# Superheating and Supercooling in Single Spheres of Tin, Indium, and Gold-Plated Indium

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An experimental study of the superheating and supercooling properties of tin, indium, and gold-plated indium spheres, typically 10 $\mu$m in diam, has been made. The results are more reliable than those obtained from experiments on powders. The effects of nucleation centers are discussed, and it is shown that in indium, at least, different nucleation centers are active in superheating and supercooling. The effect of nucleation centers vanishes as one approaches $T_c$, where the following values for the Ginzburg-Landau parameter $\kappa$ are obtained: $\kappa_{\text{Sn}}=0.0926\pm0.001$ and $\kappa_{\text{In}}=0.0620\pm0.001$. The effect of specimen size upon superheating and supercooling is also clearly demonstrated. It is found that gold plating reduces the supercooling field near $T_c$ by a factor of 1.70 ($\pm2\%$), as predicted by theory. Gold plating affects the superheating field, as a function of temperature, in a manner which is qualitatively predicted by the Ginzburg-Landau theory.

## I. INTRODUCTION

TYPE-I superconductors undergo a first-order phase transition between the normal and superconducting states in the presence of a magnetic field, and, as in other first-order transitions, one expects superheating and supercooling to occur.

Experimentally, supercooling is relatively easy to observe, whereas large superheating is difficult to observe in bulk specimens. Supercooling was first studied systematically by Faber,[1] who found that by locally lowering the magnetic field applied parallel to a cylinder of a type-I material such as Sn, In, or Al, he could keep the specimens in the normal state at fields much lower than the thermodynamical critical field $H_c(T)$. The relative amount of "supercooling" thus obtained varied significantly as a function of position of the field coil along the specimen, and it was proposed that certain flaws and defects near the surface of the specimen acted as nucleation centers for the superconducting phase. It was observed, however, that the effect of the flaws seemed to decrease as one approached the critical temperature. This is to be expected if one assumes that the flaws have dimensions such that they become of negligible size compared to the other distances involved in the problem near $T_c$. These dimensions are the coherence length $\xi(T)$ and the penetration depth $\lambda(T)$, which both diverge at $T_c$. Therefore very close to $T_c$ the supercooling observed should be typical for the material and not the defects, and useful information can be expected from the results.

Large superheating, as well as supercooling, was first[2] observed in samples consisting of a very large number of indium spheres having diameters in the range 1–5 $\mu$m. Similar experiments have since been performed on other materials.[3–6] The reason for this success is that the chance of having a defect that will act as a nucleation center decreases with size. Also, when a phase is nucleated in one sphere, it will not propagate to the others. The drawback with experiments on powders lies in the fact that one observes relatively smeared-out transitions, which makes the final interpretation of superheating and supercooling fields somewhat arbitrary. This nonideal behavior is caused by variations in size, shape, and quality of the spheres, as well as clustering and other effects that can distort the magnetic field seen by some spheres.

It is clearly desirable to look for the phase transition in one selected sphere at a time, and it is the purpose of this paper to describe the preparation and handling of small spheres of indium and tin, the gold plating of indium spheres, the observation of the superconducting transition of such spheres, and the interpretation of the experimental results.

In Sec. II we shall discuss the relevant theoretical background, followed, in subsequent sections, by the experimental details, the results, and a comparison of the results with theory.

## II. THEORY

Superheating and supercooling in superconductors have been discussed in terms of the Ginzburg-Landau[7] (GL) theory by Ginzburg.[8] In Fig. 1 we present the results of a numerical calculation, in the limit where

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[1] T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957).
[2] J. Feder, S. R. Kiser, and F. Rothwarf, Phys. Rev. Letters **17**, 87 (1966).
[3] J. P. Burger, J. Feder, S. R. Kiser, F. Rothwarf, and C. Valette, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. 2B, p. 352.
[4] J. Feder, S. R. Kiser, F. Rothwarf, J. P. Burger, and C. Valette, Solid State Commun. **4**, 611 (1966).
[5] F. W. Smith and M. Cardona, Phys. Letters **24A**, 247 (1967).
[6] F. W. Smith and M. Cardona, Solid State Commun. **5**, 345 (1967).
[7] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).
[8] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **34**, 113 (1958) [English transl.: Soviet Phys.—JETP **7**, 78 (1958)].

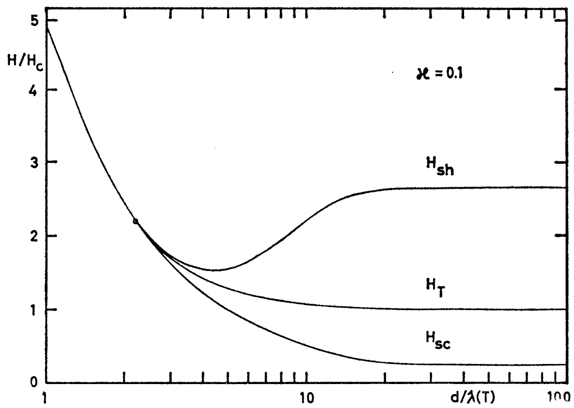


FIG. 1. Superheating field $H_{sh}$, the thermodynamic field $H_T$, and the supercooling field $H_{sc}$ for a film of thickness $d$ in a parallel field, as calculated from the GL theory in the approximation $\kappa\ll1$.

$\kappa\ll1$, for the superheating, supercooling, and thermodynamic critical fields in a type-I film of thickness $d$ in a magnetic field $H$ applied parallel to the surface. The GL parameter $\kappa=\lambda(T)/\xi(T)$ is assumed to be 0.1 in this calculation. This implies that a sufficiently thick superconducting film remains superconducting even above the thermodynamical critical field $H_T$ ($=H_c$ for a bulk specimen) where the free energies of the superconducting and the normal states are equal. There is, however, an upper limit to the superheating possible, and one can show analytically[9] that for fields larger than

$$H_{sh}=H_c/(\kappa\sqrt{2})^{1/2} \tag{1}$$

there exists no one-dimensional superconducting solution of the GL equation which minimizes the free energy. Equation (1) holds for $\kappa\ll1$ in a semi-infinite superconductor.[10] Further numerical calculations[8,11] give important deviations from Eq. (1) when $\kappa\sim1/\sqrt{2}$, and for $\kappa\rightarrow\infty$, $H_{sh}\rightarrow H_c$. In all these calculations $H_{sh}$ is the field above which the state, where the order parameter varies only in the direction transverse to the film, is unstable with respect to one-dimensional perturbations in the order parameter. Thus for type-II superconductors ($\kappa>1/\sqrt{2}$), $H_{sh}$ is the upper limit for the existence of the Meissner state above $H_{c1}$. Since the above calculations allow only one-dimensional perturbations of the order parameter, the resulting value of $H_{sh}$ must be considered to represent only an upper limit. If one allows more than one degree of freedom in the perturbations,[12] one will in general find lower instability fields. In the limit of $\kappa\gg1$ this has been attempted,[13,14] with the result $H_{sh}\sim0.75H_c$. Such calculations have not been performed for other values of $\kappa$. We believe, however, that the result (1) is correct in the limit $\kappa\ll1$. We argue below that at $\kappa=1/\sqrt{2}$, $H_{sh}$ should equal $H_c$, so that Eq. (1) should work well as an interpolation formula for $\kappa\leq1/\sqrt{2}$. It has been shown[15] that for $\kappa=1/\sqrt{2}$ there is no interface energy between a normal and a superconducting region if the interface is a plane, and also that the line energy of a single vortex is zero for this value of $\kappa$. If one then accepts that the interface energy of any normal superconducting interface involved in the nucleation process is also zero, then there will be no energy barrier inhibiting the nucleation process, and thus superheating will be impossible, giving $H_{sh}=H_c$ for $\kappa=1/\sqrt{2}$.

With a sufficiently thick film in the normal state, one can lower the applied field below the thermodynamical critical field and have the film remain in the normal state, until $H$ reaches $H_{sc}$. The field $H_{sc}$ has been calculated by Saint-James and de Gennes[16] and found for all values of $\kappa$ to be

$$H_{sc}=H_{c3}=1.695\sqrt{2}\kappa H_c, \tag{2}$$

where $H_c$ is the bulk critical field. The identification of $H_{sc}$ with $H_{c3}$ is valid for $\kappa<0.409$. It was predicted[17] that for $\kappa>0.409$, at $H_{c3}$ one will form a layer of surface superconductivity which only spreads into the supercooled material at a still lower field. This field was later calculated numerically.[18] Such peculiar supercooling effects have actually been observed.[19,20] For the experiments discussed in this paper, however, the supercooling field is $H_{c3}$.

One important feature seen in Fig. 1 is that not only the thermodynamical critical field $H_T$ but also $H_{sc}$ and $H_{sh}$ depend on the thickness of the film. With decreasing $d/\lambda$ the width of the hysteresis, $H_{sh}-H_{sc}$, diminishes and finally vanishes for $d\leq d_c=(\sqrt{5})\lambda(T)$, where the phase transition is no longer a first-order but rather a second-order one. For this reason the normal superconducting phase transition will always be a second-order one very close to the critical temperature $T_c$, because $\lambda(T)$ diverges at $T_c$.

The GL theory has been derived from the microscopic theory of superconductivity near $T=T_c$ by Gorkov,[21,22] who shows that the GL parameter $\kappa$ is given by

$$\kappa=0.96\lambda_L(0)/\xi_0, \tag{3}$$

[9] Orsay Group on Superconductivity, in *Quantum Fluids*, edited by D. F. Brewer (North-Holland Publishing Co., Amsterdam, 1966), p. 26.
[10] The expression differs slightly from the result of Ref. 8.
[11] J. Matricon and D. Saint-James, Phys. Letters **24A**, 241 (1967).
[12] P. Voetman Christiansen and H. Smith, Phys. Rev. **171**, 445 (1968).
[13] V. P. Galaiko, Zh. Eksperim. i Teor. Fiz. **50**, 717 (1966) [English transl.: Soviet Phys.—JETP **23**, 475 (1966)].
[14] L. Kramer, Phys. Letters **24A**, 571 (1967).
[15] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966).
[16] D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).
[17] J. Feder, Solid State Commun. **5**, 299 (1967).
[18] J. G. Park, Solid State Commun. **5**, 645 (1967).
[19] J. P. McEvoy, D. P. Jones, and J. G. Park, Solid State Commun. **5**, 641 (1967).
[20] F. W. Smith and M. Cardona, Phys. Letters **25A**, 671 (1967).
[21] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959)].
[22] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **10**, 998 (1960)].

where the London penetration depth is

$$\lambda_L(0)=(mc^2/4\pi Ne^2)^{1/2} \tag{4}$$

and the coherence distance $\xi_0$ is

$$\xi_0=0.18\hbar v_F/kT_c. \tag{5}$$

In these equations $N$ is the density of electrons and $v_F$ is the Fermi velocity. This calculation is based on the free-electron model of metals.

