SOVIET PHYSICS JETP VOLUME 36 (9), NUMBER 4 OCTOBER, 1959

MEASUREMENT OF THE RESISTANCE OF HIGH PURITY TIN AT HELIUM TEMPERATURES

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Submitted to JETP editor October 16, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1038-1045 (April, 1959)

The resistance of a number of single crystals of tin of various purity has been measured. The resistance was deduced from the moment of the forces acting on the specimen in a rotating magnetic field. The anisotropy and temperature dependence of the resistance between 4.2 and 3.73° K was measured and the residual resistance determined. For the purest specimen the residual resistance was about 3.7×10^{-11} ohm-cm, which corresponds to an electron mean free path of about 3 mm.

MEASUREMENT of the residual resistance of metals at low temperatures is widely used as a convenient method of checking the overall impurity concentration, especially when other methods become insufficiently sensitive ("spectrally-pure" metals).

The residual resistance method is in turn limited in sensitivity because electrons are scattered at lattice defects which are not connected with the chemical impurities.

Electrons are scattered: 1) by inter-crystallite boundaries if the specimen is not a single crystal; 2) by dislocations and other lattice imperfections; 3) by the external boundaries of the specimen. If the metal consists of a mixture of several isotopes, there must also be an "isotopic" residual resistance due to the change of zero-point vibrations of the lattice produced by the randomness of the isotope distribution.

If single crystal specimens of large enough dimensions are used, the first source of scattering is absent and the third can be considered a small correction. The experimental determination of the contributions to the residual resistance of the second and, especially, the last scattering mechanism is a much more difficult problem.

Measurements on specimens of the highest purity, such as those described below, make it possible to set an upper limit to the magnitude of these effects. We also determined the temperature variation of resistance for tin at helium temperatures, and its anisotropy.

EXPERIMENTAL METHOD

The usual dc potentiometric method of measuring resistance was not suitable for the extremely small resistivities to be measured. Also, fixing the leads would have introduced impurities and deformed the specimens.

We adopted a method which does not require the fixing of contacts, but depends on the measurement of the moment of the forces acting on a spherical specimen in a rotating magnetic field.

This method has been developed by Regel'[1] who used a frequency of 50 kcs for the rotating field. For our experiments the frequency had to be much less because at 50 kcs the field penetration depth in our samples would only be tenths of a millimeter, which is small compared both with the specimen size and with the electron mean free path. This would complicate the calculations and reduce the accuracy of the measurements.

The apparatus used is shown schematically in Fig. 1. The spherical specimen 1, of diameter 12.6 mm, was hung on the torsion balance by a quartz fiber. In most of the experiments the torsion constant of the fiber was 0.17 dyne-cm. The lower part of tube 9, which housed the balance, was enclosed by the liquid helium bath. The vapor pressure of a small quantity of liquid helium at the bottom of tube 9 served to measure the specimen temperature. The specimen was in a horizontal magnetic field, produced by the Helmholtz coils 14, which rotated about a vertical axis.

The magnitude of the field has to be chosen so that neither the Hall effect nor the magneto-resistance effect have any influence. For the purest specimens the field was 1.5 to 2.5 oe, and the effect of the magnetic field on the results only became noticeable beyond 5 oe for these specimens. Two Helmholtz coil systems (not shown in the figure) compensated the earth's magnetic field.

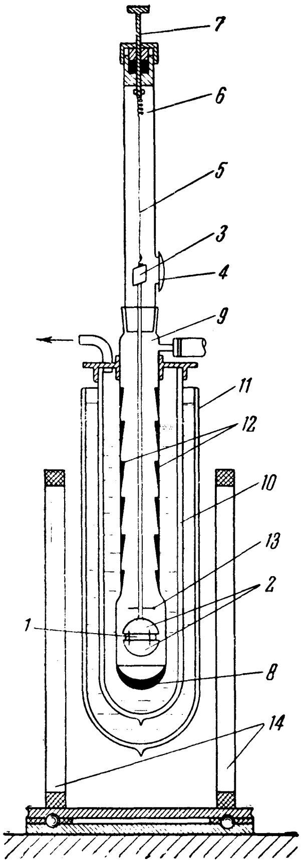

FIG. 1. 1 – specimen; 2 – quartz cups; 3 – mirror; 4 – window and lens; 5 – quartz fibre; 6 – spring protecting the quartz fibre from breaking under shock; 7 – torsion head; 8 – lining of soft material; 9 – glass tube, protecting the balance from convection currents in the liquid helium; 10 – liquid-helium Dewar; 11 – liquid-nitrogen Dewar; 12 – layer of black paper for shielding the specimen from radiation; 13 – thin aluminium shield; 14 – Helmholtz system of coils on a rotating table.

