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SUPERHEATING AND SUPERCOOLING IN THE SUPERCONDUCTING TRANSITION OF SMALL INDIUM SPHERES

J. Feder,* S. R. Kiser, and F. Rothwarf†
Laboratoire de Physique des Solides, Associé au Centre National de la Recherche Scientifique, Faculté des Sciences, Orsay, France
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Supercooling in the normal-to-superconducting phase transition has been observed experimentally,[1,2] and also has been discussed theoretically[3-6] for type-I superconductors. For a bulk sample the supercooling field is

$$H_{sc} = 1.69 H_{c2} = 1.69\sqrt{2}\,\kappa H_c, \qquad (1)$$

where κ is the Ginzburg-Landau parameter, $\kappa = \lambda/\xi$, and H_c is the thermodynamical critical field for the bulk superconductor. The supercooling characteristic of a number of metals has been observed by Faber,[1] but only near the critical temperature T_c. These results have been used[5] to give reliable values of κ near T_c.

Superheating in the superconducting-to-normal transition has been predicted theoretically.[3,4,7] The superheating field for a sphere with radius $r \gg \lambda$, where λ is the London penetration depth, is[7]

$$H_{sh} = \tfrac{2}{3} 2^{-1/4} \kappa^{-1/2} H_c. \qquad (2)$$

The factor $\frac{2}{3}$ accounts for the demagnetizing field of the sphere, and the rest of the expression is the result valid for a semi-infinite sample in parallel field, with $\kappa \ll 1$.

The large superheating predicted by (2) has been difficult to observe in the sample geometries used in previous experiments. Garfunkel and Serin[2] found $H_{sh} = 1.17 H_c$ in tin, and Burger and Valette[8] found $H_{sh} = 1.65 H_c$, also in tin. The superheating field predicted by (2) is $H_{sh} = 2.7 H_c$, using $\kappa = 0.1$ for tin[5] and omitting the factor $\frac{2}{3}$ in order to get the result for their geometry. The difficulty in obtaining superheating is in general attributed to flaws in the surface and end effects. Once the transition to the normal state has started at a "weak" point, the new phase propagates over the entire specimen and only the superheating typical for the defect is observed.

The idea of the present experiment is to observe the transition of a sample containing many small spheres. A new phase cannot propagate in such a sample, so that a nucleation process is necessary in each sphere. The minimum supercooling field and the maximum superheating field[9] measured are then characteristic of the material and not of the defects.

The sample[10] used consisted of two-thirds volume of dry indium spheres mixed with one-third volume of quartz powder. The spheres were made by sonoration of 99.999% pure indium in an organic liquid. They have diameters ranging from about 1 to 5 μ. We find a critical temperature $T_c = 3.396 \pm 0.002$°K, which is close to the values listed by Roberts.[11] The pure nuclear quadrupole resonance is observable in this sample at 4.2°K, indicating that strains and surface effects are not important enough to wipe out the resonance.

The sample was placed in the rf coil of the tank circuit of a marginal oscillator of the Pound, Knight, and Watkins[12] type, and the oscillator frequency as function of applied field was measured at various temperatures. The external magnetic field was produced by a superconducting solenoid, calibrated with a proton resonance. The axis of the solenoid was parallel to the axis of the rf coil. We obtained the curves of frequency versus field directly on an X-Y recorder by feeding the X axis with a voltage proportional to the magnet current, while the oscillator frequency was fed to a digital-to-analog converter and then to the Y axis of the recorder.

