Effect of Elastic Stress on Some Electronic Properties of Indium*

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We have measured the effect of elastic stress to 0.3 kbar on the resistance at room and helium temperatures and on the superconducting transition temperature of In whiskers. These whiskers have diameters of about 1 μ and axes parallel to a closest-packed or <101> direction. $\partial T_c/\partial\sigma$ is 51 ± 7 mK/kbar, in disagreement with results obtained by measuring the change in length of In crystals as they pass through the superconducting transition. At room temperature, $\Delta\rho/\rho\sigma=a+b\sigma$, where $a=(-0.4\pm0.2)\times10^{-5}$ bars^{-1} and $b=(14\pm2)\times10^{-9}$ bar^{-2}.

I. INTRODUCTION

WHISKERS of In have an elastic limit an order of magnitude higher than that of bulk In.[1] This makes it practical to measure the effect of elastic strain on the superconducting transition temperature and on the resistivity of In. The size of the whiskers (~1-μ diameter) makes it possible to extend the study of the effect of size on the resistivity to sizes an order of magnitude smaller than used previously.

The effects of lattice distortion on the superconducting transition temperature of In have been measured using hydrostatic pressure[2] and by measuring the change in length of a single crystal as it goes through the transition temperature.[3,4]

For the former case, only an average of the effects of changing various crystallographic dimensions can be determined, but fairly high pressures (and hence fairly large lattice distortions) may be applied. For the latter case only the initial slope of the transition temperature-lattice-dimension curve can be determined. Using whiskers, the curve may be determined to the limits of elasticity (about 0.3 kbar for In). In whiskers grow with only one crystallographic orientation, in which the long axis of the whisker is along a closest packed or ⟨101⟩ direction. Thus only one of the two components of the tensor which relates the stress to the superconducting transition temperature[5] can be determined.

The effect of lattice distortions on the resistivity of In has been studied using pressure techniques,[6,7] but presumably because of the low elastic limit of In, no work has been published on the effect of uniaxial tension on the resistivity. We report these measurements here.

II. EXPERIMENTAL PROCEDURE

The whiskers were grown by the "squeeze" technique. In (99.999% pure), furnished by the Indium Corporation of America, was vacuum deposited onto 0.25-mm-thick stainless-steel strip. The coating thickness varied from $\frac{1}{2}$ to 2 μ. Washers 25 cm in diameter were cut from the strip and compressed to a pressure of about $10^{10}N/\mathrm{m}^2$. Whiskers grew within several hours to a length of 1 mm. The whiskers which grew fastest were the thinnest. Orientations were determined from rotating crystal x-ray photographs. All samples had axes parallel to the ⟨101⟩ crystallographic direction.

The purity of the whiskers is hard to estimate. Residual resistance measurements are not a reliable indication of purity, since in samples of this size the residual resistance is predominately a surface effect. The superconducting transition temperature did not change by more than 2 mK from whisker to whisker and was 13 mK lower than the bulk value of 3.408 K as measured by Shaw, Mapother, and Hopkins.[8] If this were due entirely to impurities, it would indicate that the whiskers had less than 0.5% impurities.[9] It is also possible that the whiskers are even purer than this, and that the depression in T_c is due to the limiting of the electron mean free path by the surface of the whisker. If one assumes that the mean-free-path effect is the same for surface scattering as it is for impurity scattering, and that the residual resistance ratio, $\delta=R(4.2\text{ K})/R(300\text{ K})$, is proportional to the mean free path for surface scattering, then the theory of Markowitz and Kadanoff[10] predicts a depression in T_c of about 20 mK. The width of the resistive superconducting transition was less than 1 mK. This would indicate that the composition of an individual whisker did not change along its length.

The stressing devices used were: (1) A piezoelectric puller, in which the whisker was stretched by a pair of piezoelectric bimorphs; (2) a Mylar puller, in which the whisker was mounted on a Mylar film, which was stretched by a differential screw immersed in liquid helium; and (3) a quartz puller, a device which transmits motion generated by a micrometer at room temperature to the sample via a quartz rod and tube. (See Fig. 1.) The first two devices have been described

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elsewhere.[11] The third device was constructed to check the results obtained by the first two when it became apparent that there was a large discrepancy between these results and those obtained by others who measured the change in length of an In crystal as it passes through the superconducting transition temperature. In all these devices the sample was mounted with silver Epoxy (Waldman No. 3025) or silver paint (Du Pont No. 7713) and lowered into a small Dewar[12] which was in turn inserted in a helium storage Dewar. Liquid helium was then sucked into the small Dewar. The temperature was controlled by regulating the pressure of helium over the small Dewar bath. Temperatures of the bath were monitored with a locally calibrated CryoCal germanium resistor. This thermometer was calibrated with a helium-gas thermometer and a germanium resistor calibrated by CryoCal. Calibration results were consistent to ±2 mK.

