

## FILAMENTARY CRYSTALS WITH ALMOST THE THEORETICAL STRENGTH OF PERFECT CRYSTALS

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IN recent years many papers have been published on the growth mechanism and properties of filamentary crystals, commonly called whiskers, whose length-to-diameter ratio we shall understand to be about  $10^3$ . These recent investigations have shown that the strength of whiskers is tens of times and sometimes hundreds of times greater than the strength of ordinary crystals of the same substances, and sometimes approach the theoretical strength calculated from interatomic forces. Information concerning the electrical resistance (especially at low temperatures), ferromagnetic domain structure, and photoelectric and optical properties of whiskers is important for solid state physics.

The present review will discuss the principal methods of producing and testing whiskers, current ideas regarding their growth mechanism, and the principal results obtained from the study of their mechanical and physical properties.

### I. PRODUCTION, ORIENTATION, AND SHAPE OF WHISKERS

Accounts of the filamentary growth of crystals were published as long ago as the first half of the 18th century and are referred to in review articles by Winkler,<sup>1</sup> Kohlschütter,<sup>2,3</sup> and Ostwald.<sup>4</sup> Hardy's more recent review is very extensive.<sup>5</sup> However, the systematic investigation of the growth and properties of whiskers began comparatively recently, leading to the revelation of their extraordinary mechanical properties.

Metal whiskers can grow naturally on minerals, slag, and sulfides, as well as on thin layers of metal formed through electroplating, by deposition from a metal vapor in a vacuum or gas or by electrolytic deposition. Filaments of ionic and molecular crystals grow through precipitation from a supersaturated solution, by evaporation through a porous wall or as a result of various chemical reactions. We shall now examine in detail the principal techniques for growing whiskers.

#### 1. Techniques for the Production of Whiskers

a) Growth through the chemical reduction of metallic salts. For the purpose of growing whiskers by reducing halides Brenner<sup>6</sup> used apparatus (Fig. 1) consisting of a tubular furnace with a

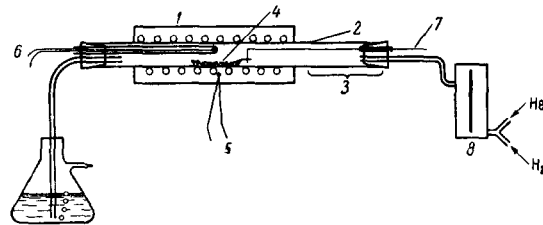


FIG. 1. Apparatus for producing whiskers by reduction of halides (Brenner): 1) furnace; 2) quartz or mullite tube; 3) cooling section; 4) vessel containing halide; 5 and 6) thermocouples; 7) tungsten wire; 8) gas flow meter.

quartz or mullite tube and a tray containing the halide to be reduced. Reduction takes place in a stream of hydrogen, or without the use of hydrogen through thermal dissociation in the case of gold and platinum crystals. Following the reduction process the tray is moved to a cooling section of the tube, which is then bathed with helium before the specimen is withdrawn from the furnace.

The disadvantage of this apparatus is that crystal growth cannot be observed visually. This shortcoming was eliminated in an improved design (Fig. 2) with strong lateral illumination and provision for preventing fogging of the window. A stereoscopic microscope is used to observe crystal growth visually, while an electron microscope is used to determine crystal diameters and to study their surface states.

Whiskers of Cu, Ag, Fe, Ni, Co and Pt were produced by reducing the salts of these metals. Analytically pure halides were used. The best results were obtained with the halides listed in Table I, which also gives the reduction temperatures. In the case of copper halides the best results were obtained by reducing CuI. The rate of hydrogen flow or its partial pressure affects crys-

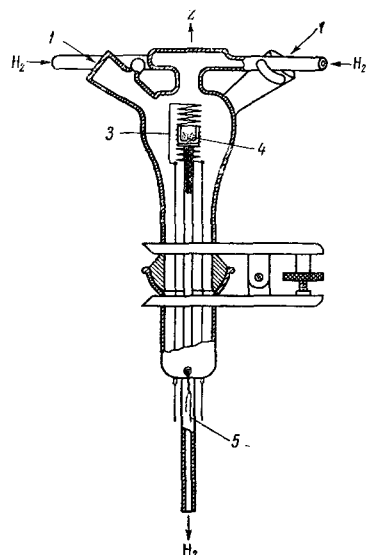


FIG. 2. Improved apparatus for producing whiskers and observing their growth from reduced halides (Brenner): 1) illumination; 2) microscope; 3) tungsten heater; 4) metal halide; 5) thermocouple.



