The Magnetic Anisotropy of Crystals of Sn, and of Sn with Added Sb, Cd, or Ga*

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The principal magnetic susceptibilities of single crystals of white (tetragonal) tin have been determined. Crystals were grown by the traveling furnace method. Perpendicular to the tetragonal axis the susceptibility (per unit volume) is $\kappa_{\rm L} = 0.197 \times 10^{-6}$; parallel to the axis it is $\kappa_{\rm H} = 0.176 \times 10^{-6}$. The ratio $\kappa_{\rm L}/\kappa_{\rm H}$ is strongly influenced by the addition of

'HAT the crystal structure of tin controls its magnetic properties is evident from the fact that white tin is paramagnetic, grey tin diamagnetic. It therefore seemed important to investigate the magnetic anisotropy of the noncubic form (white tin) and to modify this anisotropy in any feasible way. The method recently developed by Goetz and Focke¹ and applied by them to bismuth (diamagnetic) were obviously suitable with such minor changes as were made necessary by the lower absolute values of the principal susceptibilities of tin. The investigators just referred to grew single crystals suitable for magnetic measurements by the Gouy method and found how the two principal susceptibilities were affected by impurities.

Impurities which can be entrapped in crystals are of greater interest than those which cannot. Whether there is true solution in all such cases is not yet clear, but it appeared reasonable to try first impurities known to dissolve in tin. Of these it has been possible to study only antimony and cadmium. Gallium was added to the list because of its low melting point, peculiar crystal structure, and favorable position in the periodic table.

EXPERIMENTAL PROCEDURE

The tin selected for definitive experiments was a particular lot of Baker's "C. P. Analyzed" containing As 0.0000 percent; Pb 0.003 percent; Fe 0.002 percent; Zn 0.000 percent; Cu 0.000 percent. Since not over one percent of Sb, Cd, or Ga was added, ordinary commercial grades of these elements could be used. Alloys were prepared by weighing and were melted under hysmall amounts of certain elements. For tin containing no added element this ratio is 1.120. Adding 0.60 percent Sb the ratio is 1.200; 0.76 percent Cd, 0.923; 0.89 percent Ga, 0.897. The relation between the change in this ratio and the number of valence electrons of the added element is compared with available data for bismuth.

drogen in Pyrex. The low range of solid solubilities made it inconvenient to obtain a series of the desired concentrations by diluting a richer alloy. After thorough mixing a stick 7 inches (18 cm) long and 0.1 inch (0.254 cm) square was cast in a two-piece slate mold.

This polycrystalline casting was placed in a snugly fitting graphite box (Fig. 1). One end of



FIG. 1. Graphite box in which crystals were grown.

the box was closed by a steel plug. At the other end a seed crystal could be brought into contact with the casting.

This assembly was then placed in a horizontal position inside a crystal growing apparatus similar to that described by Hasler.² The tubular furnace which traverses the casting was made quite short (4 cm) and the temperature gradient on the exit side was made steeper by directing air jets against the glass wall of the tube containing the graphite box. Cooling of the furnace by this jet system was prevented by an asbestos screen. Preliminary tests showed that a steep temperature gradient is essential to success, and that 2 millimeters per minute is a suitable furnace speed. The use of a short furnace ensures against too much change in concentration of soluble impurities. Hydrogen was used to prevent oxidation. The temperature gradient was further increased by causing the hydrogen to flow past the crystal in the direction in which the furnace moved. That the temperature gradient requires

^{*} Part of a dissertation presented for the degree of Doctor of Philosophy in Yale University.

¹ A. Goetz and A. B. Focke, Phys. Rev. 45, 170 (1934), and preceding papers.

² M. F. Hasler, Rev. Sci. Inst. 4, 656 (1933).

special control was shown by the fact that it was possible to initiate the growth of crystals with the tetragonal axis at a large angle to the axis of the casting by the use of a steel plug with its end beveled at a sharp angle. This procedure was suggested by the experimental results of Palibin and Froiman,3 and was a convenient way to get seed crystals of the desired orientation, which is with the tetragonal axis perpendicular to the axis of the specimen.

