The Effect of Tension on the Electrical Resistance of Single Tetragonal Tin Crystals

MILDRED ALLEN

Physics Department, Mount Holyoke College, South Hadley, Massachusetts (Received November 1, 1937)

The adiabatic tension coefficient of resistance of single tetragonal tin crystals has been determined for various orientations. Bridgman's theory, as modified by Cookson, has been extended to the tetragonal case and the experimental points found to lie within experimental error on the curves computed according to this theory. As measured directly, the tension coefficients depend both on the primary and secondary orientations of the crystal; for $\theta = 90^{\circ}$ they depend on the secondary orientation which is contrary to what has been found in the case of the trigonal crystals studied. The tension coefficients for specific resistance are found by allowing for the change in resistance which necessarily arises from the change in dimensions and these are found to be independent of the secondary orientation whatever the primary orientation, again contrary to what holds for trigonal crystals.

 \mathbf{T} N previous papers¹ the author has studied • experimentally the effect of tension on the electrical resistance of the trigonal crystals, bismuth and antimony, and of the hexagonal crystals, zinc and cadmium. In the meantime Bridgman² has developed a general theory, consistent with these experimental results, which he applied specifically to the case of trigonal crystals, giving the tension coefficient of the specific resistance as a function of the primary and secondary orientations of the crystals with respect to the cylindrical axis of the casting. This theory was slightly modified by Cookson³ who pointed out that on the basis of the necessary symmetries the matrix representing the piezoresistive coefficients was not required to be symmetrical, in that ρ_{rs} was not necessarily equal to ρ_{sr} , as Bridgman had assumed; there is, however, as yet no experimental evidence as to this. It was easy to pass from the trigonal to the hexagonal case since some of the coefficients appearing in the case of the trigonal crystals need only be put equal to zero to give the hexagonal case. Thus it came about that the tension coefficients of the hexagonal crystals were independent of the secondary orientation. It is therefore of interest to extend both the experimental and theoretical considerations to the study of a more drastically different type of crystal; and so *tetragonal tin* was chosen. The tetragonal case, however, is not completely unrelated to those previously studied,

inasmuch as the hexagonal case may be considered a degenerate example of the tetragonal; for one may pass from the comparatively complicated theory of the tetragonal to the simpler hexagonal by postulating a suitable relation between its piezoresistive coefficients.

Application of the Bridgman Theory TO TETRAGONAL CRYSTALS

To find the dependence of the tension coefficient on the primary and secondary orientations, the procedure is similar to that for the trigonal case.² As before the change in specific resistance is taken as a linear vector function of the six components of the tension tensor:

$$\Delta r_{x} = \rho_{11}X_{x} + \rho_{12}Y_{y} + \rho_{13}Z_{z} + \rho_{14}Y_{z} + \rho_{15}Z_{x} + \rho_{16}X_{y},$$

$$\Delta r_{y} = \rho_{21}X_{x} + \rho_{22}Y_{y} + \rho_{23}Z_{z} + \rho_{24}Y_{z} + \rho_{25}Z_{x} + \rho_{26}X_{y},$$

$$\Delta r_{3} = \rho_{31}X_{x} + \rho_{32}Y_{y} + \rho_{33}Z_{z} + \rho_{34}Y_{z} + \rho_{35}Z_{x} + \rho_{36}X_{y}, \quad (1)$$

$$2\Delta r_{4} = \rho_{41}X_{x} + \rho_{42}Y_{y} + \rho_{43}Z_{z} + \rho_{44}Y_{z} + \rho_{45}Z_{x} + \rho_{46}X_{y},$$

$$2\Delta r_{5} = \rho_{51}X_{x} + \rho_{52}Y_{y} + \rho_{53}Z_{z} + \rho_{56}X_{z} + \rho_{56}X_{y},$$

$$2\Delta r_{6} = \rho_{61}X_{x} + \rho_{62}Y_{y} + \rho_{63}Z_{z} + \rho_{66}X_{y}.$$

The factor 2 is introduced into the last three equations to bring the notation into agreement with that of Bridgman which has been used throughout this work. Taking the Z axis in the direction of the crystallographic axis, the crystal has a tetragonal axis of symmetry in the Z direc-

¹ Mildred Allen, Phys. Rev. 42, 848 (1932); 43, 569 ¹ Mildred Anen, A. M. K. M. (1933); **49**, 248 (1935). ² P. W. Bridgman, Phys. Rev. **42**, 858 (1932).