The whole apparatus was carried on a massive foundation, with the Dewar vessel and rotating coil separately supported.

It can easily be shown[1,2] that if the frequency of rotation of the field is sufficiently small for the field in the specimen to differ little from the external field, the resistance of an isotropic spherical specimen is given, to a first approximation, by the simple relation

$$\rho = 10^{-9}(4\pi^2/15)(R^5H^2/TM), \tag{1}$$

where ρ is expressed in ohm-cm, R is the sphere radius in cm, H the rotating field strength in oersteds, T the period of rotation of the field in seconds and M the moment of the forces acting on the specimen, in dyne-cm. This approximation is valid for $\delta \gg R$, where $\delta = \sqrt{10^9\rho T}/2\pi$, is the field penetration depth. The error is less than 1% below $R/\delta = 0.7$.

In our experiments the period of rotation was 400 to 500 sec and R/δ was not more than 0.5 for the specimens with the smallest resistance. We verified experimentally that the moment M varied linearly with the speed of rotation over the range of speeds used.

Although the condition of slow rotation speed, required for applying Eq. (1), was fulfilled, this equation was only suitable for rough calculations in our case because A) the specimens were single crystals and therefore had anisotropic properties and B) the electron mean free paths were large at helium temperature (~ 1 mm). The relevant corrections were made in the following way.

A. One must first take into account the anisotropy in the electrical resistance of tin, the resistance parallel to the fourfold symmetry axis $\rho_\parallel$, being greater than $\rho_\perp$, the resistance in any direction perpendicular to the axis (tin has a tetragonal lattice).

Allowance must also be made for the departure of the specimen from a spherical shape due to anisotropy of the coefficient of thermal expansion. Single crystal specimens cast in a spherical glass former which departed from sphericity by less than 5 μ, became slightly flattened ellipsoids of revolution on cooling to helium temperature.

If the field rotates sufficiently slowly the calculation is straightforward. For an ellipsoidal specimen with semiaxes a, b, and c (b = c), in which the principal axes of the resistance tensor coincide in direction with the axes of the ellipsoid, and dH/dt is perpendicular to a, the moment of the forces becomes

$$M = 10^{-9}\frac{4\pi^2}{15}\frac{a^5H^2}{T}\frac{2k^4}{\rho_\parallel + k^2\rho_\perp}, \tag{2}$$

where $k = b/a$. If $\rho_\parallel = \rho_\perp$ this formula, after slight rearrangement, agrees with the relation for isotropic ellipsoids of revolution found by Gans.[2]

For our specimens $k = 1 + \epsilon$, where $0 < \epsilon \ll 1$. As ϵ is small we obtain the approximate relation

$$\bar{\rho} = 10^{-9}\frac{4\pi^2}{15}\frac{a^5H^2}{TM}(1 + 4\varepsilon) - \varepsilon\rho_\perp, \tag{3}$$

where $\rho = (\rho_\parallel + \rho_\perp)/2$. With our method of measurement this quantity is the most convenient parameter for comparing one specimen with another. In determining the moment M, which enters into Eq. (3), the fourfold axis of the crystal was placed vertical, i.e., parallel to the axis of the balance. Besides the essential quantities H, T, and M, it is also necessary, for applying Eq. (3), to know: a) the lengths of the semi-axes of the specimen at helium temperature, and b) the magnitude of $\rho_\perp$, although it can be seen from (3) that the accuracy required in ρ is not very great.

a) The specimen dimensions at helium temperature were determined from measurements at room temperature (the accuracy was $\pm 2\mu$) and data on the coefficient of expansion of single crystals of tin at room temperature,[3,4] which were extrapolated to low temperatures according to Grüneisen's rule (according to the temperature dependence of the specific heat). It was assumed that the ratios of the expansion coefficients along different axes are independent of temperature. As an example, these calculations gave for specimen No. 5 axial lengths 12.619 and 12.526 mm ($\epsilon = 7.4 \times 10^{-3}$).