The castings thus prepared were etched in hydrochloric acid solutions properly modified to prevent a too rapid attack. The etching showed at a glance whether a single crystal had been obtained, and if so, permitted its orientation to be determined by optical means. The most important etch planes were found to be $\{101\}$ and $\{301\},^4$ these indices referring to the smaller of the two commonly chosen unit cells.

Susceptibilities were measured by the Gouy method, in which the force on a long specimen of uniform cross section is given by $F = \frac{1}{2}(\kappa - \kappa_0)$ $A(H^2-H_0^2)$. Here κ and κ_0 are the susceptibilities (per unit volume) of the specimen and of the surrounding medium (air), H and H_0 are the field strengths at the two ends of the specimen, and Ais its cross section. Since κ_0 is known and H_0^2 is negligible for such long specimens, the quantities to be measured are F, A, and H.

The force F was measured by counterpoising the specimen on a sensitive microbalance, and increasing the counterpoise as necessary when the field was applied. Readings were taken to the nearest 0.01 milligram. High sensitivity was required because of the small magnitude of F, which was of the order of 3 milligrams.

The fields H and H_0 were measured with a search coil attached to a pendulum and connected to a low resistance (16 ohms) Leeds and Northrup type HS-2285e galvanometer which was calibrated with a standard mutual inductance. Field strengths H of about 24,000 gauss were employed, in which case H_0 was of the order of 650 gauss.

The cross section of the specimen was found by lowering it a known distance into a tube of ethyl alcohol and measuring the rise in the liquid level with a traveling microscope. This rise was most easily measured in a connecting side tube of small diameter. The apparatus was calibrated by immersing pieces of drill rod of known cross section.

Sections 3.5 inches (9 cm) long were cut from the good crystals, selected to give the most uniform cross section in the non-homogeneous part of the field. The bar to be cut was laid in the jaws of a pair of tin snips and allowed to fall into the hand when cut, so that all strains would be localized at the ends of the specimen.

The crystal hanger contained a device which, when the balance was arrested, allowed the crystal to be lifted, rotated about its axis, and reseated without lateral displacement. A crystal of the proper orientation could thus be set with its tetragonal axis either parallel to or perpendicular to the field. Since all directions perpendicular to the tetragonal axis are equivalent, the susceptibility in any arbitrary direction in a tetragonal crystal is given by $\kappa = \kappa_{II} \cos^2 \alpha + \kappa_{L} \sin^2 \alpha$, where α is the angle between the applied field and the tetragonal axis. Measurement of κ_{II} and κ_{I} therefore gives complete information about the magnetic properties of any crystal. Since the polycrystalline susceptibility of tin is temperature independent⁵ it seemed unlikely that small temperature fluctuations would introduce any error, and all measurements were made at room temperature.

Results

For pure tin: $\kappa_{\perp} = 0.197 \times 10^{-6}$, $\kappa_{\parallel} = 0.176 \times 10^{-6}$, $\kappa_{\rm L}/\kappa_{\rm H} = 1.120$. Taking the density of tin as 7.3 the mass susceptibilities are: $\chi_{\perp} = 0.0270 \times 10^{-6}$, $\chi_{II} = 0.0241 \times 10^{-6}$. The Voigt-Thomson⁶ relation gives for an ideal polycrystalline aggregate: $\chi = \frac{1}{3}(2\chi_{\perp} + \chi_{\parallel}) = 0.0259 \times 10^{-6}$, which is in good agreement with previously published results.⁷

The experimental data are given in Table I. Figs. 2 to 4 show the variation of the two principal susceptibilities for each impurity as a function of its concentration. Fig. 5 shows the ratio of these susceptibilities $(\kappa_{\perp}/\kappa_{\parallel})$ for each impurity as a function of its concentration. The effect of Sb is to decrease both κ_{\perp} and κ_{\parallel} , $\kappa_{\perp}/\kappa_{\parallel}$ increasing.

³ P. A. Palibin and A. I. Froiman, Zeits. f. Krist. 85, 322 (1933).

⁴ Details of the optical apparatus used and of the identification of the etch planes will be given elsewhere.

⁵ H. Endô, Sci. Rep. Tohoku Imp. Univ. 16, 201 (1927).