A typical hysteresis loop is given in Fig. 1. The decrease in oscillator frequency is proportional to the fraction of the sample that has

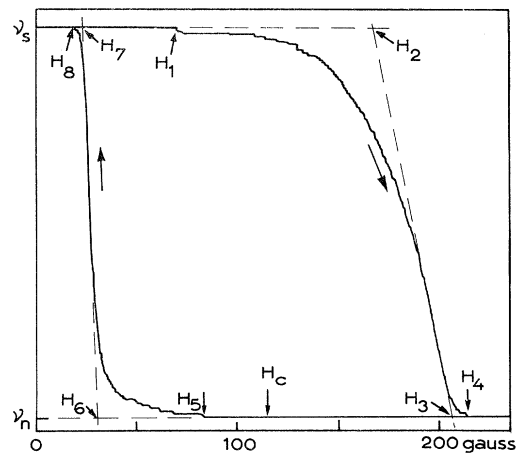

FIG. 1. Oscillator frequency as a function of applied field at $T = 2.567$°K. $\nu_S = 5.5220$ Mc/sec, $\nu_n = 5.3633$ Mc/sec.

become normal. We believe H_3 to be the superheating field, and H_6 to be the supercooling field characteristic of an ideal specimen of indium. The finite slope of the lines H_2H_3 and H_6H_7 is expected on theoretical grounds, since the field seen by a sphere in the sample is larger than the applied field because of the flux expulsion from the superconducting spheres.

It is convenient to present the results in terms of κ_3 and κ_6 as shown in Fig. 2. κ_3 is calculated using H_3 in (2) and κ_6 using H_6 in (1). The values of H_C are taken from Mapother.[13] For $T < 0.7T_C$, κ_3 and κ_6 agree[9] within 4%. Near T_C, κ_3 and κ_6 both increase rapidly with temperature. This increase is due to size effects.[14] Since κ_3 is not seriously affected by size effects, it may be safely extrapolated to T_C, giving $\kappa(T_C) = 0.070 \pm 0.005$. This value of κ obtaining from the superheating fields agrees within experimental error with Faber's value[5] $\kappa = 0.066$ obtained from a supercooling experiment at T_C. If we assume that the size effect in κ_6 is negligible at low temperatures, we can conclude that the values of κ obtained from superheating and supercooling fields are equal within experimental error at all temperatures.

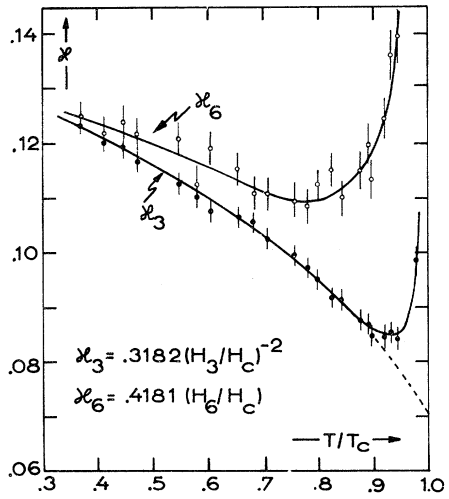

FIG. 2. The Ginzburg-Landau parameter κ in indium as a function of the reduced temperature. κ_3 and κ_6 are derived from superheating and supercooling fields, respectively. The increase of κ near T_C is a size effect.

It is important to remember that (1) and (2) are derived on the basis of the Ginzburg-Landau equations which are valid only near T_C in pure superconductors. For $T < T_C$ we take Eq. (1) to define $\kappa = \kappa_{SC}$ from the supercooling field, and (2) to define $\kappa = \kappa_{sh}$ from the superheating field, in a phenomenological way. We then note that from a theoretical point of view κ_{SC} and κ_{sh} thus defined may well be different for $T < T_C$, but they must coincide at T_C. In view of this it is very interesting to see that our results on indium indicate that κ_{SC} and κ_{sh} are equal at all temperatures. We note that κ shows a strong temperature dependence. Using different methods, Paskin et al.[15] and Chang and Serin[16] have seen similar behavior in type-I materials. The latter investigators find for indium a value of $\kappa(T_C) = 0.11$, which is quite different from our result.

In conclusion we point out that our method of observing superheating and supercooling offers a powerful technique for studying the variation of κ as function of temperature in type-I materials. Details concerning the temperature dependence of κ, as well as a more thorough discussion of other topics presented in this Letter, will appear in a later publication.