Resistances were measured by a four contact method using a Rubicon six-dial potentiometer and a Keithley 147 null detector. The sample current during resistivity measurements was typically 100 μA and during superconducting transition temperature measurements 10 μA. The nonlinear behavior of the piezoresistance at 300°K was determined by using a differential technique which measured the slope of the strain-resistivity curve directly. In this technique, a small oscillating stress was superposed on the steady stress applied to the sample. Since the current in the sample was held constant, the changes in resistance due to the oscillating stress resulted in an oscillatory voltage across the sample. This oscillatory voltage was at the phase and frequency of the oscillatory stress. The reference output of a Princeton Applied Research HR-8 lock-in amplifier was superposed on the steady voltage across the piezoelectric puller. This oscillated the stress in the sample about a fixed stress. The resulting oscillatory voltage across the sample was measured by the same lock-in amplifier. Since the oscillations in stress were small compared with the steady stress, the signal measured by the lock-in amplifier was proportional to the slope of the stress-resistance curve.

Stresses were inferred from the measured axial component of the strain using the elastic constants of In as measured by Winder and Smith.[13] It has been found that bulk elastic constants adequately describe the behavior of small strong whiskers.[14] The major source of uncertainty in the measurement of the strain (and hence of the stress) was the measurement of the length of the whisker. The uncertainty in determining the edge of the glue contact gave a 5% uncertainty in the strain (and stress) measurements. Whisker cross sections were calculated from the room-temperature resistance and length of the sample between potential contacts, assuming a resistivity of 9.0 $\mu\Omega$ cm.[15] Size effects on the resistivity at room temperature were negligible, since at this temperature the electron mean free path is much smaller than the sample diameter. The uncertainty in the measurement of the cross section is estimated to be 8%, including the stated 5% uncertainty in the elastic constants.

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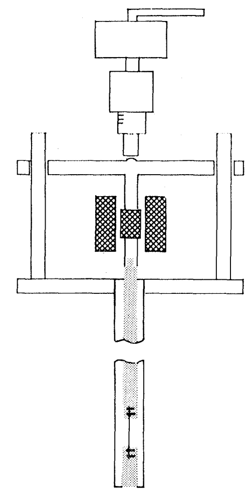

FIG. 1. Quartz puller. The whisker is strained by moving the quartz rod in the quartz tube. The motion is measured with a differential transformer at room temperature. The motion comes from a micrometer operated through a 200:1 speed reducer.

III. RESULTS

A. Resistivity

Resistivity changes were measured using the piezoelectric puller. The resistivity ρ at room temperature was found to be a nonlinear function of stress. The

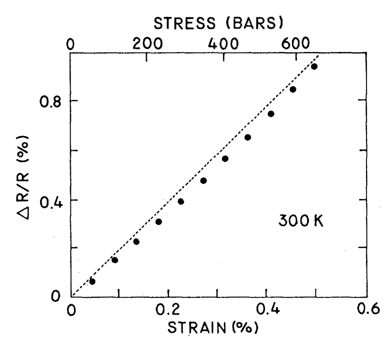

FIG. 2. Change of resistance in In at room temperature with stress. The increase in length of the sample is shown on the lower scale. The effect of geometric changes of the sample is shown by the dotted line. The difference between the experimental results and this line is the change in resistivity of the sample. This difference is negative and nonlinear for this orientation on In Uncertainties in the relative values of ΔR and of the stress are indicated by the symbol size. Absolute accuracy is about 5%.

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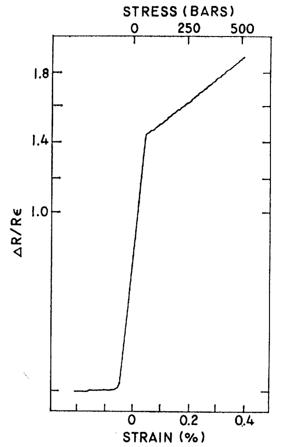

FIG. 3. Recorder tracing of the slope ($\Delta R/R\epsilon$) versus elongation (ϵ) for an In whisker at room temperature. $\Delta R/R\epsilon$ represents the slope of the scaled-resistance-versus-elongation curve. This slope is measured by an oscillatory technique (explained in the text) which averages over a small region of the $\Delta R/R\epsilon$ curve. The apparent value of $\Delta R/R\epsilon$ below zero strain is caused by this averaging. If there were no change in the resistivity of the sample, $\Delta R/R\epsilon$ (due to increases in the length and decreases in the cross section of the whisker) would be 1.96.