Gorkov[23] has also calculated the temperature variation of the parameter $\kappa_1(t)$ involved in the relation for the bulk nucleation field $H_{c2}$, below which the normal state is unstable with respect to the formation of superconductivity even in an infinite sample. Defining

$$H_{c2}(t)=\sqrt{2}\kappa_1(t)H_c(t), \tag{6}$$

he finds that

$$\kappa_1(t)=\kappa(1.25-0.30t^2+0.05t^4), \tag{7}$$

where $t=T/T_c$.

This equation is valid in the clean limit $l/\xi_0\gg 1$, where $l$ is the mean free path. Abrikosov[24] has shown, also in the clean limit, that $H_{c3}/H_{c2}>1$ for all temperatures. Ebneth and Tewordt[25] demonstrate that

$$\left[\frac{d}{dt}\left(\frac{H_{c3}}{H_{c2}}\right)\right]_{t=1}=-1.040 \tag{8}$$

in the clean limit, so that the factor 1.695 in Eq. (2), valid only for $t=1$, increases with decreasing temperature. Lüders[26] finds that, if the electrons are diffusely reflected at the surface, then

$$\frac{H_{c3}}{H_{c2}}=1.695\left[1+p\frac{45\zeta(4)}{224\zeta(3)}1.36(1.695)^{1/2}\times\left(\frac{12}{7\zeta(3)}(1-t)\right)^{1/2}+\cdots\right], \tag{9}$$

near $t=1$, where $p$ is the diffuse scattering coefficient and $\zeta(n)$ is the Riemann $\zeta$ function. Lüders[27] also discusses the effect of finite specimen size.

For the superheating field, no microscopic calculation has been performed outside the GL regime.

It can be seen that the measurement of $H_{sh}$ and $H_{sc}$ gives $\kappa$ directly, provided that $H_c$ is known. Since we shall be interested in comparing experimentally obtained values with those obtained from theory, we present the experimental results in terms of the following parameters:

$$\kappa_{sc}(T)\equiv 0.418[H_{sc}(T)/H_c(T)], \tag{10}$$

[23] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].
[24] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **47**, 720 (1964) [English transl.: Soviet Phys.—JETP **20**, 480 (1965)].
[25] G. Ebneth and L. Tewordt, Z. Physik **185**, 421 (1965).
[26] G. Lüders, Z. Physik **202**, 8 (1967).
[27] G. Lüders, Z. Physik **209**, 219 (1968).

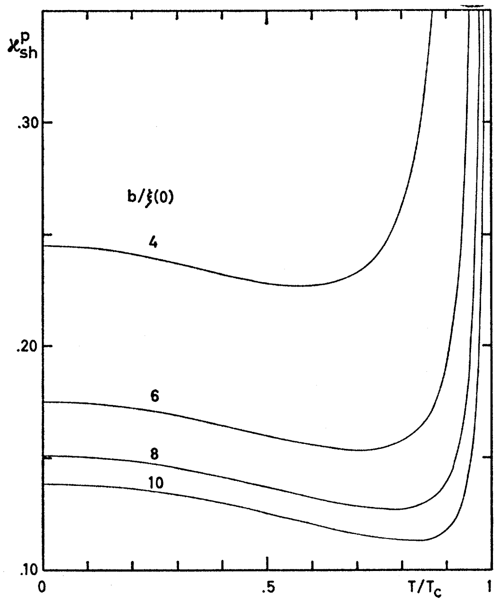


FIG. 2. $\kappa_{sh}^P$ as a function of reduced temperature, calculated (Ref. 9) from the GL theory, assuming a temperature-independent extrapolation length $b$, $\xi(T)=\xi(0)/[1-(T/T_c)^4]^{1/2}$ and $\kappa(T)=0.06\{1+0.7[1-(T/T_c)^2]\}$.

$$\kappa_{sh}(T)\equiv 0.314[H_{sh}(T)/H_c(T)]^{-2}, \tag{11}$$

$$\kappa_R(T)\equiv 0.382[H_{sc}(T)/H_{sh}(T)]^{2/3}. \tag{12}$$

The expression (10) is simply obtained from Eq. (2), $\kappa_{sh}(T)$ is defined using Eq. (1) after the insertion of a factor $\frac{2}{3}$ to take into account the demagnetizing field of a sphere, and $\kappa_R$ is obtained by eliminating $H_c(T)$ between Eqs. (10) and (11).

The parameters $\kappa_{sc}(T)$ and $\kappa_{sh}(T)$ thus defined should converge to a common value, the GL parameter $\kappa$, as $T$ approaches $T_c$, provided that the sphere is large enough to prevent size effects. It can be seen from Fig. 1 that size effects occur when $\xi(T)$ becomes comparable to the dimensions of the sample. As a result of the size effect, the parameters $\kappa_{sc}$ and $\kappa_{sh}$ will both increase above $\kappa$ and finally diverge as $T\rightarrow T_c$. The parameter $\kappa_R(T)$ should also approach $\kappa$ as $T\rightarrow T_c$ and has the advantage that it is independent of $H_c(T)$.

For thin films, $H_{sc}=(\sqrt{24})(\lambda/d)H_c$, and equating this to $H_{c3}$, which is $H_{sc}$ for thick films, gives $d=2.04\times\xi(T)$ as an estimate of the thickness above which size effects are unimportant. For spheres,[8] $H_{sc}=(8\sqrt{5})\times(\lambda/D)H_c$, giving $D=7.5\xi(T)$ as the diameter above which size effects are unimportant. For indium and tin $D$ is of the order 5 $\mu$m at $T=0.95T_c$. If the superconductor is plated with a normal material, then $H_{sc}=H_{c2}=H_{c3}/1.695$ as discussed later, and thus the corresponding dimensions will be 1.7 times larger.

Experiments were also performed on superconducting spheres coated with a normal metal. The effect of the normal coating is to change the boundary condition for

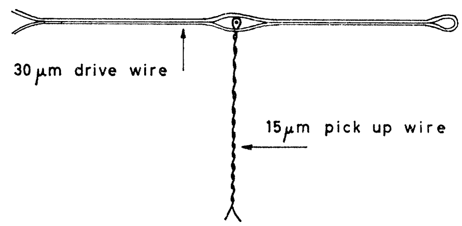


FIG. 3. The sample h...

the order parameter at the surface. de Gennes[28] has derived the following boundary condition for the order parameter in the dirty limit:

$$\frac{1}{\psi}\frac{d\psi}{dx}\bigg|_{x=0}=-\frac{1}{b}, \tag{13}$$

where the extrapolation length, $b$, depends on the properties of the two metals and the transmission coefficient for electrons between them. Zaitsev[29] has derived a similar relation,

$$\frac{1}{\psi}\frac{d\psi}{dx}\bigg|_{x=0}=-\frac{1}{\tilde{\beta}}\frac{\kappa}{\lambda(T)}\left(\frac{T_c}{T_c-T}\right)^{1/2}, \tag{14}$$

where $\tilde{\beta}=C_l\beta$ and $C_l=[12/7\zeta(3)]^{1/2}$ for $l\rightarrow+\infty$, and $C_l=2/\pi$ for $l\ll\xi_0$, where $l$ is the mean free path in the superconductor. $\beta$ is a parameter which involves the diffuse scattering coefficient and the transmission and reflection coefficients for the electrons at the interface. If the transmission coefficient goes to zero, $\beta$ goes to infinity, and one obtains the usual boundary condition for $\psi$. If there is good contact, so that

$$\tilde{\beta}[(T-T_c)/T_c]^{1/2}\ll 1,$$

Zaitsev finds that

$$H_{sc}{}^P=H_{c2}\left(1+\frac{(1-T/T_c)^{1/2}}{2\sqrt{\pi}}\tilde{\beta}\exp\frac{-1}{\tilde{\beta}^2(1-T/T_c)}\right); \tag{15}$$

hence, according to this theory, the surface superconductivity is completely suppressed near $T_c$. This conclusion has also been reached by Hurault[30] for the dirty case. It is interesting to see from Eq. (14) that the extrapolation length $b$ is temperature-independent close to $T_c$, because $\lambda(T)$ diverges as $1/(1-T/T_c)^{1/2}$ in this vicinity.

For the presentation of the experimental results on plated spheres we introduce a new parameter,

$$\kappa_{sc}{}^P(T)=\tfrac{1}{2}\sqrt{2}[H_{sc}{}^P(T)/H_c(T)], \tag{16}$$

where $H_{sc}{}^P(T)$ is the observed supercooling field for the plated sphere. If the factor 1.695 really vanishes close to $T_c$, we should find that $\kappa_{sc}{}^P(T)$, $\kappa_{sc}(T)$, and $\kappa_{sh}(T)$ all converge at $T_c$. Equation (15) predicts that, below $T_c$, $H_{sc}{}^P$ will not be suppressed by the full factor 1.695, so that at lower temperatures $\kappa_{sc}{}^P>\kappa_{sc}$.