The value of ϵ at helium temperature can also be obtained directly with the apparatus, if the specimen is made superconducting. As a magnetic field does not penetrate into a superconductor, a mechanical moment will act on an ellipsoid in an external steady field. Naturally, the field must not destroy the superconductivity. If the specimen is fixed to the balance so that the fourfold axis is horizontal, then the moment of the force is a maximum, $M^S_{\max}$, when the angle between the field direction and the axis is 45°. If $\epsilon \ll 1$

$$\varepsilon = M^s_{\max} / 0.15\, H^2 a^3. \tag{4}$$

The value of ϵ, obtained in this way, agreed well with the extrapolation method described. For the same specimen No. 5, Eq. (4) gave $\epsilon = 7.7 \times 10^{-3}$.

b) The measurement of $\rho_\perp$ was made, in a rotating magnetic field, with the specimen hung in the same way as for determining ϵ, i.e., with the axis horizontal. The deflection of the mirror is then not constant, since the angle between the field and the fourfold axis varies with the rotation of the field. The suspension system carries out oscillations with a period T/2. The largest deflection occurs when the field is perpendicular to the specimen axis. The currents then flow everywhere perpendicular to the axis, and $\rho_\perp$ can be derived from the greatest deflection of the mirror, using the equation

$$\rho_\perp = 10^{-9} \frac{4\pi^2}{15} \frac{a^5 H^2 k^4}{T M_{\max}} \approx 10^{-9} \frac{4\pi^2}{15} \frac{a^5 H^2}{T M_{\max}} (1 + 4\varepsilon). \tag{5}$$

The deflection is a minimum when the field is parallel to the axis and is then equal to the stationary deflection in the case of the axis being vertical, as it should be since Eqs. (2) and (3) hold for $M_{\min}$.

In determining $\rho_\perp$ we neglected the effect of the inertia and damping of the balance, in a magnetic field, on the amplitude of oscillation of the suspended system. For our conditions, when the period τ of free oscillation in zero field was only 0.05 T and the damping in the magnetic field was near critical, the error involved is small. By solving the differential equation for the motion of the balance in a rotating magnetic field, this error is found to be proportional to $(\tau/T)^2$ and is only 1 or 2% of the amplitude of oscillation of the pointer in the rotating field.

B. The corrections for the long electron mean free path, l, were made in the following way. As the scattering of electrons at the boundaries of the metal appears to be diffuse, a surface layer of the specimen, with thickness of the order of l, has a higher effective resistance ρ_{eff} than the interior of the specimen. It is not difficult to solve numerically the problem of the magnetic moment of a sphere, for which ρ depends on R, placed in a slowly rotating field. As $l \ll R$, Sondheimer's formula[14] for a plane can be used for $\rho_{\text{eff}}(R)$. We neglected the anisotropy in conductivity and took $\rho l = 1.05 \times 10^{-11}$ ohm-cm for tin from Chambers' data.[15]

The corrections calculated in this way are considerable (8 — 14% for the purest specimens) as a result of which the large mean free path is the greatest source of error in our measurements. The overall accuracy in the absolute values of $\bar{\rho}$ are about 5%, while the random errors in individual measurements (due to irregularities in rotation of the field, vibration of the balance etc) are less than 0.5%.

MEASUREMENT RESULTS

Table I shows the results of measurements of the resistance of a number of single crystal specimens of increasing purity. The resistances of the purest specimens, Nos. 4 — 6, depend appreciably on temperature in the helium region (see Table II).

For specimen No. 6 $\bar{\rho}_{20°\text{C}} / \bar{\rho}_{4.2°\text{K}}$ was 1.0×10^5, but $\bar{\rho}_{20°\text{C}} / \bar{\rho}_{3.75°\text{K}} = 1.4 \times 10^5$. Owing to the superconducting transition at 3.73° K, the residual resistivity of these specimens could not be determined. The values of residual resistivity given in Table I, were obtained by extrapolating the temperature dependence of resistance to T = 0. Over the range of our measurements (4.2 to 3.73° K) the dependence of $\bar{\rho}$ on T fits the relation $\bar{\rho} = \bar{\rho}_0 + \bar{b}T^n$ with n = 5 (see Table II). If we take n = 5 and derive the values of $\bar{\rho}_0$ and $\bar{b}$ by the method of least squares, the scatter of the points from the curve is not more than 0.2%. If n is taken as 4, the corresponding de-