relation $\Delta\rho/\rho\sigma = a + b\sigma$, where $a = (-0.4\pm0.2)\times10^{-5}$ bars^{-1}, $b = (14\pm2)\times10^{-9}$ bars^{-2} and σ is the applied tensile stress, describes the room-temperature results of these experiments. The large uncertainty in the linear coefficient of $\Delta\rho/\rho\sigma$ results from having to subtract a geometrical correction (due to increased length and decreased cross section) from the measured value of $\Delta R/R\sigma$ that is very nearly equal to $\Delta R/R\sigma$; Figs. 2 and 3 show the results of these experiments graphically. The influence of pressure, p, on the resistivity of In has also been reported. Bridgman[6] finds $\Delta R/Rp = 1.0\times10^{-5}$ bars^{-1} at 10^4 bars pressure and that the resistance is nonlinear in pressure.

The helium temperature stress-resistivity is complicated by surface scattering. The resistance of whisker samples at helium temperature is mainly due to surface scattering, and correcting the measured resistance changes for geometrical effects involves a knowledge of the crystallographic orientation of the surfaces and of the polish of these surfaces. Microscopic examination indicates that the whiskers have a form like fluted prisms and that the flutes do not have low index crystallographic orientations. Thus, a geometric correction cannot be made. This may explain the fact that there are large variations in $\Delta\rho/\rho\sigma$ from whisker to whisker in helium temperature experiments, but not in room temperature experiments. Typical experimental results are shown in Fig. 4. Figure 5 shows a plot of the residual resistance ratios, $\delta = R(4.2\text{ K})/R(300\text{ K})$, versus $A^{-1/2}$, where A is the cross-sectional area calculated from the room-temperature resistance and length using 9.0 $\mu\Omega$ cm[15] for the resistivity of In. If all of the whiskers had circular cross sections, the Nordheim relation would predict $\delta \propto \delta_{\text{bulk}}\lambda A^{-1/2}$, where δ_{bulk} is the residual resistance ratio of bulk material of the same purity, and λ the electron mean free path in this bulk material. The scatter in the data is presumably due to the variation in cross-sectional shape from sample to sample. It is unlikely that this scatter is due to varying impurity content since the superconducting transition temperatures were within 2 mK of each other. This indicates that the purity of the whiskers were within ~0.05% of each other.[9] Some of the larger whiskers were amenable to optical measurements, and the cross sections of these was approximately rectangular, with length to width ratios from ~1 to ~10. The fact that some of the whiskers have less resistance at helium temperature (putting them to the right of the line that represents the results of Aleksandrov) than is predicted by the work of Aleksandrov[15] on larger single crystals indicates that there is some specular reflection in these samples,

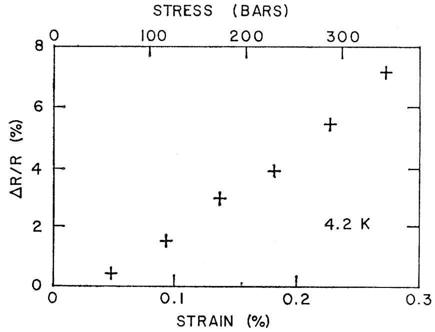

FIG. 4. Change in the resistance of a typical In whisker with stress at 4.2K. This result varied by a factor of 2 from whisker to whisker, presumably due to surface scattering differences.

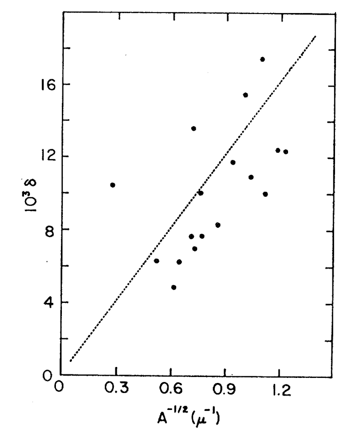

FIG. 5. Plot of δ, resistance at helium temperature divided by the resistance at room temperature, versus the reciprocal of the "diameter" of the sample. These samples have a form similar to a fluted prism and the square root of the cross section was taken as a measure of the diameter. The scatter in the data may be due to the inaccuracy of the diameter measurement or to differences in surface reflectivity from sample to sample. The dashed line represents the results of Aleksandrov (Ref. 15) on wires extended to larger valves of the reciprocal of the diameter.

or that the mean free path for this orientation is longer than for the (unspecified) orientation of Aleksandrov's samples.