The superheating of the superconducting half-space, coated with a normal metal, has been discussed by the Orsay group[9] for the case $\kappa\ll 1$, using the boundary conditions of Eq. (13) on the assumption that the extrapolation length $b$ is independent of temperature and magnetic field. We choose to present their results in the following way. The predicted superheating field from Ref. 9 is corrected by a factor $\frac{2}{3}$ to account for the demagnetizing field of a sphere and inserted in the expression (11). Hence we define

$$\kappa_{sh}{}^P=0.314[H_{sh}{}^P(T)/H_c(T)]^{-2}. \tag{17}$$

A plot of $\kappa_{sh}{}^P$ as a function of temperature and for various values of $b/\xi(0)$ is presented in Fig. 2. It is seen that the effect of the normal coating is strongly dependent on temperature and the parameter $b/\xi(0)$. In Fig. 2 we have used $\xi(T)\sim\xi(0)/(1-t^4)^{1/2}$ and $\kappa(T)=0.06[1+0.7(1-t^2)]$, which corresponds closely to our observed temperature variation of $\kappa_{sc}(T)$ for indium. It should be remembered at this point that these results, based on the GL theory, are valid only close to $T_c$ and are extended by the insertion of an empirical temperature dependence of the parameters in the theory. However, it will later be shown that the qualitative behavior of the experimental results is indeed remarkably well described using such a procedure.

## III. EXPERIMENTAL

### A. Preparation of the Spheres

The spheres were produced by ultrasonic dispersion of the molten metal[31] in high-purity glycerol for indium and in 1,2,6-hexantriol for tin. The liquid volume was typically 3 $cm^3$ for 1 g of metal. The small ceramic vessel containing the liquid and the metal was placed on a hot plate, where the tip of an ultrasonic drill could be made to touch the molten metal. A specially prepared glass tip was used on the drill in order to avoid contamination. The ultrasonic power was turned on only after the metal was molten and in less than 1 min most of the metal was dispersed. The best results were obtained when the dispersion was quenched by pouring it into a mixture of glycerol and alcohol in equal proportions. For tin we obtained the best spheres using pure 1, 2, 6-hexantriol. On the other hand, for indium a basic solution was found to give better results. This was obtained by adding 4% by weight of $\beta$-phenylaethylamin to the glycerol. The quality of the spheres was improved in the sense that wrinkles and pits on the surfaces of the spheres were seen

[28] P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964).
[29] R. O. Zaitsev, Zh. Eksperim. i Teor. Fiz. 50, 1055 (1966) [English transl.: Soviet Phys.—JETP 23, 702 (1966).]
[30] J. P. Hurault, Phys. Letters 20, 587 (1966).
[31] Indium 99.9999% pure from the Consolidated Mining and Smelting Company Ltd., Montreal, Quebec, Canada; tin 99.9999% pure from L. Light & Co., Colnbrook, England.

less frequently. An addition of 0.2% KOH by weight instead of the above-mentioned organic base gave compatible results.

The spheres were cleaned by rinsing with alcohol a number of times. In this way one could also easily wash away the spheres less than 5 $\mu$m in diam, which were not needed. It turned out to be important to keep the spheres in alcohol, because upon drying they tended to collect on the bottom of the vessel and leave small deformations on one another.

### B. Handling of the Spheres

With a brush, a large number of spheres were put on a well-cleaned glass plate covered with alcohol. The spheres were nicely distributed by adding alcohol carefully at the proper places. The spheres were then allowed to dry and put under a good metallurgical microscope, which gave magnifications up to 500. At this magnification, using monochromatic light, the resolution was better than 1 $\mu$m.

The spheres were handled with a 15-$\mu$m nylon fiber which was clamped in a mechanical stage such that it could be moved in the vertical and horizontal directions by means of micrometer screws. The fiber was cleaned with alcohol, and with some patience one could roll the spheres around and pick them up more or less at will. It is important to turn the spheres over before picking them up, because the big defects tend to lie towards the glass and cannot be seen from above. Having picked up a sphere, there was normally no difficulty involved in placing it in the pickup loop of the detection system. As may be easily appreciated, it is of vital importance that all surfaces be clean, or else the spheres will stick to the glass and make it impossible to pick them up. Roughly 30% of all spheres mounted got lost in the liquid helium, and in one case we have evidence that the sphere was moving during the experiment. We found no way of avoiding these frustrating losses, since sticking the spheres down would possibly cause strains upon cooling. The diameter of the spheres was estimated using a graduated eyepiece in the metallurgical microscope.

### C. Gold Plating of the Spheres

A small quantity of spheres was placed in a graphite vessel containing a few cm$^3$ of gold electroplating solution.[32] The liquid was stirred with a platinum electrode and 4–6 V was applied between the vessel and the electrode. The spheres were removed using a fine brush.

Concentrated nitric acid was found to break open the gold coating of the spheres. We were thus able to observe that the coating thickness varied from 3 down to less than 1 $\mu$m, having a uniform thickness for any given sphere. The gold shells had smooth shiny insides and we concluded that the indium had not been etched in

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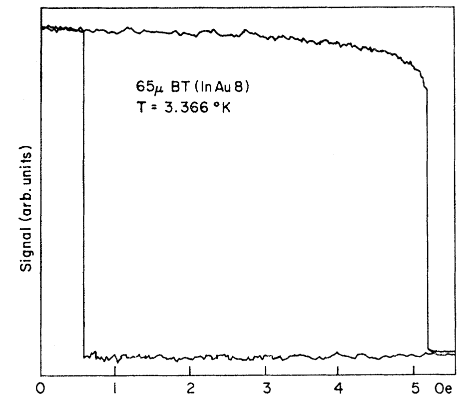


FIG. 4. Amplifier output as a function of applied magnetic field for a 65-$\mu$m gold-plated indium sphere, aged 20 h at room temperature after plating. The a.c. field is parallel to the static field. The depression of the signal before the transition to the normal state is not present for unplated spheres.

the plating process. On the outside the thicker shells exhibited a structure as if composed of small, approximately 2-$\mu$m, crystallites. Concentrated hydrochloric acid did not attack the spheres so violently, and the 21-$\mu$m sphere, for which we later present results, was selected from a powder of coated spheres that had been over 10 min in concentrated HCl. From the acid treatment and optical observation we believe the coating on our spheres to be both continuous and fairly uniform.

### D. Detection System

Each sample holder consisted of an insulated copper drive wire 30 $\mu$m in diam and a pickup loop of 15-$\mu$m wire (see Fig. 3). The whole system was mounted on a piece of Plexiglass with a varnish.

The drive current was obtained from a PAR H-8 lock-in amplifier and typically gave a field of 0.1 G at the position of the sphere. The pickup loop was connected to the primary of the torodial transformer placed in the helium. The transformer had a step-up ratio of 700 and was shielded by a niobium tube. The secondary was connected to the input of the lock-in amplifier, the output of which was fed to the $Y$ axis of an $X$-$Y$ recorder. Further details on the detection system have been published elsewhere.[33] The $x$ axis was driven by a voltage proportional to the current through the superconducting Helmholtz pairs that provided the magnetic field used to induce the phase transitions of the sphere. The output obtained for a gold-plated sphere is shown in Fig. 4; the output for an unplated sphere was, for a sufficiently slow sweep rate, completely square.

The earth magnetic field was cancelled by sending bias currents through the horizontal and vertical Helmholtz pairs. The horizontal pair had been oriented along the horizontal component of the earth magnetic

[33] D. S. McLachlan and J. Feder, Rev. Sci. Instr. 39, 1340 (1968).

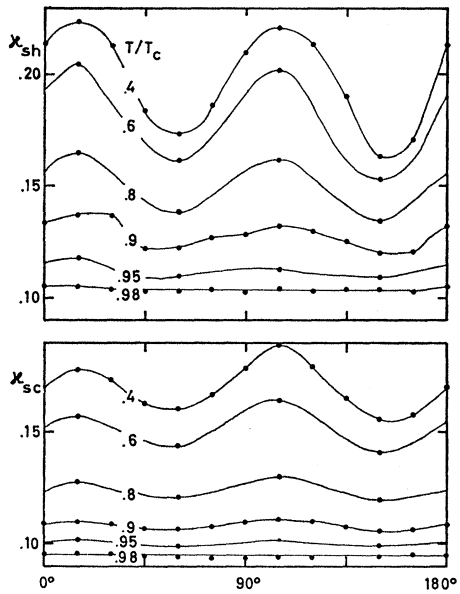


FIG. 5. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for a 21-$\mu$m tin sphere. $T_c = 3.719$°K.

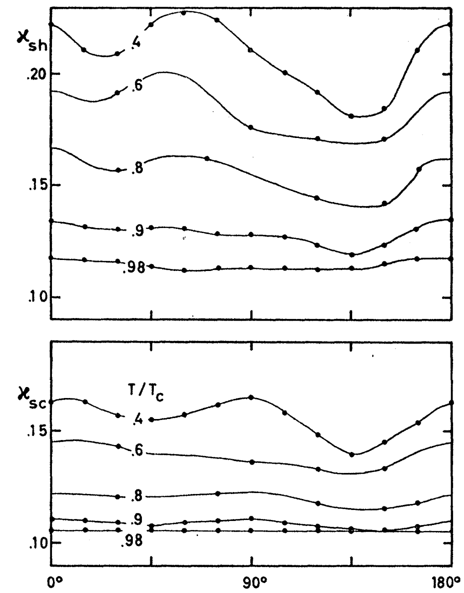


FIG. 7. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for an 8-$\mu$m tin sphere. $T_c = 3.720$°K.

field. The probe holder could be rotated about a vertical axis, so that observations were made for different field directions using the horizontal Helmholtz coil. The a.c. field was parallel to the static field when using the vertical Helmholtz coils.

### E. Temperature Measurements

The temperature of the bath was controlled by means of a heater at the bottom of the Dewar, in which the current was controlled by a differential oil manometer monitored by a photoresistor.[34] The temperature was obtained by measuring the vapor pressure of liquid helium in a small bulb placed close to the sample, using a mercury manometer. A germanium thermometer (Texas Instruments) was placed close to the sample to provide easy observation of temperature drifts and instabilities. The temperatures could be stabilized to $\frac{3}{10}$ of 1 mdeg near $T_c$. We believe the absolute error in our temperature readings to be less than 3 mdeg and the relative error less than 1 mdeg.