⁶ W. Voigt, Lehrbuch der Kristallphysik (1928), p. 960. ⁷ International Critical Tables, Vol. 6, p. 355.

| Crystal No. | Alloy wt. % | Orien- tation | CROSS SECTION | Force1* | Forcen* | Field (gauss) | ${}^{H^2-H_0{}^2}_{	imes 10^{-8}}$ | к_1‡×10-6 | <i>к</i> п‡×10 ^{−6} | <i>к</i> т/кп |
|----------------|----------------|------------------|-------------------------|-------------------|-------------------|--------------------|------------------------------------|-----------------|------------------------------|---|
| 19 | 0.09 Sb | 89.9° | 0.06493 cm ² | 3.371 mg 3.375 | 2.920 mg 2.925 | 24,700 24,700 | 6.0967 6.0967 | 0.1959 .1961 | 0.1736 .1738 | 1.127 1.128 |
| 20 | .26 Sb | 86° | .06278 | 3.135 3.138 | 2.660 2.663 | 24,400 24,400 | $5.9494 \\ 5.9494$ | .1935 .1937 | .1686 .1687 | $1.148 \\ 1.148$ |
| 18 | .09 Sb | 89.9° | .06278 | 3.143 3.130 | 2.705 2.703 | 24,304 24,378 | 5.9026 5.9386 | .1952 | .1721 | $1.134 \\ 1.131$ |
| 17 | Stock B | 90° | .06329 | 3.198 3.193 | 2.795 2.788 | 24,353 24,304 | $5.9265 \\ 5.9026$ | .1961 .1965 | .1751 .1753 | $\substack{1.120\\1.121}$ |
| 13# | Stock B | 89.9° | .06046 | 3.265 | 2.865 | 24,304 | 5.9026 | .2083 | .1864 | 1.117 |
| 8 | Stock B | 87° | .06193 | 3.103 | 2.745 | 24,378 | 5.9386 | .1944 | .1753 | 1.109 |
| 21 | 0.76 Cd | 85.5° | .06244 | 2.823 2.830 | 3.105 3.108 | 24,378 24,378 | $5.9386 \\ 5.9386$ | .1782 .1786 | .1931 .1933 | .9228 .9240 |
| 23 | .50 Cd | 87° | .06391 | 3.033 | 3.104 | 24,333† | 5.9167 | .1862 | .1899 | .9805 |
| 16 | Stock B | 89° | .06123 | 3.130 3.135 | 2.725 2.733 | 24,324† 24,324† | 5.9123 5.9123 | .1985 .1987 | .1765 .1770 | $\substack{1.125\\1.123}$ |
| 27 | 0.25 Cd | 89° | .05631 | 2.775 2.775 | 2.683 2.675 | 24,324 24,294 | 5.9123 5.8978 | .1924 .1928 | .1870 .1869 | 1.029 1.032 |
| 28 | .12 Cd | 88° | .06391 | 3.153 3.143 | 2.888 2.863 | 24,294† 24,294 | $5.8978 \\ 5.8978$ | .1930 .1924 | .1792 .1779 | 1.077 1.082 |
| 31 | .60 Sb | 88° | .06262 | 2.963 2.945 | 2.383 2.360 | 24,259 24,259† | $5.8808 \\ 5.8808$ | .1867 .1857 | .1558 .1546 | 1.198 1.201 |
| 32 | .42 Ga | 87° | .06193 | 3.075 3.058 | 3.035 3.020 | 24,288 24,288† | $5.8948 \\ 5.8948$ | .1941 .1932 | .1919 .1911 | $\begin{array}{c} 1.011\\ 1.011\end{array}$ |
| 33 | .89 Ga | 88° | .06262 | 3.133 3.128 | 3.555 3.553 | 24,298 24,298† | 5.8997 5.8997 | .1952 .1949 | .2176 .2175 | .8971 .8961 |

TABLE I. Susceptibility data on alloys if single crystals of tin.

* After subtracting suspension correction of 0.1 mg. \ddagger After adding air correction of 0.029 $\times10^{-6}$.

When Cd is added κ_{\perp} decreases and κ_{Π} increases; $\kappa_{\perp}/\kappa_{\Pi}$ therefore decreases. At 0.4 percent cadmium $\kappa_{\perp} = \kappa_{\Pi}$ and the crystal is magnetically isotropic. When Ga is added κ_{\perp} changes very little while κ_{Π} increases rapidly; $\kappa_{\perp}/\kappa_{\Pi}$ decreases as it does when Cd is added.