We thank J. P. Burger and C. Valette, who are now doing similar work on mercury using this method, for a number of useful discussions. We also thank M. Cyrot and P. G. de Gennes for stimulating discussions.

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*NATO Science Fellow, on leave from the University of Oslo, Oslo, Norway

†On a U. S. Secretary of the Army Research and Study Fellowship. Permanent address: Pittman-Dunn Research Laboratories, Frankford Arsenal, Philadelphia,

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are indebted to Professor W. D. Knight, University of California, Berkeley, California, for the loan of the sample.

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[14]Equations (1) and (2) are valid when $r/\lambda > 2.6\kappa^{-1}$. When r/λ is small, the superheating field decreases and the supercooling field increases with decreasing r/λ.[3,4] As λ increases rapidly with temperature near T_c, r/λ becomes small so that values of κ calculated from (1) and (2), using the observed fields near T_c, are too large. The size effect is more marked in κ_6 than in κ_3, because the supercooling field H_6 is characteristic of the smaller spheres, whereas the superheating field H_3 is characteristic of the larger spheres.

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THEORY OF THE SELF-CONSISTENT HARMONIC APPROXIMATION WITH APPLICATION TO SOLID NEON

Thomas R. Koehler
IBM Research Laboratory, San Jose, California
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Mathematical techniques have been described[1,2] by which one can perform an exact calculation in coordinate space of the matrix elements of a crystal Hamiltonian

$$H = -\tfrac{1}{2}\lambda^2\sum_i \nabla_i^2 + \tfrac{1}{2}\sum_{i\neq j} V(r_{ij}), \tag{1}$$

between the eigenfunctions $|a;n\rangle$ of a harmonic Hamiltonian[3]

$$H^{(1)}(a) = \tfrac{1}{2}\lambda^2\tilde{p}p + \tfrac{1}{2}a^2\tilde{q}\Phi q \tag{2}$$

appropriate to a crystal of the same symmetry. Here a is a parameter which is essentially a scale factor for the generation of a set of harmonic Hamiltonians whose eigenfunctions and eigenvalues are simply related, $\lambda^2 = \hbar^2/(m\sigma^2\epsilon)$, and the Mie-Lennard-Jones potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ has been used, with σ and ϵ as units of distance and energy, respectively. We will also use

$$V = \tfrac{1}{2}\sum_{i\neq j} V(r_{ij}).$$

A notation is used in which q is a supervector whose components are the vectors q_i, and the Cartesian components of q_i are denoted by q_i^{α}. A similar notation is used for other vectors and matrices. The coordinate of the ith particle is given by r_i and its equilibrium position by R_i, and $q_i = r_i - R_i$.

It was found that $W(a) \equiv \langle a;0|H|a;0\rangle$ and $E_k^{\alpha}(a) \equiv \langle a;k|H|a;k^{\alpha}\rangle - W(a)$ were readily obtained, where $|a;0\rangle$ is the ground-state eigenfunction of $H^{(1)}(a)$, and $|a;k^{\alpha}\rangle$ is the state with one phonon of wave vector k, belonging to the αth branch, excited. Thus, a variational calculation can be performed to determine the optimum value a_0 of a and the ground-state energy $W_0(a_0)$ of the crystal. The $E_k^{\alpha} \equiv E_k^{\alpha}(a_0)$ then give the phonon spectrum to first order.

In this Letter it will be shown that a logical extension of the calculation described above leads to the construction of a "self-consistent harmonic Hamiltonian" for a crystal, which we shall define as that Hamiltonian

$$H^{(c)} = \tfrac{1}{2}\lambda^2\tilde{p}p + \tfrac{1}{2}\tilde{q}\Phi^{(c)}q \tag{3}$$

in which

$$\Phi_{ij}^{(c)\alpha\beta} = \left\langle c,0\left|\frac{\partial^2 V}{\partial r_i^{\alpha}\partial r_j^{\beta}}\right|c,0\right\rangle. \tag{4}$$