. The results of Wey-Yen after scraping under helium (lower curve) and annealing four months at 300 K (upper curve) are shown for comparison

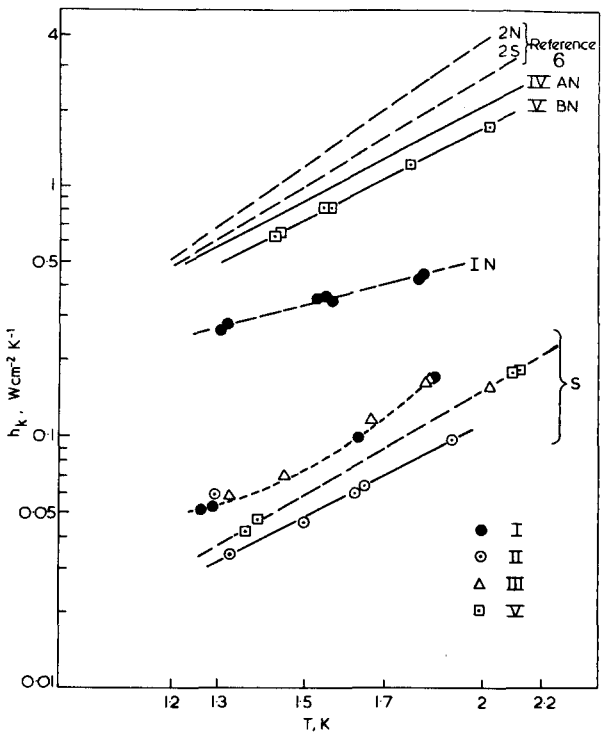


Figure 4. Conductance of the other cut specimens as a function of temperature, with the best treated specimens from reference 6 and specimen IV included for reference. The initial condition of the specimens is given in Table 2

the virgin-cut superconducting data is self-consistent and also consistent with the result of a similar experiment made by Kuang Wey-Yen.[5] In addition a weeks' annealing in helium gas at 300 K showed a rise in h to exactly the same value as that obtained by Wey-Yen [5] after four months' annealing. This is considered as a satisfactory check on the experimental results as well as giving an indication that there may be a saturation of the observed superconducting state conductance after a short annealing at 300 K. We note further that the comparative variation in the N state data is extremely small and that there is a measurable decrease in the conductance after room temperature annealing, which is presumably due to oxide growth or other contamination.

Field passes of specimen IV B and D at about 1·3 K are shown in Figure 5. As the behaviour in the normal state both near and well above H_c have already been systematically studied,[6] this question was not pursued here. We note however that the values of H_c deduced from the Kapitza resistance of specimen IV were: A 850 Oe, B 940 Oe, C 830 Oe, D 790 Oe. Due to various technical considerations we can place an absolute accuracy of only ±5% on these figures. However, it does seem that the observed H_c of the unannealed samples is significantly higher than the accepted thermodynamic critical field at 1·3 K (~ 780 Oe) which is not the case for the annealed specimen. An elevation of H_c due to cold working has been observed in other experiments.[2,1]

Another possible explanation of the elevated values of H_c observed could be a resistive contribution by the