It may be seen that Cd and Ga, the two elements having fewer valence electrons than tin, cause a decrease in $\kappa_{\rm L}/\kappa_{\rm H}$. On the other hand Sb, which has one more valence electron than tin, causes an increase in this ratio. The significance of this finding is increased by the fact that $\kappa_{\rm L}/\kappa_{\rm H}$



FIG. 2. Susceptibilities of tin containing antimony.

† Fluxmeter calibrated at time of taking this reading. # Not averaged.



FIG. 3. Susceptibilities of tin containing cadmium.



FIG. 4. Susceptibilities of tin containing gallium.

is not subject to errors made in measuring either field strength or crystal cross section, since these variables cancel out. Therefore, although the probable error in κ may be as high as 2 percent, the probable error in $\kappa_{\perp}/\kappa_{\parallel}$ is considerably less. The precision in measurement of κ was checked by determining the mass susceptibilities of distilled water and fused quartz. Results were, for water, $\chi = -0.738 \times 10^{-6}$ compared with the accepted value of -0.720×10^{-6} ; and for fused quartz $\chi = -0.420 \times 10^{-6}$ compared with a value of -0.42×10^{-6} obtained by Dr. C. T. Lane in these laboratories but with other apparatus.

DISCUSSION

It is interesting to compare Fig. 5 with the corresponding data given by Goetz and Focke for bismuth. With tin, elements toward the alkali side of the periodic table decrease $\kappa_{\rm L}/\kappa_{\rm H}$, while those toward the halogen side increase this ratio. The exact opposite was found for bismuth. However, when account is taken of the fact that the susceptibilities of tin are both positive, while those of bismuth are both negative, this difference is perhaps to be expected. Assume for definiteness that an added impurity contributes diamagnetism parallel to the principal axis and nothing at all perpendicular to it. Then in the case of tin we are adding a negative quantity to the smaller of two positive quantities, while in the case of bismuth we are adding it to the smaller of two negative quantities. The ratio for tin will be increased and for bismuth will be decreased. Something more complicated than this actually occurs, for the magnitudes of κ_{\perp} and κ_{\parallel} both change.

Goetz and Focke explained their results with



FIG. 5. $\kappa_{\perp}/\kappa_{II}$ ratios for tin containing impurities.

the aid of the Ehrenfest-Raman^{8, 9, 10, 11} large electron orbit hypothesis, which had previously proved useful in explaining the abnormally high diamagnetism of bismuth, antimony, and graphite crystals, and the diminution in these values when the crystals were made submicroscopic or melted. Assuming the impurity to collect in certain crystallographic planes, Goetz and Focke pointed out that these planes might act as reflecting walls to electrons moving in large orbits. A reorientation of these orbits would result, and since they are presumably large enough to surround many atomic nuclei, the diamagnetic susceptibility in certain crystallographic directions would be considerably increased at the expense of that in other directions.

Processes of this kind are adequate to explain some of the effects of impurities on tin. The five planes having the greatest atom densities are, in order: {100} {110} {112} {101} {210}. By assuming impurities to be concentrated in {110} planes, the changes in κ_1/κ_0 may be explained. Planes of the form {110} are suggested as more probable than $\{100\}$ by the fact that several of the crystals were covered after etching by fine lines which corresponded to traces of {110} planes. These traces were most regular and conspicuous on the lateral faces of the crystal, and were best developed in the direction most nearly parallel to the sloping isothermal surfaces in the freezing melt. That is, one of the planes (110), $(1\overline{1}0)$ was conspicuous; the other was not. It is difficult to explain these lines without attributing them to impurities, particularly since they were most pronounced in crystals containing the largest amounts of impurities. Although the lines were so widely spaced as to be visible without magnification, they certainly do not make less plausible the existence of planes of impurity spaced more or less uniformly at much smaller intervals throughout the crystal. A considerable amount of work indicates the presence of some sort of secondary structure in metals, so that there is no longer much question of its existence. We are now more interested in the sizes, causes, and regularity of these secondary patterns.

- ⁸ P. Ehrenfest, Physica 5, 388 (1925).
 ⁹ P. Ehrenfest, Zeits. f. Physik 58, 719 (1929).
 ¹⁰ C. V. Raman, Nature 123, 945 (1929).
 ¹¹ C. V. Raman, Nature 124, 412 (1929).