TABLE I

Specimen No.	Impurity concentration according to analysis, % by weight	Further purification: Heating in vacuo, t°C	Further purification: Zone melting; number of passes	Temperature, T °K	$\rho \times 10^{10}$ ohm-cm at T°K	$\rho_{\parallel}/\rho_{\perp}$ at ~4.2°K	$\rho \times 10^{10}$ ohm-cm	$(\overline{\rho_{20°C}/\overline{\rho}_0}) \times 10^{-3}$	Estimated impurity concentration after purification, %
1	0.1	1000	10	4.23	42±3 %	1.3±5%	41	2.95***	$7\cdot10^{-3}$
2	0.002	1000	—	4.22	13.7±3%	1.30±4%	12.8	9.5	$2\cdot10^{-3}$
3	0.002*	1200—1400	—	4.22	6.4±5%	1.40±5%	5.5	24.2	$8\cdot10^{-4}$
4	0.002	1200—1400	43	4.215	1.68±5%	—	0.77	157	$1\cdot10^{-4}$
5				4.227	1.67±5%	1.56±7%	0.75	162	
6	0.1	1200—1400**	166	4.216	1.23±5%	1.5±7%	0.37	330	$<6\cdot10^{-5}$
				3.75	0.87±6%				

*The value determined by analysis is not shown. Preliminary measurements gave $\rho_{4.2}/\rho_{20°C} = 1 \times 10^{-4}$ for this kind of tin, i.e., the impurity concentration ~0.002%.

**Purification consisted of double electrolysis, heating and zone melting, and was carried out by N. N. Mikhaĭlov in the Technical Section of the Institute for Physical Problems, as were the purifications of the other specimens.

***For all specimens $\overline{\rho}_{20°C} = 1.21 \times 10^{-5}$ ohm-cm.[4]

TABLE II. $\overline{\rho}(T)$ for specimen No. 5 $\overline{\rho}_{calc} \times 10^{10} = 0.753 + 6.762 \times 10^{-4}\,T^5$ ohm-cm

T°K	$\rho_{meas} \times 10^{10}$ ohm-cm	$\rho_{calc} \times 10^{10}$ ohm-cm
4.227	1.668	1.666
4.192	1.629	1.628
4.120	1.554	1.556
4.062	1.500	1.501
3.992	1.435	1.439
3.883	1.351	1.350
3.730	1.243	1.241

partures reach 0.5 to 0.6% and take on a systematic appearance. Van den Berg[5] has found that the resistance of single crystals of tin obeys the relation $\rho = \rho_0 + bT^5$ between 4.2 and 10°K, but the value of b which he found is 35% greater than ours. It is possible that this difference is due to a difference in crystal orientation, which was not determined by van den Berg.

From our measurements of $\rho_{\parallel}/\rho_{\perp}$ for specimens Nos. 5 and 6 at 4.2 K (see Table I) it follows that the anisotropy in b is considerable, with $b_{\parallel}/b_{\perp} = 1.5$ to 1.6. At room temperature $\rho_{\parallel}/\rho_{\perp} = 1.45$ (Bridgman[4]). The value $\rho_{\parallel}/\rho_{\perp} = 1.3$ for the least pure specimens (Nos. 1 and 2) presumably represents the anisotropy of the residual resistance for these specimens. Faber and Pippard[9] found $(\rho_{\parallel}/\rho_{\perp})_0 = 1.14$ for tin with indium impurity. The difference from our data for specimens No. 1 and 2 must presumably be ascribed to the different impurities.

The value of $\overline{\rho}_0$ which is given in Table I was, for all our specimens, calculated on the basis of the data for specimen No. 5, given in Table II.

The accuracy with which $\overline{\rho}_0$ can be determined is, clearly, small in view of the uncertainties in the theory of the temperature dependence of resistance. If we assume that there is also a term proportional to T^2 in the expression for the resistivity (due to electron-electron collisions), and its upper limit is determined from the possible errors of measurement, then we obtain an uncertainty in $\overline{\rho}_0$ for specimens No. 4 and 5 of about 10 to 15%. For specimen No. 6 the uncertainty in $\overline{\rho}_0$ reaches 20 to 30%. It would be difficult to obtain values of $\overline{\rho}_0$ of any reliability for tin specimens of even lower resistivity, using this method.