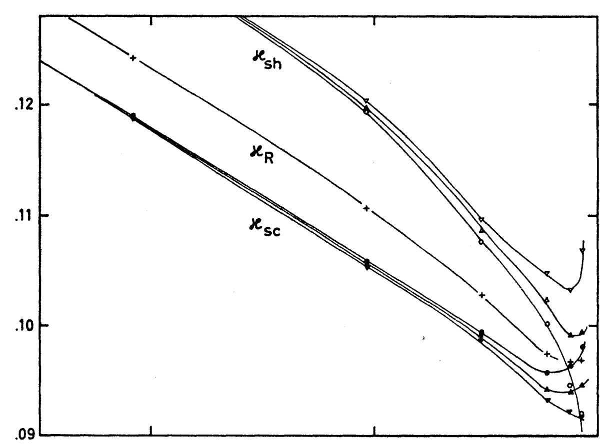


FIG. 6. $\kappa_{sh}$, $\kappa_{sc}$, and $\kappa_R$ as a function of reduced temperature for a 21-$\mu$m tin sphere. ● ○, $T_c = 3.718$°K; ▲ △, $T_c = 3.719$°K; ▼ ▽, $T_c = 3.720$°K.

[34] C. J. Adkins, J. Sci. Instr. **38**, 305 (1961).

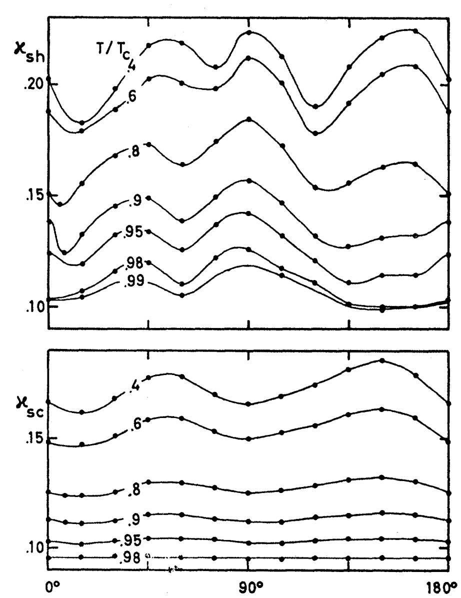


FIG. 8. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for a 48-$\mu$m tin sphere. $T_c = 3.717$°K.

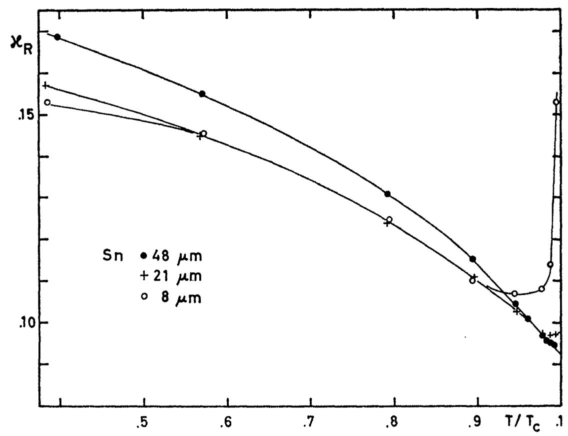


FIG. 9. $\kappa_R$ as a function of reduced temperature for the three tin spheres.

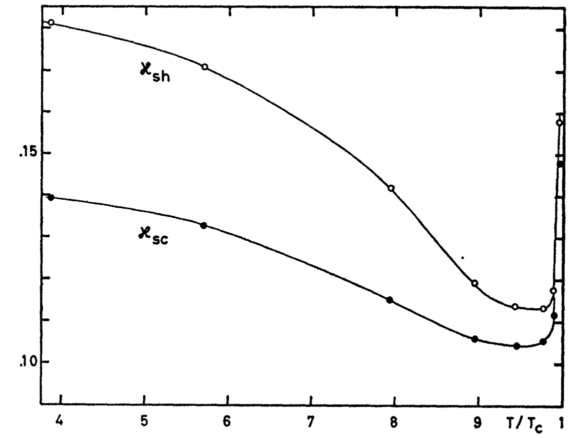


FIG. 11. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for an 8-$\mu$m tin sphere. $T_c$=3.720°K.

## IV. RESULTS

Experiments have been performed on 12 tin, 28 indium, and 11 gold-plated indium spheres. The raw data consist of the superheating and supercooling fields, as read from hysteresis loops of the type seen in Fig. 4 for a number of directions of the applied magnetic field and for a series of temperatures. For a given direction and temperature we found the hysteresis loops to be completely reproducible when the temperature was properly stabilized, and there was therefore no difficulty involved in the interpretation of the hysteresis loops. Only for the gold-plated spheres did we occasionally observe different superheating fields near $T_c$, but then a slow field sweep always gave reproducible results. We only present the results for a few spheres representing the best and/or most illustrative samples.

Since we are basically interested in the GL parameter $\kappa$, we choose to present the data in terms of the parameters $\kappa_{sc}(T)$, $\kappa_{sh}(T)$, and $\kappa_R(T)$ (as defined in Sec. II), which should all converge to $\kappa$ as $T \rightarrow T_c$. In all expressions but the one for $\kappa_R$, the thermodynamical critical field $H_c(T)$ appears. This field was not directly measured in these experiments and we used Mapother's[35] in the form

$$H_c(T)=H_c(0)[1-(T/T_c)^2]+H_c(0)D(T/T_c), \quad (18)$$

where $H_c(0)=305.5$ Oe for tin and $H_c(0)=282.7$ Oe for indium. The term $D(T/T_c)$ is taken from a graph given in Ref. 35. It turns out that the results obtained for $\kappa_{sc}(T)$ and $\kappa_{sh}(T)$ versus reduced temperatures depend strongly on the choice of $T_c$, in the vicinity of $T_c$, through the expression for $H_c(T)$. The absolute accuracy of our temperature measurements is of the

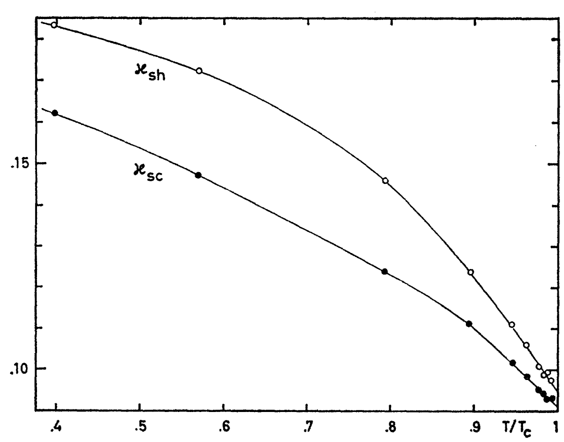


FIG. 10. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for a 48-$\mu$m tin sphere. $T_c$=3.717°K.

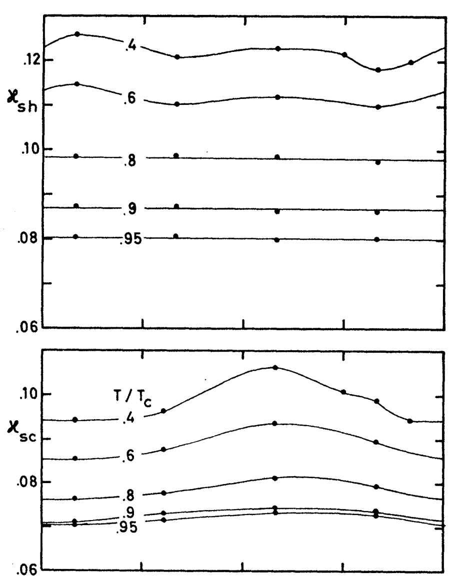


FIG. 12. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for a 8-$\mu$m indium sphere. $T_c$=3.407°K.

[35] D. E. Mapother, IBM J. Res. Develop. 6, 77 (1962).

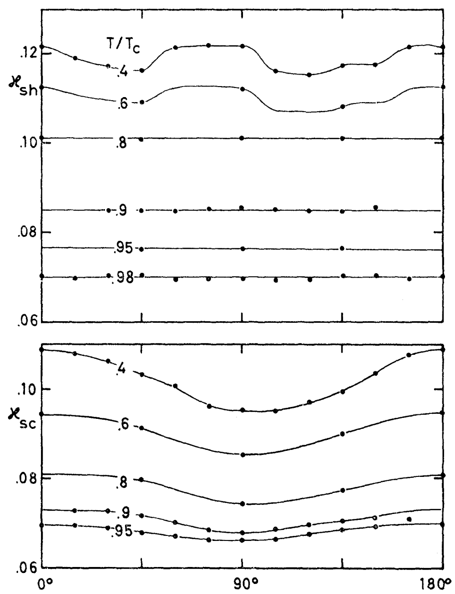


Fig. 13. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for an 16-$\mu$m indium sphere. $T_c = 3.404$°K.

order of 3 mdeg, whereas the accuracy of the relative measurements was considerably better than this. We have therefore adopted a procedure for presenting the results which is illustrated below for a tin sphere 21 $\mu$m in diam.

First, the parameters $\kappa_{sc}(T)$ and $\kappa_{sh}(T)$ are calculated, using an approximate value for $T_c$, and the plot in Fig. 5 is obtained. $\kappa_{sc}$ and $\kappa_{sh}$ in the direction which gives the lowest values, the 150° direction in Fig. 5,

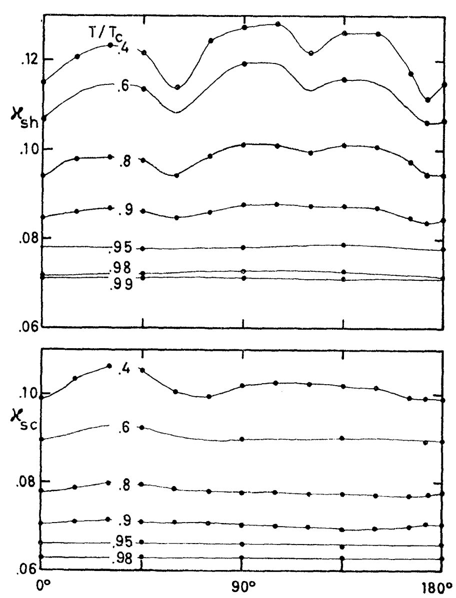


FIG. 14. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of field direction for a 35-$\mu$m indium sphere. $T_c = 3.404$°K.