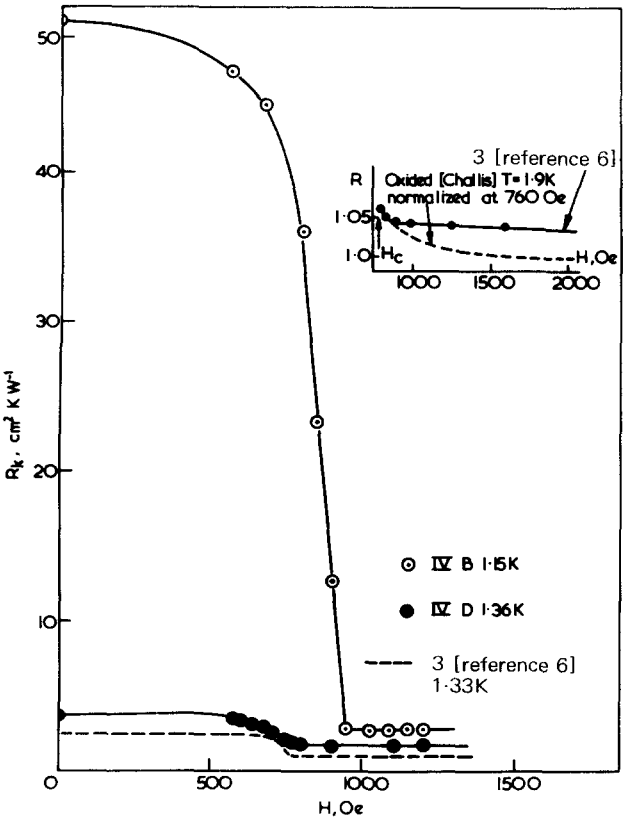
superconducting surface sheath.[28 29] However, in view of the thinness of the sheath ($2\zeta \lesssim 1\,500$ Å for lead) and the inconsistent and small variations observed, this does not seem to be a likely explanation. Examination of Figure 5 shows the absence in these results of 'tails' in the transition which were noted by Challis [2] for a heavily oxided specimen (see inset Figure 5).

Kapitza resistance of PbIn alloys

This is of interest for experiments which use superconducting bolometers, such as heat pulse propagation experiments,[31] as well as those to verify Andreev's conclusion [13] that h_{el} should be negligible for the impure metal.

Preliminary measurements on 2 and 20 atomic % indium in lead show the same general behaviour although considerable difficulty was experienced in removing surface oxide for the 2% specimen. The magnetic field variation of the 20% specimen at 1·3 K is shown in Figure 6. The specimen was annealed in vacuo for about 24 hours at 150 C, polished chemically (H_2O_2 + acetic acid) and rinsed in acetone just before cooling. The surface was bright with few traces of residual oxide.

The apparent increase of R_K with magnetic field is at first surprising. However the measured bulk thermal resistivity has the same form as that often found in the mixed



IV B as cut + ~2 days at 77 K
IV D as cut + ~3 days at 77 K + ~5 days at 330 K

Figure 5. The resistance of specimen IV as a function of magnetic field. The resistance of specimen 3 (reference 6) is shown for comparison and the inset shows the absence of 'tails' for a surface cleaned by ion bombardment as opposed to their presence for an oxidized surface (Challis[2])

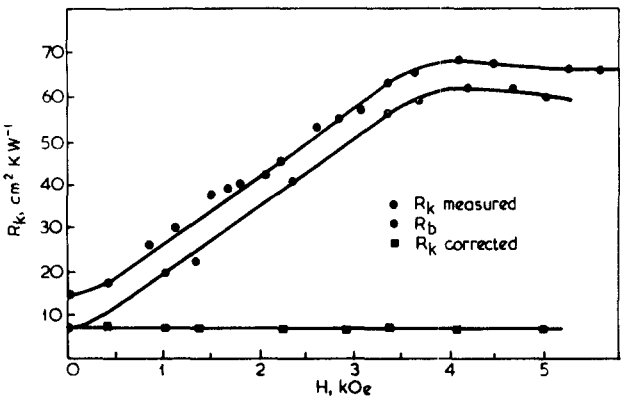


Figure 6. The Kapitza resistance of a Pb–20% at In specimen as a function of magnetic field at ~1·3 K showing the importance of the correction for the extrapolated bulk resistance R_b between thermometer and surface

state.[5 7] Correcting for the bulk temperature gradient between thermometer and surface we then find a Kapitza resistance independent of field to about 15%. The correction is clearly of over-riding importance in this case and illustrates the difficulty in measuring R_K for high thermally resistive materials.