B. Superconducting Transition Temperatures

The change in superconducting transition temperature with stress was measured using all three pulling devices. The results obtained from the quartz and Mylar pullers did not differ, and were used to calibrate the piezoelectric puller. A typical transition is shown in Fig. 6. The temperature at which the resistance had decreased to half its normal value was taken as the transition temperature. The results are shown in Fig. 7. The slope gives a value of $(\partial T_c/\partial\sigma)_{\langle 101\rangle}$ equal to (51±7) mK/kbar. This result is considerably larger than that predicted from the measurements of the change in length of In as it passes through the critical field, using the equations

$$\partial T_c/\partial\sigma_\theta = -(\partial H_c/\partial\sigma_\theta)[(\partial H/\partial T)_{T=T_c}]^{-1},$$

$$\partial H_c/\partial\sigma_\theta = \cos^2\theta\,(\partial H_c/\partial\sigma_0)+\sin^2\theta\,(\partial H_c/\partial\sigma_{90}),$$

$$(H_c/4\pi)\partial H_c/\partial\sigma_\theta = [(l_n-l_s)/l_n],$$

where θ is the angle between the fourfold axis and the sample axis, and l_s and l_n are the sample lengths in the superconducting and normal phases, respectively.

Using the data of Finnemore and Mapother[16] we estimate $(\partial H_c/\partial T)_{T_c} = -154\pm7$ Oe/K. The data of Rohrer[3] then predict $(\partial T_c/\partial\sigma)_{\langle 101\rangle}$ to be 22.5 mK/kbar; and the data of Collins, Cowan, and White[4] predict it to be 29.6 mK/kbar. These measurements of the change in length give only the initial slope of ΔT_c versus stress. In fact, the first value of the ΔT_c that could be measured with the Mylar puller was at a stress of about 70 bar. To check the possibility that the ΔT_c-versus-stress curve changes slope near zero stress, the results were checked using the piezoelectric puller. The piezoelectric puller is difficult to calibrate at helium temperature, so that absolute values of the stress measured on this apparatus are not very accurate. Over motions of 10 μ (1% strain on a 1-mm-long whisker) the motion is linear in voltage to within 3%. The changes in transition temperature of In as measured by both the Mylar puller and the quartz puller were used to calibrate the motion of the piezoelectric puller over large (several μ) motions, and this calibration enabled small regions to be studied. The piezoelectric puller thus can give a continuous record of ΔT_c versus stress. Since it is not possible to align the whisker perfectly, when the whisker first tightens the stress is nonuniform and the transition temperature is nonlinear in puller motion. This covered about 10 bar of stress. Except for this region, the piezoelectric puller showed ΔT_c to be a linear function of stress. It may be that the slope of the transition-temperature-versus stress curve changes by a factor of 2 in this small region, but it seems unlikely. The results of Makarov[17] on the effect of pressure on the transition temperatures of dilute alloys of In preclude a nonlinear effect in this region due to an electron transition.

Because of the discrepancy between these results and those obtained by the change in length method, special care was used in checking the Mylar and quartz pullers and in calibrating the thermometers. Several different pieces of Mylar gave identical results as shown in Fig. 7, and these agreed with the results obtained with the quartz puller. The elasticity of the sample was checked during each run by measuring the transition tempera-

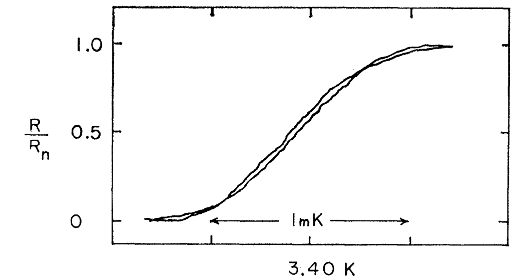

FIG. 6. A typical superconducting transition curve. The narrowness in temperature of the transition indicates that the sample purity did not change along the whisker length. Results obtained by increasing and by decreasing the temperature are shown. The cross section of this whisker was 0.86 μ^2.