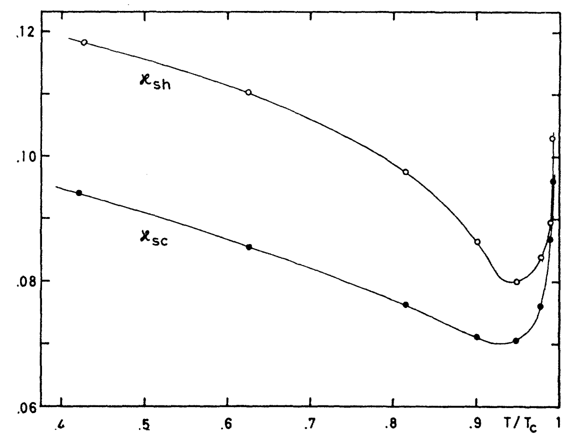


FIG. 15. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for an 8-$\mu$m indium sphere. $T_c = 3.407$°K.

are plotted as a function of reduced temperature, together with the $\kappa$ values obtained when the assumed $T_c$ is changed by a few mdeg. On a largely expanded scale the results will look like those of Fig. 6. It is seen that a change of only 1 mdeg gives rise to variations in $\kappa_{sc}$ and $\kappa_{sh}$ that are larger than the experimental inaccuracies for $T/T_c > 0.95$.

On the other hand, $\kappa_R(T)$ is insensitive to such a small variation in $T_c$, since it does not depend on $H_c$. We therefore assume that we have picked the correct $T_c$ when the curves for $\kappa_{sc}$ and $\kappa_{sh}$ have the same general appearance as the $\kappa_R$ curve, that is, the curves for $\kappa_{sc}$ and $\kappa_{sh}$ should neither cross nor split apart. This procedure gives us $T_c$. In the example shown in Fig. 6 we pick $T_c = 3.719$°K, which is 3 mdeg lower than the value $T_c = 3.722$°K given by Finnemore and Mapother.[36]

As both the normal and the superconducting phases are preferably nucleated in a region near the equator whose plane is transverse to the applied field, the

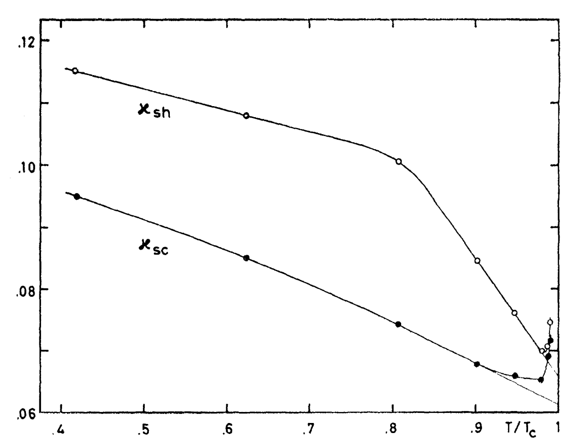


FIG. 16. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for a 16-$\mu$m indium sphere. $T_c = 3.404$°K.

[36] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).

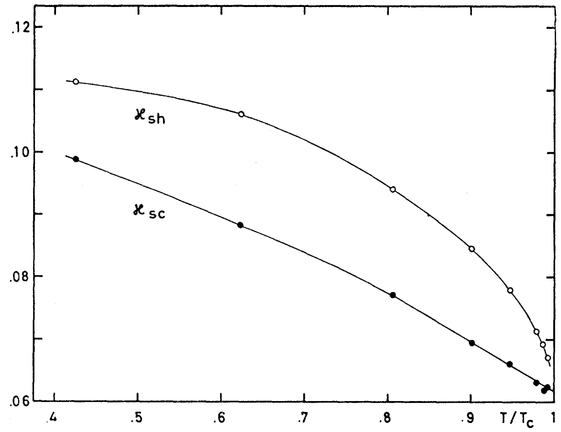


FIG. 17. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for a 35-$\mu$m indium sphere. $T_c=3.404$°K.

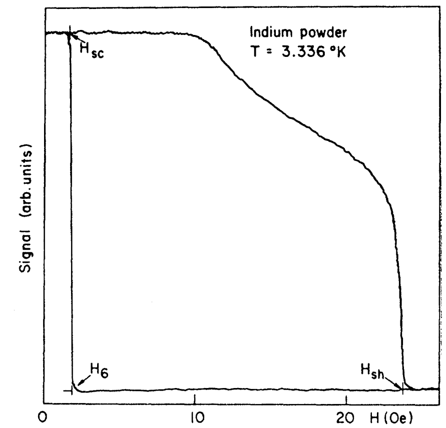


FIG. 19. Hysteresis loop for a powder of indium spheres 10–50 $\mu$m in diameter.

rotational diagrams reveal the presence of nucleation centers. Both the 21-$\mu$m sphere already discussed and the 8-$\mu$m and 48-$\mu$m spheres of Figs. 7 and 8 have a fourfold symmetry in their rotational diagram, and the variations in $\kappa_{sh}$ and $\kappa_{sc}$ are clearly correlated, the structure vanishing as one approaches $T_c$. In $\kappa_{sh}$ for the 48-$\mu$m sphere, another structure showing no symmetry is superimposed and this structure remains even very close to $T_c$. This big sphere was, however, somewhat deformed in a small region ($<10$ $\mu$m in diam). We could not obtain any big spheres free of such defects, which look like small scars that often have fourfold symmetry. Such defects were not observed in the other spheres even after the spheres had been turned around several times under the microscope. The rotational diagrams for the tin spheres are qualitatively different from those of indium spheres which fail to exhibit any rotational symmetry and whose variations of $\kappa_{sc}$ and $\kappa_{sh}$ are not correlated (see Figs. 12–14). Note that in Faber's experiments,[1] on supercooling, he found that two types of flaws were active as nucleation centers in tin, whereas no such evidence was found for indium. One might speculate that the variations showing symmetry are due to anisotropic properties of the material in the sphere, whereas the other variations are due to very small defects and pits.

The effect of specimen size on superheating and supercooling as discussed in Sec. II is borne out qualitatively in Fig. 9, where $\kappa_R$ for the three tin spheres is shown. The 8-$\mu$m sphere has a very pronounced size effect above $T/T_c\sim0.9$, the 21-$\mu$m sphere shows only a small size effect very near $T_c$, and in the 48-$\mu$m sphere no size effect has been observed. At low temperatures, $\kappa_R$ for the 21-$\mu$m and 8-$\mu$m spheres fall closely together except at the lowest temperature, where the smallest sphere is a little better. The big sphere is clearly not so good as the other two spheres at low temperatures, but the values of $\kappa_R$ for it and the 21-$\mu$m sphere converge at $T_c$.

In order to obtain the GL parameter $\kappa$ we have extrapolated $\kappa_{sc}$, $\kappa_{sh}$, and $\kappa_R$ to $T_c$ in such a way that the size effect is neglected. In Fig. 6 we find that $\kappa_{sc}(T_c)$

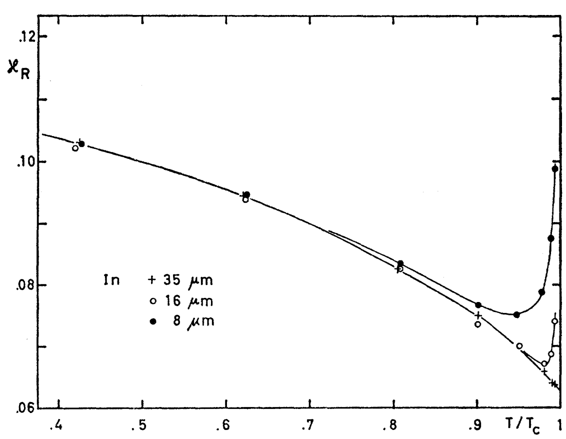


FIG. 18. $\kappa_R$ as a function of reduced temperature for three indium spheres.

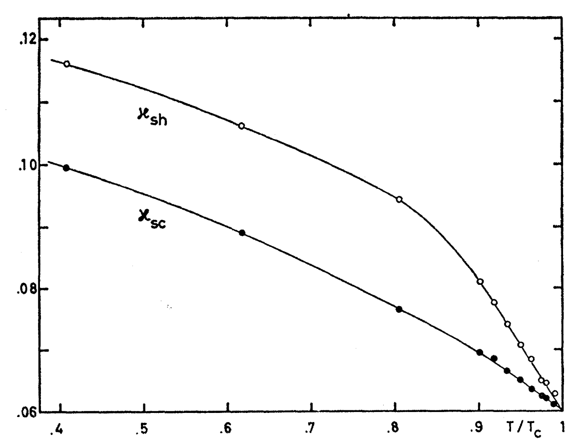


FIG. 20. $\kappa_{sh}$ and $\kappa_{sc}$ as a function of reduced temperature for an indium powder sample.

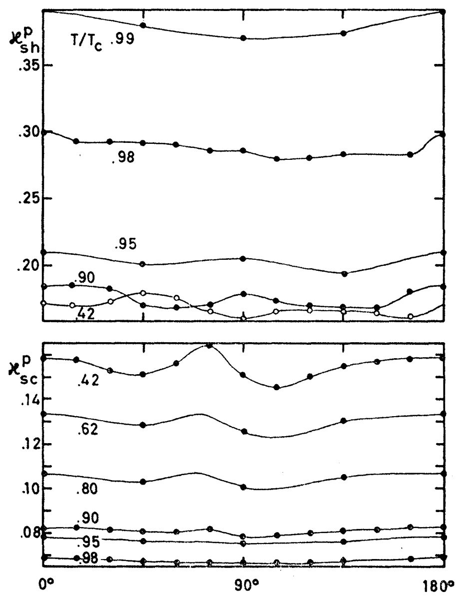


FIG. 21. $\kappa_{sh}{}^{P}$ and $\kappa_{sc}{}^{P}$ as a function of field direction for an 65-$\mu$m gold-plated indium sphere aged 6 h at room temperature after plating. $T_c = 3.404°$K.