Estimating $\ell_e \sim 8 \times 10^{-7}$ cm,[34] we find $\omega\tau \ll 1, q\ell \sim 1$ which suggests that the electronic contribution is very small for $q\ell \ll 1$ as proposed by Andreev.[13] Due to the very large correction the region $q\ell \ll 1$ should clearly be sought at lower temperatures. The situation is also complicated by the possibility of surface concentration gradients. A complete report of further developments of this work will be given at a later date.

Discussion

As the extrapolation of the temperature gradient to the surface is fundamental to the interpretation, we will consider this question in some detail.

We note firstly that from measurements of the thermal conductivity of pure lead for T in the range 1–2 K, K_N is determined essentially by the purity and K_S by the degree of mechanical strain.[35] Assuming now ideal conditions in which we measure the 'true' Kapitza conductance for $T \ll T_c$, we can assume $h_N = h_\phi + h_{el}$, $h_S = h_\phi$. For a real surface with strain and oxide, water, etc present, we would have bulk thermal resistances in R^b in series and

$$h_N^{-1} = R_N^b + \frac{1}{h_{el} + h_\phi}, \qquad h_S^{-1} = R_S^b + h_\phi^{-1},$$

where R_N^b is determined mainly by the contaminated layers and R_S^b by the deformed surface layer. For a very strained surface, where T is not much less than T_c, we should see a K_{es} contribution in R_S^b. The above equivalent circuit has been chosen primarily because of its simplicity.

For the results of reference 6 it seems reasonable to suppose that R_N^b and R_S^b are small compared to the Kapitza resistance. Due to the high value of K_N, the correction to h_N is extremely small, and a simple linear extrapolation seems justified. For h_S however, from Mont-

gomery [35] we can suppose the phonon mean free path $l \sim 0{\cdot}5$ mm, and the extrapolation of ∇T is not clear here as this is of the same order as the thermometer–surface separation, d. These results [6] were corrected appropriately using Montgomery's values of K_S for pure unstrained lead; in view of the small size ($\lesssim 10\%$) of the correction and the large scatter in the results, this seemed to be a reasonable and not too dangerous procedure. In principle for $l > d$ and heat flow in the diffusion region, it may well be that the thermometer is in fact measuring the true average surface temperature. In any case as $l \ll R$ and $l \sim d$, we do not feel that the correction procedure given by Neeper and Dillinger [24] is appropriate here.

The correction procedure appropriate to the results of reference 8 is a different matter. As in that case we suppose here that R_N^b is small while R_S^b is extremely large and indeed $R_S^b \gg h_\phi^{-1}$ for the freshly cut specimens. Since the deformation seems to be extremely large and inhomogeneous, it does not seem possible experimentally to correct for R_S^b in order to arrive at h_ϕ for the undeformed surface. The results of reference 8 seem consistent with a bulk deformation effect rather than a deformation effect on the intrinsic Kapitza conductance (as suggested by Wey-Yen); this is indicated by the relative sensitivity of h_S and insensitivity of h_N to room temperature annealing. In view of the uncertainties which now seem associated with the correction procedure, we have not corrected the normal state values, which would in any case have been only a correction of a few %.

It seems highly probable that values of $h_N/h_S > 1$ are due to the role played by R_S^b. Support for this comes from preliminary results by Challis and Sherlock [9] on relatively unstrained lead foils. The situation is seen also by the results of Figure 5, where values of $h_N/h_S \sim 25$ at 1 K have been observed while h_N has about the same value observed in reference 6 and in earlier results. The anomalously high values of h_N/h_S are thus most clearly due to depressed values of h_S of the damaged specimens, as is seen in Figure 3 and Table 2. Kuang Wey-Yen, on the basis of superconducting state data alone, suggested that this was due to the formation of an amorphous surface layer and subsequent alteration of the surface elastic constants which resulted in an increase of the true Kapitza resistance. In view of the present experimental and theoretical picture of the small size of the electronic contribution in this temperature range, h_N should also be reduced by surface damage in this picture, and by the same amount as h_s. The fact that this is not so seems to rule out Wey-Yen's suggestion and confirm our model of an artificially introduced bulk thermal resistance in the superconducting state of a damaged specimen surface.