Returning to the causes of the residual resistance in our specimens, we should point out that lattice defects, unconnected with impurities, make no significant contribution in specimens 1 — 5, since specimen No. 6 was produced with a significantly lower residual resistance.

We carried out special experiments to make sure that accidental damage to the specimen did not influence the results. For example, dropping a specimen onto the floor from a height of 1.5 m produced no noticeable increase in $\overline{\rho}_0$. In general, mechanical deformation did not affect $\overline{\rho}_0$ appreciably. We give in Table III some values of ρ for a specimen initially shaped with a chisel, then recrystallized, hammered and turned in a lathe and finally heated. It can be seen from the table that the maximum increase in ρ_0 is not more than a factor of ten.

TABLE III. Influence of various treatments on resistance (in 10^{-10} ohm-cm)

Specimen treatment	$\rho_{4.2°K}$	ρ_0	ρ_0/ρ_0 single crystal
Initial shaping	3.5	2.6	3.35
Single crystal	1.69	0.78	1
Violently hammered and turned at 20°C	8.3	7.4	9.5
After 40 hrs at 20°C	7.3	6.4	8.2
Heating for 8 hrs at 220–225°C. (The specimen consisted of 10–20 crystals with dimensions 4–8 mm)	2.3	1.4	1.8

The residual resistance of specimens 1 — 5 must, therefore, be due to chemical impurities. In the last column of Table I we give rough values for the total impurity concentration C in parts per cent, using the relation $C \approx 20\,\bar{\rho}_0 / \bar{\rho}_{20^\circ\text{C}}$, which is based on data in the literature for the residual resistance of tin with small impurities of In, Bi, and Sb, and also for some specimens with known total impurity concentrations (see Fig. 2). This calculation only gives an upper limit to the impurity concentration in the purest specimen, No. 6, since a significant fraction of its residual resistance could be due to "non-chemical" lattice imperfections. The possible imperfections are vacancies and other defects, produced in the lattice as a result of thermal motion at high temperatures and retained on quenching the specimen (see Lazarev and Ovcharenko,[16] who studied the residual resistance of quenched gold and platinum wires), and also isotopic disorder, mentioned above. It is difficult to evaluate the part played by these factors with sufficient accuracy. As tin has a high boiling point ($\sim 2500^\circ$ C) and a low melting point, we may expect the concentration of vacancies on our specimens to be insignificant (10^{-4} to 10^{-8}%, according to rough calculation if we take the heat of formation of vacancies to be $\frac{1}{4}$ the heat of vaporization, as found by Lazarev and Ovcharenko). It is not impossible that such a vacancy concentration has a noticeable effect on the resistance of specimen No. 6. This is even more so for the isotopic source of resistance. Natural tin consists of a mixture of many isotopes with atomic weights ranging from 112 to 124. Pomeranchuk[17] has given a theoretical estimate of the electron mean free path in an isotopically impure metal, and for tin this comes to 1 — 10 mm, while in specimen No. 6 the mean free path at 0° K is 3 mm.

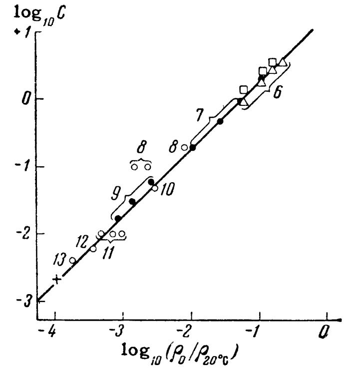

FIG. 2. The dependence of the residual resistance of tin on impurity concentration C (in % by weight). ● – Sn + In, Δ – Sn + Sb, □ – Sn + Bi, ○, + – upper limit of concentration according to the suppliers' analysis or from the conditions of preparation (+ – our measurements on specimen No. 2). The numbers against the points indicate the literature references.

We would like to express our thanks to N. N. Mikhaĭlov, director of the Technical Department of the Institute for Physical Problems, who carried out the purifications, to I. Ya. Pomeranchuk for informing us of his results prior to publication, and to A. I. Shal'nikov for his interest and valuable advice.

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Translated by R. Berman
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