$= 0.0914$, $\kappa_{sh}(T_c) = 0.0960$, and $\kappa_R(T_c) = 0.0930$ for the 21-$\mu$m sphere. For the 48-$\mu$m sphere (see Fig. 10) the values are $\kappa_{sc}(T_c) = 0.0914$, $\kappa_{sh}(T_c) = 0.0946$, and $\kappa_R(T_c) = 0.0923$. For the 8-$\mu$m sphere (Fig. 11) extrapolations are not meaningful, because of the large size effect. Clearly the extrapolation of $\kappa_{sh}$ is the least reliable one, and in order to test whether $\kappa_{sc}$ and $\kappa_{sh}$ do converge at $T_c$ it is more sensible to compare $\kappa_{sc}$ and $\kappa_R$, since this minimizes the inaccuracies introduced by the use of $H_c(T)$, which have not been directly measured. We see that there is only a 2% difference between $\kappa_{sc}$ and $\kappa_R$ at $T_c$, conclude that $\kappa_{sh}$ and $\kappa_{sc}$ should converge to within a few percent for tin, and obtain the value for tin

$$\kappa = 0.0926 \pm 0.001. \tag{19}$$

The slope of $\kappa_{sc}$ at $T_c$ is of some theoretical interest, and we have for the 21-$\mu$m tin sphere

$$\frac{1}{\kappa} \frac{d\kappa_{sc}(T/T_c)}{dT/T_c}\bigg|_{T/T_c=1} = -1.5. \tag{20}$$

It is clear, however, that this slope is larger than the characteristic value for tin, since the effect of defects has been demonstrated to vanish only gradually as $T_c$ is approached. This is clearly illustrated by the fact that for the 48-$\mu$m tin sphere, which has a visible defect, the slope is $-2.1$, considerably larger than that of the 21-$\mu$m sphere. The magnitude of the slope given should therefore be considered only as an upper limit.

Results for indium have been reported in an earlier paper,[37] but are included here for completeness and comparison. We again discuss the results of three spheres, 8, 16, and 35 $\mu$m in diam. The rotational diagrams are presented in Figs. 12–14 and the $\kappa$ curves are presented in Figs. 15–18. We have used $T_c = 3.404$ °K, which again is about 3 mdeg lower than the value given by Finnemore and Mapother.[36]

The rotational diagrams exhibit no symmetry, and in all spheres investigated there seems to be no evidence for a correlation between the variations in $\kappa_{sh}$ and $\kappa_{sc}$. Compared with tin, the amplitude of the variations are smaller and the variations have usually vanished at $T/T_c = 0.9$. Again the size effect is clearly seen in the $\kappa_R$ plot (Fig. 18), and is about as important as in tin.

Extrapolating $\kappa_{sc}$ to $T_c$ gives $\kappa_{sc}(T_c) = 0.0625$ for the 35-$\mu$m sphere and $\kappa_{sc}(T) = 0.0620$ for the 16-$\mu$m sphere. For the smallest sphere $\kappa_{sc}(T_c) = 0.065$ is obtained, but this is clearly too high, because of the large size effect in this sphere. Extrapolation of $\kappa_{sh}$ to $T_c$ gives values of the order 0.065, but these extrapolations are rather difficult to perform with a high degree of confidence, and again we consider it better to compare the extrapolated values of $\kappa_{sc}$ with those of $\kappa_R$, which are completely independent of the precise choice of $T_c$. We find that $\kappa_R(T_c) = 0.0625$ (see Fig. 18). We therefore again conclude that $\kappa_{sh}$ and $\kappa_{sc}$ should converge to within a few per cent, and obtain the $\kappa$ value for indium

$$\kappa = 0.0620 \pm 0.001. \tag{21}$$

The slope of $\kappa_{sc}$ at $T_c$ is found to be

$$\frac{1}{\kappa} \frac{d\kappa_{sc}(T/T_c)}{dT/T_c}\bigg|_{T/T_c=1} = -1.4. \tag{22}$$

For indium, experiments were also done on a powder using a mutual-inductance technique. The powder consisted of spheres 10–50 $\mu$m in diam diluted with a plastic powder so that the spheres occupy about $\frac{1}{6}$ of the volume of the sample. The fields interpreted as $H_{sh}$ and $H_{sc}$ are marked in Fig. 19. Note that in the original paper on superheating and supercooling in powders,[2] the field denoted $H_6$ was used as a conservative estimate of the supercooling field, because no quantitative estimate could be made of the effective field seen by a normal sphere surrounded by superconducting spheres in the relatively dense sample. It is now clear, in view of the results on single spheres, that $H_{sc}$ defined as in Fig. 19 is a better interpretation of the powder results. We do not believe that the small tails on the hysteresis loop of the powder represent particularly good superheating and supercooling, but rather superheating and supercooling of aspherical grains and clusters of spheres. In Fig. 20 the results for the powder are plotted, using the definitions of $H_{sc}$ and $H_{sh}$ introduced above. $\kappa_{sc}(T_c) = 0.060$, but we have more confidence in the results obtained from experiments on single spheres.

The experiments on gold-plated indium spheres show a number of interesting effects. The supercooling field is

[37] J. Feder and D. S. McLachlan, Solid State Commun. 6, 23 (1968).

lower than in the uncoated case and the superheating is completely suppressed close to $T_c$, whereas far from $T_c$ the effect on $\kappa_{sh}$ is not so dramatic. Also, since the superheating and supercooling properties change with time, we stored freshly coated spheres at liquid-nitrogen temperatures and aged them at room temperature. A few hours of aging at room temperature gave large changes in the superheating and supercooling fields. We consider this to be a result of diffusion of gold into indium, thereby changing the boundary conditions with age. Small spheres are found to have a lower $T_c$ when coated, as do large spheres if sufficiently aged. We also find that size effects are more important in coated than in uncoated spheres.

The rotational diagram for the 65-$\mu$m gold-plated indium sphere, the diameter of which includes the gold layer, is presented in Fig. 21, which again shows irregular and uncorrelated variations in $\kappa_{sc}^P$ and $\kappa_{sh}^P$. Also, the structure in $\kappa_{sh}$ appears to change with $T/T_c$. Aging does not change the structure in $\kappa_{sc}$, but in $\kappa_{sh}$ the structure does change somewhat with time. Choosing the lowest $\kappa_{sc}^P$ and $\kappa_{sh}^P$ for every temperature, we obtain the plot in Fig. 22 of $\kappa_{sc}^P$ and $\kappa_{sh}^P$ for the 65-$\mu$m sphere. For this sphere we measured $T_c=3.404°$K after 20 h of aging, so that this value was chosen for the presentation of the data. Note that for coated spheres $\kappa_R$ does not have any simple interpretation, and we cannot use the same procedure for finding $T_c$ that was used for unplated spheres.

By extrapolation one finds that $\kappa_{sc}^P(T_c)=0.0685$ after $1\frac{3}{4}$ h of aging and that $\kappa_{sc}^P(T_c)=0.0620$ after both 6 and 20 h of aging. For lower temperatures the surface superconductivity is not completely suppressed and the result is that $\kappa_{sc}^P>\kappa_{sc}$ for $T<T_c$. We interpret the increase in $\kappa_{sc}^P$ near $T_c$ as a size effect. As explained in Sec. II, plated and unplated spheres will show similar size effects when the ratio of the diameter is about 1.7, so that it is not very surprising to find a small size effect near $T_c$ even for a 65-$\mu$m sphere.

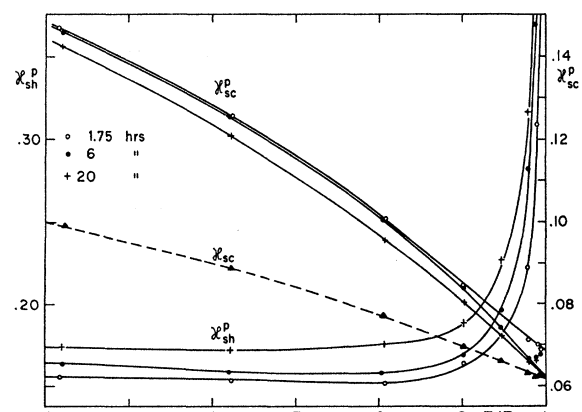


FIG. 22. $\kappa_{sh}^P$ and $\kappa_{sc}^P$ as a function of reduced temperature for a 65-$\mu$m gold-plated indium sphere aged 1.75, 6, and 20 h at room temperature after plating. $T_c=3.404°$K. The dotted line shows $\kappa_{sc}$ for the 35-$\mu$m indium sphere for comparison.

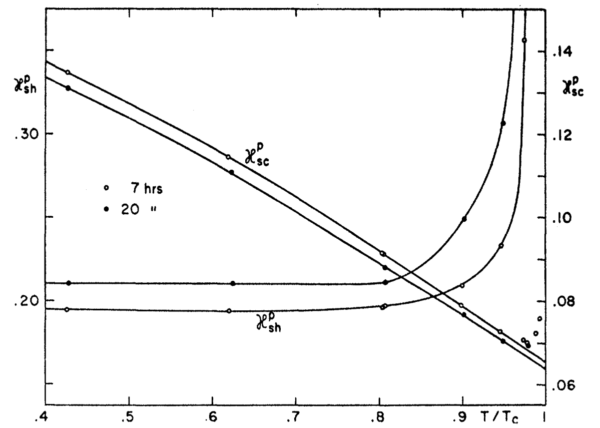


FIG. 23. $\kappa_{sh}^P$ and $\kappa_{sc}^P$ as a function of reduced temperature for a 31-$\mu$m gold-plated indium sphere aged 7 and 20 h at room temperature after plating. $T_c=3.404°$K.

The $\kappa_{sh}^P$ curves in Fig. 22 are markedly different from the $\kappa_{sh}$ curves of the unplated case. It is seen that the general appearance is qualitatively described by the simple theoretical model discussed in Sec. II and presented in Fig. 2. From Figs. 2 and 22 one would estimate that $b/\xi(0)\sim 8$, and $b$ is also seen to decrease upon aging as expected.