³ John W. Cookson, Phys. Rev. 47, 194 (1935).

tion and digonal axes of symmetry in the X and Y directions. When these conditions are applied to the general relations of Eq. (1) these take the simplified form :

$$\begin{aligned} \Delta r_{x} &= \rho_{11} X_{x} + \rho_{12} Y_{y} + \rho_{13} Z_{z}, \\ \Delta r_{y} &= \rho_{12} X_{x} + \rho_{11} Y_{y} + \rho_{13} Z_{z}, \\ \Delta r_{z} &= \rho_{31} X_{x} + \rho_{31} Y_{y} + \rho_{33} Z_{z}, \\ \Delta r_{4} &= \frac{1}{2} \rho_{44} Y_{z}, \\ \Delta r_{5} &= \frac{1}{2} \rho_{44} Z_{x}, \\ \Delta r_{6} &= \frac{1}{2} \rho_{66} X_{y} \end{aligned}$$

The total change in the specific resistance ΔR is then found from these values using the relation

$$\Delta R = \Delta r_x \cos^2 \alpha + \Delta r_y \cos^2 \beta + \Delta r_z \cos^2 \gamma + 2\Delta r_4 \cos \beta \cos \gamma + 2\Delta r_5 \cos \alpha \cos \gamma + 2\Delta r_6 \cos \alpha \cos \beta, \quad (3)$$

where α , β and γ are the angles made by the X, Y and Z axes with the axis of figure of the cylindrical casting and so are related to the primary orientation θ and the secondary orientation¹ φ in the following way:

$$\cos \alpha = \sin \theta \sin \varphi, \qquad \cos \beta = \sin \theta \cos \varphi, \\ \cos \gamma = \cos \theta. \qquad (4)$$

Carrying out these indicated substitutions, the final equation connecting the tension coefficient β (the relative change in specific resistance per unit applied tension) with the orientation angles is

$$\beta \rho_{\theta} = \frac{6\rho_{11} + 2\rho_{12} + \rho_{66}}{8} \sin^4 \theta + \rho_{33} \cos^4 \theta + (\rho_{13} + \rho_{31} + \rho_{44}) \sin^2 \theta \cos^2 \theta + \frac{2\rho_{11} - 2\rho_{12} - \rho_{66}}{8} \sin^4 \theta \cos 4\varphi, \quad (5)$$

where ρ_{θ} is the specific resistance for the primary orientation θ . Since the term in $\cos 4\varphi$ is multiplied by $\sin^4 \theta$ it is immediately evident that the tension coefficient must vary with φ when θ is 90°. In this it differs markedly from the trigonal case where the coefficient of $\cos 3\varphi$ was a function of $\sin \theta \cos \theta$ and so was necessarily zero for $\theta = 90^{\circ}$.

To pass from the tetragonal case with its seven characteristic coefficients to the hexagonal one with six it is only necessary to substitute for ρ_{66} its value for the hexagonal case $2(\rho_{11}-\rho_{12})$. This causes the coefficient of the term in $\cos 4\varphi$ to vanish, as it must to agree with both theory and experiment according to which the tension coefficients of hexagonal crystals are entirely independent of the secondary orientation, and reduces the coefficient of $\sin^4 \theta$ to its value ρ_{11} for the hexagonal case.

EXPERIMENTAL PROCEDURE

The experimental procedure in the case of tin crystals was much the same as that used for zinc and cadmium.

The crystals themselves were made of Kahlbaum metal by the author in Bridgman's laboratory by slowly lowering the bent glass mold containing the tin through an electric furnace in an atmosphere of CO₂ to prevent oxidation. They had a diameter of approximately a sixteenth of an inch and a length of from one to two inches. They were also very pliable and needed to be handled with great care to prevent undesirable bending. The sensitivity of the galvanometer used, with the scale at about five meters, was 0.98×10^{-7} volts per centimeter deflection, or about twice the sensitivity of the one that had been available previously. The readings could not be made closer than to one-half a millimeter. Even under these favorable conditions, since the specific resistance of tin is small, the tension coefficients not large, and the elastic limit of tin crystals very low, it was rare to get a deflection greater than 2 cm and many of the measurements made involved deflections much smaller than this.