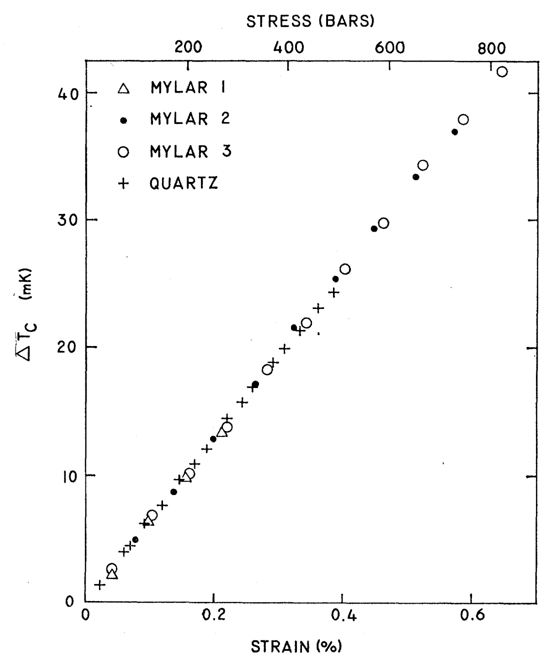

FIG. 7. Change in superconducting transition temperature with stress. Three separate experiments on different Mylar strips are shown. The lower axis shows the elongation of the sample. Uncertainties in the values are indicated by the symbol size.

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ture with both increasing and decreasing stress. The transition temperature at a given stress varied by less than 0.4 mK. A similar Mylar puller was used by Davis, Skove, and Stillwell[18] and gave results for tin which were consistent with Grenier's[19] work with bulk tin single crystals. The different methods of calibrating the thermometer were consistent within 1 mK from 2.5 to 4.2°K, and changes in temperature in the region around 3.4°K were consistent to within 0.2 mK.

There seems to be no simple explanation for the factor of 2 difference between these results and those of Rohrer and of Collins *et al.* The thermodynamic reversibility of the transition is well established. Whiskers of Sn give results that are consistent with those of bulk Sn, and thus there is no reason to suppose that whiskers do not act as bulk material does. Indeed, even in the smallest whiskers ($\sim 0.1\ \mu$ diameter) fluctuation effects are negligible.[20] The extrapolation procedure used in finding the ratio $(l_s - l_n)/H_c$ at T_c (where both $l_s - l_n$ and H_c are zero) does not appear to give difficulties. There may be others difficulties in the measurement of $(l_s - l_n)/H_c$, since Collins *et al.* and Rohrer find values of $(l_s - l_n)$ with differing signs for rods whose axes lie in the base plane.

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Observed Large Deviation of the Superconductive Critical-Field Ratio H_{c3}/H_{c2} from the Existing Theories near T_c†

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The ratio H_{c3}/H_{c2} is calculated in the presence of a phonon-mediated interaction which is slightly depressed in a surface layer. It is shown that if the surface layer has a thickness of order ξ_0, then this ratio will drop rapidly to unity as the transition temperature is approached from below. This result is in good agreement with the recent observation by Ostenson and Finnemore, who reported that for temperatures very close to T_c, the ratio H_{c3}/H_{c2} falls far below the factor 1.7 of Saint-James and de Gennes. The present paper gives a mean-field-theory explanation of this phenomenon.

I. INTRODUCTION

By solving the linearized Ginzburg-Landau (GL) equation[1] in a half space, with the boundary condition that the solution should have a vanishing slope at the surface, Saint-James and de Gennes[2] first predicted that the ratio H_{c3}/H_{c2} for a superconductor should always be equal to 1.695, independent of many properties of the sample. The surface nucleation critical field H_{c3} is the maximum magnetic field that can be applied, parallel to one of the surfaces of a bulk sample, without suppressing all superconducting properties of the sample. It also marks the first appearance of a thin superconducting sheath near the sample surface, which is parallel to an applied field, when the applied field is lowered continuously from above. The upper critical field for the vortex state H_{c2} is also called the bulk nucleation critical field, because it also marks the onset of a localized superconducting region deep inside a bulk sample, at decreasing field. For pure materials, Saint-James and de Gennes's prediction is valid only in a narrow temperature region near the transition temperature T_c, satisfying the criterion $T_c - T \ll T_c$, which is commonly referred to as the GL region. Ebneth and Tewordt,[3] and Lüders[4] subsequently extended the work of Ref. 2 to just below the GL region and found a correction term 1.041 $(1-t)$, where $t \equiv T/T_c$, to the ratio H_{c3}/H_{c2} for a sample with a specular surface. Hu and Korenman[5] then succeeded in showing that the expansion parameter near T_c is actually $(1-t)^{1/2}$, and in addition to reproducing the above conclusions, have found that the next order term is $-0.978\ (1-t)^{3/2}$. As $T \to 0$°K, the ratio was also found to approach a value equal to or larger than 1.925 with vanishing slope. The following interpolation

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