Some caution should be taken when the divergence near $T_c$ is discussed. One cannot have $H_{sh}<\frac{2}{3}H_c$, and for $\frac{2}{3}H_c<H_{sh}<H_c$ one should enter the intermediate state. This means that for $0.314<\kappa_{sh}^P<1/\sqrt{2}$ we should have no sharp transition, but rather a transition to the intermediate state.[38] We have indeed observed the intermediate state for gold-plated indium spheres. For the 65-$\mu$m sphere after 20 h of aging the transition at about 0.5 mdeg below $T_c$ for $H_{sh}^P$ was gradual, and for the case with the tickling field parallel to the static field the differential paramagnetic effect could be observed (the signal increasing relative to that obtained for the normal state). The differential paramagnetic effect[39] is characteristic of the intermediate state. For all the points presented in Fig. 22 the transitions at both $H_{sc}^P$ and $H_{sh}^P$ were sharp and abrupt. In Fig. 4 we have presented a hysteresis loop for the 65-$\mu$m gold-plated indium sphere aged 20 h at $T/T_c=0.989$. The only remarkable thing with this curve as compared to similar curves for unplated spheres is the slight decrease of the signal just before the abrupt transition at $H_{sh}^P$. It is believed that this decrease is due to the gradual depression of the weak superconductivity in the normal metal induced by the superconducting sphere. The divergence close to $T_c$ must represent the proximity and size effects in combination, and, seeing that the size effect in $\kappa_{sc}^P$ is small, the proximity effect must give the dominating contribution.

[38] Strictly speaking, $H_c$ in the above argument should be replaced with a thermodynamical critical field $H_T{}^P$ appropriate for the plated sphere. This field can be less than $H_c$ because of proximity effects.

[39] R. A. Hein and R. Falge, Jr., Phys. Rev. 123, 407 (1961).

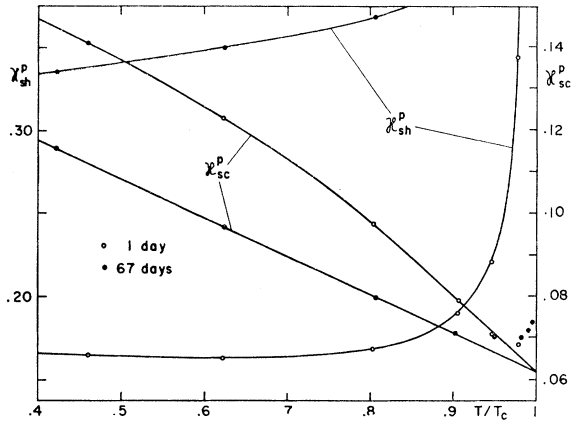


FIG. 24. $\kappa_{sh}{}^P$ and $\kappa_{sc}{}^P$ as a function of reduced temperature for a 21-$\mu$m gold-plated indium sphere aged 1 and 67 days at room temperature after plating. $T_c = 3.404$°K.

In Figs. 23–25 the results for other gold-plated indium spheres are presented. The general appearance is the same as for the large sphere. For the 31-$\mu$m sphere of Fig. 23 we have used $T_c = 3.404$°K (it was found to be 3.400°K after 100 h at room temperature) and extrapolation gives $\kappa_{sc}{}^P(T_c) = 0.0640$ after 20 h at room temperature. The 21-$\mu$m sphere gives $\kappa_{sc}{}^P(T_c) = 0.0620$ both after 1 and 67 days of aging. It is seen that extrapolation for the 67-day curve is performed with points rather far away from $T_c$, but all these lie on a straight line, so that the extrapolated value should be reliable. For the 67-day curve the differential paramagnetic effect was observed for $T > 0.98T_c$.

Finally, the results for a 14-$\mu$m gold-plated sphere are presented in Fig. 25. The transition temperature for this sphere was found to be somewhat suppressed, since the measured value was 3.380°K. This value has been used in the calculation of $\kappa_{sc}{}^P$ and $\kappa_{sh}{}^P$. The size effect is very marked, and, as one should expect, the extrapolation of $\kappa_{sc}{}^P$ clearly gives too high a value.

From the results presented we find that, for gold-plated indium, the GL parameter $\kappa$ after sufficient aging has the value

$$\kappa = \kappa_{sc}{}^P(T_c) = 0.0610 \pm 0.001. \quad (23)$$

This agrees remarkably well with the result already presented for unplated spheres, Eq. (21), and we can conclude that

$$(H_{c3}/H_{c2})_{T_c} = (H_{sc}/H_{sc}{}^P)_{T_c} = 1.70 \pm 0.03. \quad (24)$$

## V. DISCUSSION

From supercooling experiments on cylinders, Faber[1] obtained $\kappa_{sc}(T_c) = 0.097$ with 2% accuracy for tin, and states with absolute confidence that $\kappa$ cannot be greater than this, and indeed the present results are only about 4% lower than his value. For indium his results give $\kappa_{sc}(T_c) = 0.066$, which is 6% above our result. From his results we can conclude that almost as much supercooling can be obtained in experiments on cylinders as on spheres very close to the critical temperature, but far away from the critical temperature small spheres supercool much better than cylinders.

Superheating in cylinders is much more difficult to achieve; however, Doll and Graf[40] have recently, in a very ingenious experiment, observed large superheating in tin cylinders 7, 19, and 122 $\mu$m in diam. They find that $\kappa_{sh}(T_c) = 0.165$, which differs by considerably more than the experimental errors from the present result of 0.0926, and we must conclude that the results on cylinders do not represent ideal superheating; nor did Doll and Graf[40] observe the size effect near $T_c$ one would expect in the 7-$\mu$m cylinder. Although they state that there were no defects on the surface of the samples that could be resolved by a light microscope, one knows from the rotational diagrams that there seem to be defects, active as nucleation centers, that cannot be seen in a very good light microscope. We therefore believe that the cylindrical geometry is less favorable for superheating than the spherical geometry, because of the relatively larger surface and hence the larger possibility for active nucleation centers.

In the original work[2] on superheating and supercooling of powders, indium was investigated. Extrapolation gave $\kappa_{sh}(T_c) = 0.070 \pm 0.005$. It is now clear that this value is too high because of the relatively important size effect in this sample, the spheres being 1–5 $\mu$m in diameter.

Later, Smith and Cardona published similar experiments on tin,[5] indium,[6] and mercury and lead.[41] Their hysteresis loops[6] for indium powders are relatively smeared-out, and this makes a reliable interpretation in terms of superheating and supercooling fields very difficult. Smith and Cardona[5,6] have also studied copper-plated spheres in powder samples and find a lowering both in superheating and in supercooling. However, they use inconsistent definitions of $H_{sc}{}^P$ and $H_{sc}$. In terms of the fields defined in Ref. 2, they use $H_7$ for $H_{sc}{}^P$ and $H_6$ for $H_{sc}$. Using these definitions, they find $H_{sc}/H_{sc}{}^P = 1.53$ for indium and 1.49 for tin, instead of 1.7. Had they used a consistent definition of $H_{sc}$ and $H_{sc}{}^P$, they would have obtained even lower values. From experiments on uncoated powers they conclude that $\kappa_{sh} = \kappa_{sc} = 0.088 \pm 0.005$ for indium and $\kappa_{sc} = 0.125 \pm 0.005$ for tin at $T_c$. These values are well above the present results, being 40 and 13% too high, respectively.[42] Also, their observed temperature variation of $\kappa$ is too large, since they obtain $-3.1$ and 1.8 for $(1/\kappa)d\kappa/dt|_{t=1}$

[40] R. Doll and P. Graf, Phys. Rev. Letters **19**, 897 (1967).

[41] F. W. Smith and M. Cardona, Solid State Commun. **6**, 37 (1968).

[42] *Footnote added in proof.* F. W. Smith, A. Baratoff, and M. Cardona, in Proceedings of the Eleventh International Conference on Low-Temperature Physics, St. Andrews, 1968 (to be published), find that $\mathcal{K}_{Sn} = 0.087 \pm 0.002$ and $\mathcal{K}_{In} = 0.060 \pm 0.002$, and these values, which agree with our results, supersede their previous results. They also discuss nonlocal effects.

TABLE I. Superconductive properties of In and Sn.

| | In | Sn | Unit |
|---|---|---|---|
| $T_c$, superconducting transition temperature | $3.407\pm0.001$[a] | $3.7216\pm0.001$[a] | °K |
| $H_c(0)$, thermodynamical critical field at $T=0$ | $282.66\pm0.12$[a] | $305.5\pm0.1$[a] | Oe |
| $v$, molal volume at 4°K | 15.37[b] | 16.06[c] | $cm^3$/mole |
| $N$, number of electrons/$cm^{33}$ | $1.179\times10^{23}$ | $1.500\times10^{23}$ | $cm^{-3}$ |
| $\gamma_0=\frac{1}{3}k_B{}^2mk_F/\hbar^2$, electronic specific-heat coefficient | 780 | 846 | erg $°K^{-2}$ $cm^{-3}$ |
| $\gamma/\gamma_0$ | {1.51[d]<br>1.38[a] | 1.29[d]<br>1.28[a] | |
| $S/S_0=(\sigma/l)/(\sigma/l)_0$,[e] free area of Fermi surface relative to free-electron value | {0.48[f]<br>0.39–0.95[g] | 0.31[f]<br>0.22–0.44[g] | |
| $\xi_0=0.18\hbar v_F/k_BT_c$, coherence distance in free-electron model | 7070 | 7670 | Å |
| $\xi_0{}^*=0.18\hbar v_F{}^*/k_BT_c=(\gamma_0S/\gamma S_0)\xi_0$,[e,h,i] renormalized coherence distance | 2460 | 1860 | Å |
| $\xi_0{}^{\mathrm{expt}}$, experimental coherence distance | 2000[j] | 2300[k] | Å |
| $\lambda_L(0)=(mc^2/4\pi Ne^2)^{1/2}$, London penetration depth in the free-electron model | 155 | 270 | Å |
| $\lambda_L{}^*(0)=(\gamma/\gamma_0)^{1/2}(S_0/S)\lambda_L(0)$,[i,f] renormalized penetration depth | 380 | 985 | Å |
| $\lambda_L{}^{\mathrm{expt}}(0)$, experimental penetration depth | 250[l] | 350[k] | Å |
| $\kappa=0.96\lambda_L(0)/\xi_0$, GL parameter in free-electron model | 0.021 | 0.034 | |
| $\kappa^*=0.96\lambda_L{}^*(0)/\xi_0{}^*$, renormalized GL parameter | 0.148 | 0.51 | |
| $\kappa=0.96\lambda_L{}^{\mathrm{expt}}(0)/\xi_0{}^{\mathrm{expt}}$ | 0.120 | 0.146 | |
| $\kappa^{\mathrm{expt}}$ [m] | $0.0620\pm0.001$ | $0.0926\pm0.001$ | |