In the present work the magnitude of the observed changes (20 percent in $\kappa_{\rm L}/\kappa_{\rm H}$ for less than 1 percent added impurity) makes it possible to associate the changes not with the mere presence of the impurity but with the effect of its presence on the rest of the crystal. Goetz and Focke point out that a distribution of impurity in widely separated planes could be expected to produce a larger effect than a uniform volume distribution. Furthermore, a distribution in planes accounts much more readily for anisotropic changes in susceptibility.

To explain why an element having more valence electrons than tin should have an opposite effect to one having less, we may assume either that different impurities go into different planes, or that they go into the same planes but affect the crystal differently.

One limitation of the large orbit hypothesis should be pointed out. A mere rearrangement of existing orbits cannot affect the calculated ideal polycrystalline susceptibility, for any increase in κ_{\perp} would result in a corresponding decrease in $\kappa_{\rm II}$, and *vice versa*. As can be seen from Figs. 2 to 4, the corresponding polycrystalline susceptibility (which would be given by a line 1/3 the distance from κ_{\perp} to $\kappa_{\rm II}$) does not remain constant.

If all added impurities form reflecting walls, then to explain changes in $\kappa_{\rm L}/\kappa_{\rm II}$ we must assume that Cd or Ga collects in planes parallel to the axis while Sb collects in planes perpendicular to it. For example, the addition of Cd decreases $\kappa_{\rm L}/\kappa_{\rm II}$. If Cd collects in any set of planes parallel to the tetragonal axis, we would expect an increase in the area of large orbits projected on these planes, and an increased diamagnetism perpendicular to the axis. The net positive value of $\kappa_{\rm L}$ would therefore be lowered relative to $\kappa_{\rm II}$, and $\kappa_{\rm L}/\kappa_{\rm II}$ would decrease, as is actually observed.

One limitation of the large orbit hypothesis has already been mentioned. Another appears when we assume that impurity collects in planes parallel to the tetragonal axis, for unless conditions of growth favor one plane more than another there is no reason to expect impurity to collect in, say, (110) and not to collect in $(1\overline{10})$. If it collects in both the planes of form $\{110\}$ the crystal is divided by walls of impurities into narrow rectangular prisms, and no large orbits can exist at all. We may avoid this situation only by assuming that all impurities collect in (001) planes, which divide the crystal not into prisms but into layers. But if we do so there is still the difficulty of explaining the opposite effects of different impurities.

Honda and Shimizu¹² have suggested that increase in lattice constants may produce diamagnetism. In this connection the results of Bowen and Morris Jones¹³ have some bearing on the present work. By x-ray investigation they found that when Sb is added to tin there is a gradual expansion of the tin lattice up to the limit of solid solubility, with no change, however, in the ratio of the lattice parameters. Fig. 2 shows a decrease in paramagnetism, as this line of argument would predict. It would be interesting to see if Ga, which increases the paramagnetism of tin, simultaneously decreases its lattice constants.

In comparing the effects of impurities on tin with the effects on bismuth it should be pointed out that there is little evidence in the present work for a critical concentration of impurity corresponding to the complete filling of a set of uniformly spaced planes with a one- or two-atom layer of impurity. The nearest thing to such evidence is the dip in the Cd curves (Fig. 3) near the origin. Since all the critical concentrations reported by Goetz and Focke lay below 0.1 percent, it is not impossible that minima in these curves occur at lower concentrations than any yet used. The stock tin was not, however, pure enough to warrant studies at such low concentrations. It will be observed that the changes in $\kappa_{\rm L}/\kappa_{\rm H}$ for tin are much smaller and much more nearly linear than those for bismuth over the same range in concentration. The approximate linearity may be due merely to the smaller range of κ_{\perp} , κ_{μ} , and of their ratio, in the present case.

In conclusion the author wishes to express his appreciation to Professor L. W. McKeehan, director of the research, for his ready advice and suggestions. He is also indebted to Dr. C. T. Lane and Dr. A. B. Focke for much valuable aid.

¹² K. Honda and Y. Shimizu, Nature 135, 108 (1935).

¹³ E. G. Bowen and W. Morris Jones, Phil. Mag. **12**, 441 (1931).