An important consideration is the origin and extent of the surface damage. It has been suggested by Challis and Sherlock [9] that the differential contraction between specimen and specimen holder is a possible cause of surface strain in the classical arrangement (as in reference 6). This seems a very reasonable possibility but to observe its effects it is necessary to remove surface damage of a more primary origin, that due to lathe turning etc during fabrication before the specimen is mounted. It is known that in lead this damage may extend at least as far as 100 μ, the actual depth depending in a complicated way on specimen pre-history.[30]

As the specimens in reference 6 were annealed and many hundreds of microns of the surface layer were removed, we can consider that the 'primary' damage has been removed. The proposed differential contraction on cooling is certainly one reasonable explanation of the $h_N/h_S > 1$ ratios that were still observed in reference 6. The variation 1 A – E suggests that electro-polishing and bombardment are slowly removing residual damage, but a precise interpretation seems difficult.

In the cutting experiments the origin of surface damage obviously lies in the shearing force needed to cut the specimen. It seems reasonable to suppose that at 1 K there is insufficient kT to anneal out these defects, so they are frozen in. Indeed the results indicate that this is still true at 77 K, while most of the annealing effect appears to be achieved on warming to 300 K. If this interpretation is correct, then a series of measurements such as those carried out on specimen IV could provide a sensitive means of studying surface annealing stages, especially for the case of soft superconductors.

The above conclusions indicate that there seems little hope of extracting h_{el} by present techniques. It is interesting however to compare the normal state values with the predictions of the Khalatnikov model. We find [14]

$$h_\phi = h_{\text{khal}} = \frac{1{\cdot}375 \times 10^{14} F T^3}{\rho c_t^3} \qquad \ldots (1)$$

Here F = numerical factor $\sim 1{\cdot}5$

ρ = solid density,

c_t = solid transverse wave velocity, cm s^{-1}

For lead using Poisson's ratio $\sigma = 0{\cdot}45$ and θ_D at O K = 105 K [26], $F = 1{\cdot}38$ [15] we find

$$h_{\text{khal}} = \frac{6{\cdot}6 \times 10^6 \, F T^3}{l M \theta_D^3}$$

with

$$= 1{\cdot}8 \times 10^{-2} T^3 \qquad \ldots (2)$$

$$l = 2 + \frac{ct^3}{c^3}$$

Following Johnson and Little [20] we can account for the dense layer of helium near the surface using the results of Challis, Dransfeld, and Wilks.[25] Using interaction energies

$$W_1 = +0{\cdot}104 \text{ eV Å}^3 \text{ and } W_2 = -0{\cdot}377 \text{ eV Å}^3$$

and a free electron model with four free electrons per atom, we obtain for lead [7]

$$h_\phi = 4{\cdot}5 \times 10^{-2} T^{4{\cdot}2} \text{ W cm}^{-2} \text{ K}^{-1} \text{ for T} \sim 2 \text{ K} \quad (3)$$

While the model chosen is undoubtedly too simple it should give at least a good order of magnitude estimate of the enhanced heat flow due to the dense layer. An analogous calculation for PbO gives

$$h_\phi = 3 \times 10^{-2} T^{4{\cdot}2} \qquad \ldots (4)$$

which indicates that oxide layers could appreciably reduce the true Kapitza conductance; in practice the thermal

resistance of the oxide would probably mask the dense layer effect, and the latter will in any case only be important at high temperatures (1–2 K).