[a] See Ref. 36.
[b] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).
[c] J. A. Rayne and Chandrasekhar, Phys. Rev. **120**, 1658 (1960).
[d] See Ref. 1.
[e] See Ref. 45.
[f] K. R. Lyall and J. F. Cohran, Phys. Rev. **159**, 517 (1967).
[g] Results of other work quoted in Ref. f.
[h] Using results from Refs. a and f.
[i] See Ref. 44.
[j] E. Guyon, F. Meunier, and E. S. Thompson, Phys. Rev. **156**, 452 (1967).
[k] J. Burger, G. Deutscher, E. Guyon, and A. Martinet, Phys. Rev. **137**, A853 (1965).
[l] K. Fossheim, Phys. Rev. Letters **19**, 81 (1967).
[m] This work.

in indium and tin, respectively. In tin, Smith and Cardona[5] obtain perfect agreement between $\kappa_{\mathrm{sh}}$ and $\kappa_{\mathrm{sc}}$ for low temperatures. This agreement is obtained upon using $H_6$ instead of $H_7$ (see Sec. IV) as the supercooling field, and is thus accidental. There is no theoretical reason for assuming that $\kappa_{\mathrm{sh}}=\kappa_{\mathrm{sc}}$ except at $T_c$.

Chang and Serin[43] have measured $H_\perp$, the transverse critical field for thin evaporated films of various purities. Interpreting $H_\perp$ as $H_{c2}$ and extrapolating to the pure limit, they find $\kappa(T_c)=0.11$ for indium and 0.15 for tin, which is much higher than the results obtained from superheating and supercooling.

It is interesting to compare the experimental results with the predictions of the microscopic theory. The relevant data are collected in Table I. Using a free-electron model with a spherical Fermi surface, values for the coherence distance $\xi_0$ are obtained which are very much larger than the values obtained by experiments on the properties of thin films. It has been argued[44,45] that quantities like the Fermi velocity $v_F$ and the density of states $N(0)$ should be renormalized in order to take into account the effects of the electron-electron and electron-phonon interaction. For instance,[45] $v_F{}^*=(\gamma_0S/\gamma S_0)v_F$, where $\gamma$ and $S$ are the observed specific-heat coefficient and the free area of the Fermi surface, respectively, while $\gamma_0$ and $S_0$ are the same quantities calculated from the free-electron model. The renormalized density of states is $N^*(0)=(\gamma/\gamma_0)N(0)$. Using $v_F{}^*$ instead of $v_F$ gives a renormalized coherence distance $\xi_0{}^*$, which is in reasonable agreement with the experimental values. The London penetration depth calculated from the free-electron model gives values somewhat lower than the experimental results. Using the form[46] $\lambda_L(0)=[3c^2/8\pi N(0)v_F{}^2e^2]^{1/2}$ and renormalizing $N(0)$ and $v_F$ gives $\lambda_L{}^*(0)=(\gamma/\gamma_0)^{1/2}(S_0/S)\lambda_L(0)$, which turns out to be higher than the observed values. It is seen in Table I that the $\kappa$ values calculated using the free-electron model are about $\frac{1}{3}$ of the experimental value obtained from superheating and supercooling. The renormalized $\kappa$ is very much larger than the experimental value, as is the $\kappa$ obtained from separate experiments giving $\xi_0$ and $\lambda_L(0)$. The various quantities which

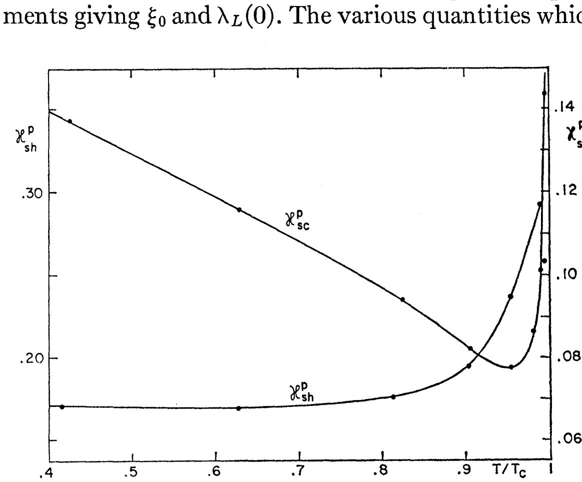


FIG. 25. $\kappa_{\mathrm{sh}}{}^P$ and $\kappa_{\mathrm{sc}}{}^P$ as a function of reduced temperature for a 14-$\mu$m gold-plated indium sphere aged 7 h at room temperature after plating. $T_c=3.380$°K.

[43] G. K. Chang and B. Serin, Phys. Rev. **145**, 2741 (1966).
[44] B. B. Goodman, Phys. Letters **1**, 215 (1962).
[45] G. Eilenberger and V. Ambegaokar, Phys. Rev. **158**, 322 (1967).
[46] See Ref. 15, p. 224.

are renormalized represent, in general, different averages over the Fermi surface, and in view of the poor agreement between the simply renormalized $\kappa$ and the experimental value, a detailed calculation, taking the actual Fermi surface properly into account, would be desirable.

For the slope of $\kappa_{sc}$ at $T_c$ we can obtain a theoretical prediction by combining Eqs. (7), (8), and (10):

$$\frac{1}{\kappa_{sc}}\frac{d\kappa_{sc}(T/T_c)}{dT/T_c}\bigg|_{T/T_c=1}=-1.0\,, \qquad (25)$$

valid for pure superconductors. The present experiments giving 1.5 for tin and 1.4 for indium represent upper limits for the magnitude of the slope. A part of the discrepancy could possibly be accounted for by renormalization effects, but, as already discussed, minor defects present even in the best spheres result in too large a value for the magnitude of the slope. In pure niobium, a type-II superconductor, Webb[47] recently found the slope of $H_{c3}/H_{c2}$ to be somewhat less than predicted by Eq. (8). The very strong temperature dependence [see Eq. (9)] proposed by Lüders[26,27] does not seem to be in agreement either with the present results or with the results of Webb.[47]

Experiments on gold-plated indium spheres gave $(H_{sc}/H_{sc}{}^P)_{Tc}=1.7\pm0.03$, so that $H_{sc}{}^P/H_{c2}=1.00\pm0.02$, in excellent agreement with the prediction by Zaitsev, Eq. (15). The experimental results (Fig. 22) also show that $H_{sc}{}^P/H_{c2}\sim\kappa_{sc}{}^P/\kappa_{sc}$ increases with decreasing temperature as expected from Eq. (15). It is clear that the temperature dependence of $\kappa_{sc}{}^P/\kappa_{sc}$ in general does not represent the temperature dependence of $H_{c3}/H_{c2}$ calculated by Ebneth and Tewordt, which is valid only for the unplated case [see Eq. (8)], but rather a combination of their temperature dependence and the variation of $H_{sc}{}^P/H_{c2}$ with temperature as calculated by Zaitsev, which represents the temperature variation of the boundary condition. For dirty superconductors, $H_{c3}{}^P/H_{c2}$ is again 1 under certain conditions discussed by Hurault.[30]

The superheating of type-I superconductors, plated with a normal metal as a function of temperature, has not been observed earlier. It is satisfying to see the qualitative agreement between the simple GL picture for this situation (see Fig. 2) and the experimental results of Figs. 22–25. Since the GL theory can be justified only very close to $T_c$ for pure superconductors, no quantitative comparison is attempted.

[47] G. W. Webb, Solid State Commun. 6, 33 (1968).

## VI. CONCLUSION

Experimental studies on the superconducting phase transition of single spheres down to about 5 $\mu$m in diam have been carried out. The results are more reliable than those obtained by the original powder method,[2] since there are no difficulties in interpretation.

In the type-I superconductors investigated, large superheating and supercooling effects have been observed; also, the presence and effect of invisible nucleation centers have been established by the study of the variation of superheating and supercooling with field direction and temperature. In indium, different nucleation centers are active in superheating and supercooling. The effect of nucleation centers vanishes as the critical temperature is approached, and the $\kappa$ values deduced from superheating and supercooling converge within a few percent for indium and tin. If in deriving $\kappa_{sh}$ from $H_{sh}$ one uses the numerically calculated relation[8] instead of Eq. (1), then $\kappa_{sh}(T_c)$ will be increased by 16% for tin and $\kappa_{sh}$ would differ from $\kappa_{sc}$ by more than the experimental error. Thus we conclude that the superheating field calculated in a way that allows only one-dimensional fluctuations of the order parameter is too large for $\kappa\sim0.1$. Also, Eq. (1) used as an interpolation formula appears to agree with experiment.

For gold-plated indium spheres, it is demonstrated that the supercooling field is lowered by a factor 1.695 to within 2%, i.e., from $H_{c3}$ to $H_{c2}$ as predicted by theory. The effect of plating upon the superheating field as a function of temperature qualitatively follows the simple GL calculation by the Orsay group.[9]

The size effect in superheating and supercooling, as predicted by the GL theory, is borne out qualitatively in these experiments.

The observed values for the GL parameter $\kappa$, $\kappa_{Sn}=0.0926$ and $\kappa_{In}=0.0620$, are significantly lower than those predicted by microscopic theory, using values for the Fermi velocity and the density of states which are renormalized using experimental results on the electronic specific heat and the anomalous skin effect.