RESULTS

Some two dozen tin crystals of varying orientations were measured, their temperature being kept close to 30.0°C. The reading with one crystal was discarded since it was found to be twice as large as any other and so indicated some discrepancy.

Computations were made from the observed tension coefficients of resistance in two ways. In the first the observed values of β were introduced directly into Eq. (5) and the ρ' 's determined from the twenty-three measurements using the method of least squares. Logically this procedure is scarcely defensible, since the theory does apply to the change in specific resistance and not to the observed resistance which is affected by the changes in dimensions which must accompany the application of tension. However, since the change in dimensions produced by the tension



FIG. 1. Relative change of resistance per unit tension due only to changes in dimensions and orientation and computed from Bridgman's determination of the elastic constants of tin. a, $\varphi = 45^{\circ}$; b, $\varphi = 22\frac{1}{2}^{\circ}$; c, $\varphi = 0^{\circ}$.

has a symmetry very similar to that of the change in resistance the observed values fit Eq. (5) very well, and the ρ' 's found in this way enable one to compute directly the change in resistance which will be *actually observed* by the application of a given tension to a crystal of a given orientation. The primes are used to indicate that the changes in resistance have *not* been corrected for the change in dimensions and are therefore not the piezoresistive coefficients which appear in the theory. Their values as found for tin are

$$\begin{array}{l} (6\rho_{11}'+2\rho_{12}'+\rho_{66}')/8 = (0.69\pm0.44)\times10^{-11}, \\ \rho_{33}' = (11.36\pm0.76)\times10^{-11}, \\ \rho_{13}'+\rho_{31}'+\rho_{44}' = (28.5\pm2.2)\times10^{-11}, \\ (2\rho_{11}'-2\rho_{12}'-\rho_{66}')/8 = (-1.88\pm0.52)\times10^{-11}. \end{array}$$

The tension is as usual expressed in kg/cm^2 .

The second method of computation is to subtract from every observed relative change in resistance the computed relative change in resistance which would result from the change in dimensions and orientation caused by the application of the tension. That which remains then gives the relative change of specific resistance, arising perhaps from a slight rearrangement of the atoms in the crystal lattice, and is that change of resistance to which Bridgman's theory directly applies. To compute the relative change in resistance per unit applied tension which arises directly from the change in dimensions and orientation the theory sketched in the antimony paper¹ is developed for the tetragonal case and the values of the elastic constants given for tin by Bridgman⁴ are used. The resulting values are presented in Fig. 1. It is to be noted that these values depend on the secondary orientation for $\theta = 90^{\circ}$ and that at $\theta = 90^{\circ}$ the maximum spread with variation of secondary orientation is 3.84×10^{-6} . From every observed tension coefficient there is then subtracted the appropriate value as interpolated from this graph, and the result is substituted in Eq. (5). Least squares are again applied and the ρ 's determined which are now the real piezoresistive coefficients to which the theory sketched above applies. The numerical values found for these coefficients of specific resistance are

$$(6\rho_{11}+2\rho_{12}+\rho_{66})/8 = (-4.41\pm0.45)\times10^{-11}, \rho_{33} = (8.96\pm0.77)\times10^{-11}, \rho_{13}+\rho_{31}+\rho_{44} = (19.5\pm2.3)\times10^{-11}, (2\rho_{11}-2\rho_{12}-\rho_{66})/8 = (0.07\pm0.53)\times10^{-11}.$$
(7)

The significance of these experimental results for the tension coefficient of resistance for tin can perhaps best be presented graphically in Fig. 2, where the curves marked a, b and c give the directly observed tension coefficients as a function of the primary and secondary orientations θ and φ , and the curve d the tension coefficients of the specific resistance. The directly observed curves are seen to depend on the secondary orientation φ at $\theta = 90^{\circ}$ (as did also the so-called correction curve of Fig. 1). The maximum spread with variation of φ is 3.62×10^{-6} which is within experimental error of the maximum spread of the correction curve. Hence it is to be expected that when the method of least squares is applied to the data for the tension coefficients of the specific resistance alone they will cease to be a function of the secondary orientation φ . This is shown to be true both graphically in Fig. 2(d) and in the numerical values of Eq. (7) where the coefficient of the term in $\cos 4\varphi$ is zero well within the probable error. This lack of dependence of the tension coefficients of the specific resistance on the secondary orientation for all values of the primary orientation is the most striking and unexpected result of this work on tin.