For the fully treated specimens of reference 6 we have $h_N \sim 0{\cdot}3\,T^{3{\cdot}5}$ which gives a discrepancy of ~5 at 1 K between theory and experiment, if we include the dense layer. Comparison is complicated by the disagreement in the temperature dependence. However it is probably true to say that the agreement is at least as good as that usually found with other materials, and that a T dependence stronger than T^3, which characterizes the data, is compatible with the effect of a dense layer. As has been noted several times agreement between theory and experiment seems better for low acoustic impedance materials, which is the case here. For high acoustic impedance materials the observed heat flow is usually much higher than that calculated. For at least one material (copper [27]) the agreement with the theory becomes very much better in the very low temperature (long phonon wavelength) limit. These general observations suggest that there exists a parallel mechanism which becomes comparatively increasingly important as the Khalatnikov conductance mechanism grows smaller and which is more effective at higher temperatures. This point has been elaborated elsewhere.[32]

As there are now several results for surfaces prepared or cleaned under liquid helium, it would be interesting to compare these with the theory. These have been tabulated in Table 3. While there is some agreement between the results for Pb(S), the observed conductances for Pb(N) (which should be more appropriate for comparison with theory), Cu[20], and KCl[22] are about an order of magnitude higher. The agreement with theory is thus not appreciably better than is usual, although it would be interesting to carry out further measurements on other materials to confirm this point. We note that as the observed conductances are always too high, and as cutting or scraping tends to depress the apparent conductance due to the surface damage, the better 'agreement' with theory obtained could be quite fortuitous. Also if we assume that the scraped or cut values correspond to agreement with the theory, many unlikely assumptions become necessary in order to explain the present results on the cut specimens.

A final general remark is in order concerning the possibility of observing h_{el}. The standard treatment [12,13] leads one to assume that the only effect of applying a magnetic field $H > H_c$ for $T \ll T_c$ is to introduce the electronic component in parallel. This simple picture is complicated by at least two difficulties. Firstly it is not evident *a priori* that many processes which may be operative in the superconducting state (dense layer modification, heat transfer by the intermediary of absorbed gas atoms[20] etc) are unaffected by a transition to the normal state. Secondly to observe a large electronic contribution, the energy stored in the surface wave in the superconducting state must not be removed. Should the surface wave be 'fully' scattered by non-electronic defects (for example, surface asperities) then even in the presence of a highly effective electron–phonon interaction in the normal state we would expect to see at most only a very small increase in h_K. From the point of view of surface roughness this scattering should be reduced at lower temperatures, which gives a second reason why the observation of h_{el} should be more favourable at ultra-low temperatures. Needless to say, the existence of a direct interaction such as proposed by Bloch is not necessarily affected by these considerations.

Table 3. List of conductances of specimens cut, cleaved or scraped under liquid helium and comparison with the Khalatnikov model

Solid	h_{obs}, W cm^{-2} K^{-1}	h_{Khal}	*Experimental reference*
Cu	$5{\cdot}3 \times 10^{-2} T^{3{\cdot}6}$	$2 \times 10^{-3} T^3$	20
Pb(S)	$2{\cdot}4 \times 10^{-2} T^{3{\cdot}2}$		5
Pb(S)	$10^{-2} T^5$	$1{\cdot}8 \times 10^{-2} T^3$	8 (IV)
Pb(N)	$2{\cdot}5 \times 10^{-1} T^3$		8 (IV)
KCl	$8{\cdot}3 \times 10^{-2} T^{3{\cdot}3}$	$5{\cdot}5 \times 10^{-3} T^3$	R. C. Johnson, private communication

Conclusion

All of these results show the importance of surface damage in determining the apparent Kapitza resistance, and we conclude that this is the dominant factor in the change seen at the superconducting-to-normal phase transition in lead. The results likewise point to the difficulties to be expected in the measurement of the Kapitza resistance of high thermally resistive materials.

In a general sense it seems clear that too little attention has been paid up to now in producing a detailed description of the physical and chemical state of the surface. We are hoping to apply better techniques to the preparation of specimen surfaces, as well as to develop more satisfactory methods for the measurement of the mean surface temperature.

The author gratefully acknowledges the collaboration of Dr L. J. Challis in the early part of the work reported here which formed part of a PhD thesis submitted at the University of Nottingham 1965, and would also like to thank B. Hebral for collaboration in the measurement of the PbIn specimens and for many helpful discussions.