One or two other points deserve note. As is indicated in Fig. 2 negative values of the tension coefficients occur for certain orientations, giving further evidence that negative tension coefficients are not abnormal. These negative values were actually found for five of the crystals measured. As regards the order of magnitude of the results,

⁴ P. W. Bridgman, Proc. Am. Acad. 60, 379 (1925).

Tomlinson⁵ gives for the tension coefficient of polycrystalline tin the value 5.89×10^{-6} which appears reasonable in the light of these present results. Rolnick's value⁶ of 10.6×10^{-6} causes one to wonder whether his specimen was actually polycrystalline.

One test of the success of a theory lies in the agreement of the observed values with those computed according to the theory. Using the numerical values of the ρ 's (or ρ 's) in Eq. (5) to compute the tension coefficients it was found that the average deviation between these computed values of the tension coefficients and the corresponding ones found experimentally is about 1.05×10^{-6} , where the actual values range from -1.33×10^{-6} to $+10.12 \times 10^{-6}$, the largest actual difference between the two being 3.0×10^{-6} . Various factors contribute to this somewhat large discrepancy which is consequently seen not to be exorbitant. The lower limit to which the galvanometer scale can be read introduces an uncertainty in the measured value of the tension coefficient of about 0.5×10^{-6} , the exact value depending of course on the size of the total resistance involved. The average deviation of the individual values of a single determination of the coefficient found with different tensions and with reversed current is only in three cases greater than this, so that 0.50×10^{-6} represents well the uncertainty arising from the galvanometer readings alone. A further uncertainty of about the same magnitude is caused by the difficulty of measurement of the orientations which had to be determined, as in the case of cadmium, by the reflection pattern method since tin does not cleave. The primary orientation is probably good to 3° while the secondary is uncertain to 4° or 5°. An uncertainty of a few percent in the area of cross section of the crystals is relatively not of great importance.

As noted in the paper on zinc and cadmium,¹ sufficient data are lacking, without further experimental work involving the torsion of the crystals, to allow one to disentangle the piezoresistive coefficients further. However, in the interests of collecting all the known data concerning the effect of stresses on the resistance of the tetragonal tin crystals, the pressure coef-



FIG. 2. Tension coefficients of tin directly observed: a, $\varphi = 45^{\circ}$; b, $\varphi = 22\frac{1}{2}^{\circ}$; c, $\varphi = 0^{\circ}$. Coefficients of *specific* resistance—curve d.

ficients of specific resistance as determined by Bridgman⁷ are given for reference.

$$-\frac{2\rho_{13}+\rho_{33}}{\rho_{0^{\circ}}} = \left(\frac{1}{p}\frac{\Delta R}{R}\right)_{\theta=0^{\circ}} = -10.96 \times 10^{-6},$$
$$-\frac{\rho_{11}+\rho_{12}+\rho_{31}}{\rho_{90^{\circ}}} = \left(\frac{1}{p}\frac{\Delta R}{R}\right)_{\theta=0^{\circ}} = -10.28 \times 10^{-6}.$$

These pressure coefficients give two relations between the seven piezoresistive coefficients in addition to the four relations given by the application of longitudinal tensions described in this paper. The seventh necessary relation can be furnished by experiments on torsion which have not yet been carried out.

The author is much indebted to the National Research Council for a generous grant towards acquiring apparatus and supplies; in particular it made it possible to have one of the Leeds and Northrup galvanometers of high voltage sensitivity (HS No. 2285-a) as well as a large capacity 6-volt storage battery. She is also much indebted to Miss Haigouhi Haigazn, a graduate student at Mount Holyoke College in the year 1933–1934, who reassembled the apparatus after its removal from Harvard and who made the measurements on six of the crystals.

⁷ P. W. Bridgman, Proc. Am. Acad. 60, 371 (1925).

⁵ Tomlinson, Phil. Trans. 174, 1 (1883).

⁶ H. Rolnick, Phys. Rev. **36**, 506 (1930).