REFERENCES

1. CHALLIS, L. J. Proc LT 7, 476 (1960)
2. CHALLIS, L. J. *Proc Phys Soc* (London) **80**, 759 (1962)
3. GITTLEMAN, J. I., and BOZOWKI, S. *Phys Rev* **128**, 646 (1962)
4. BARNES, L. J., and DILLINGER, J. R. *Phys Rev Lett* **10**, 287 (1963)
5. KUANG WEY-YEN, *Soviet Physics JETP* **15**, 635 (1962)
6. CHALLIS, L. J., and CHEEKE, J. D. N. *Prog Refrig Sci* **1**, 227 (1965)
7. CHEEKE, J. D. N. Thesis (unpublished) Nottingham (1965)

8. CHEEKE, J. D. N. Proc LT 11, St Andrews, 567 (1968)
9. CHALLIS, L. J., and SHERLOCK R. Proc LT 11, St Andrews, 571 (1968) and *Jour Phys C* 3, 1193 (1970)
10. POLLACK, G. *Rev Mod Phys* **41**, 48 (1969)
11. LITTLE, W. A. *Canadian J Phys* **37**, 334 (1959)
12. LITTLE, W. A. *Phys Rev* **123**, 435 (1961)
13. ANDREEV, A. F. *Soviet Physics JETP* **16**, 1084 (1963)
14. KHALATNIKOV, I. M. *M. Zh Eksp Teor Fiz* **22**, 687 (1952)
15. CHALLIS, L. J. and CHEEKE, J. D. N. *Proc Roy Soc* **A304**, 479 (1968)
16. HOLLAND, L. Vacuum Deposition of Thin Films (Chapman and Hall, London, 1966)
17. CARRUTHERS, J. A., COCHRAN, J. F., and MENDELSSOHN, K. *Cryogenics* **2**, 160 (1962)
18. PRESI, 101 Rue Ampere, Grenoble, France
19. BLOCH, F. reported by W. A. Little, *IBM J Res and Devel* **6** 31 (1962) and reference 20
20. JOHNSON, R. C., and LITTLE, W. A. *Phys Rev* **130**, 596 (1963)
21. JOINER, W. C. H. *Phil Mag* **20**, 807 (1969)
22. JOHNSON, R. C., private communication
23. CARTER, G., and COLLIGON, J. S. (ed) Ion Bombardment of Solids. Chapter 6 (Heineman, London, 1968)
24. NEEPER, D. A., and DILLINGER, J. R. *Phys Rev* **135**, A 1028 (1964)
25. CHALLIS, L. J., DRANSFELD, K., and WILKS, J. *Proc Roy Soc* **A 260**, 31 (1961)
26. VAN DER HOEVEN, B., and KEESOM, P. H. *Phys Rev* **137**, A 103 (1965)
27. ANDERSON, A. C., CONNOLLY, J. I., and WHEATLEY, J. C. *Phys Rev* **135**, A 910 (1964)
28. CHALLIS, L. J. *Phys Lett* **13**, 20 (1964)
29. SEIDEL, T., and MEISSNER, H. *Phys Rev* **137**, 272 (1966)
30. SAMUELS, L. E. Surface Chemistry of Metals and Semiconductors, 82 (1960)
31. ANDREWS, J. M., and STANDBERG, M. W. P. *Proc Inst Elec Engrs* **54**, 523 (1966)
32. CHEEKE, J. D. N. *Journal de Physique*, special issue on helium (forthcoming 1970)
33. SNYDER, N. S. *Cryogenics* **10**, 89 (1970)
34. LIVINGSTON, J. D. *Phys Rev* **129**, 1943 (1963)
35. MONTGOMERY, H. *Proc Roy Soc* **A 244**, 85 (1958)
36. SEIN, 57 rue Eugène Carrière, Paris 18e, France
37. DUBECK, L., LINDENFIELD, P., LYNTON, E. A., and ROHRER, H. *Rev Mod Phys* **36**, 110 (1964)