FIG. 3. Copper whiskers (Brenner) from the reduction of CuI ( $\times 20$ ).

TABLE I

Metal	Halide	Temperature of whisker growth	Optimum temperature, °C	Maximum length, microns
Cu	CuCl	430—850	650	~50
	CuBr			
	CuI			
Ag	AgCl	700—900	800	~10
	AgI			
Fe	FeCl <sub>2</sub>	730	—	~20
	FeBr <sub>2</sub>	760	—	
Ni	NiBr <sub>2</sub>	740	—	2
Co	CoBr <sub>2</sub>	650	—	3
Pt	PtCl	800	—	3
Au	AuCl	550	—	2

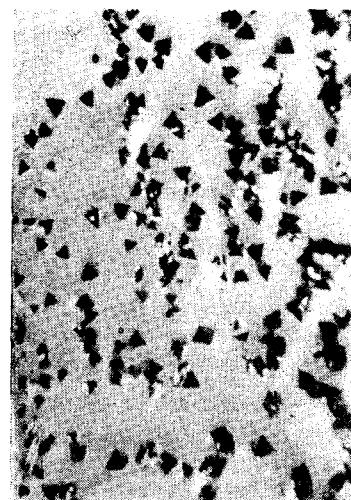


FIG. 4. Large forms of copper crystals from high-temperature (850°C) reduction (Brenner) ( $\times 26$ ).

tal growth in this method only below certain values.

Brenner made the most thorough study of the conditions for producing copper whiskers. The rate of halide reduction increases with temperature. CuI at 850°C is reduced by hydrogen in minutes, while at 430°C a few days are required. The reduction temperature strongly affect whisker shapes and sizes. Smooth thin whiskers result from reduction at 430 — 700°C (Fig. 3), whereas at higher temperatures lamellar structures appear in addition. Above 850°C whiskers are not produced; well-developed large copper crystals are formed instead (Fig. 4). The whiskers most frequently have a hexagonal cross section, and when the time of CuI reduction is prolonged at a temperature below 600°C the whiskers tend to expand (Fig. 5). Observation of the growth of bent crystals showed that in most metals growth usually takes place at the tip. Silver is an exception.

Webb and Riebling<sup>7</sup> investigated the kinetics



FIG. 5. Hexagonal cross section of whisker ( $\times 60$ ).

of the reduction reaction during this mode of whisker growth. They grew crystals of Ag, Cu, Fe, Co, Ni and Mn at different temperatures in the reaction zone and with different rates of hydrogen flow. The activity of the metal could be

computed from measurements of the flow of hydrogen and of the halide gas and from thermodynamic data on vapor pressures and the equilibrium constant of the reaction.

b) Growth by deposition from vapor. Volmer and Estermann<sup>8</sup> showed that very thin layers of mercury could be formed on a glass surface by condensing the mercury vapor at  $-63.5^{\circ}\text{C}$ . The condensation of metallic vapors has been used to produce crystals of mercury,<sup>9</sup> zinc, cadmium, silver and cadmium sulfide,<sup>10,11</sup>

Figure 6 shows the vessel in which mercury crystals were grown by Sears,<sup>9</sup> who noted that at the mercury vapor temperature  $T = 25^{\circ}\text{C}$  thin mercury platelets grew, but that at  $T = -50^{\circ}\text{C}$  and lower whiskers usually grew.

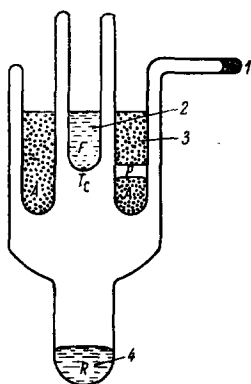


FIG. 6. Vessel for growing mercury whiskers (Sears): 1) soldered end; 2) liquid and solid  $\text{CHCl}_3$ ; 3) acetone baths ( $T_v$ ); 4) mercury ( $T_c$ ).

Whiskers of the remaining metals grew in a certain temperature gradient produced by two furnaces (Fig. 7).<sup>11</sup> The vessel used for growing

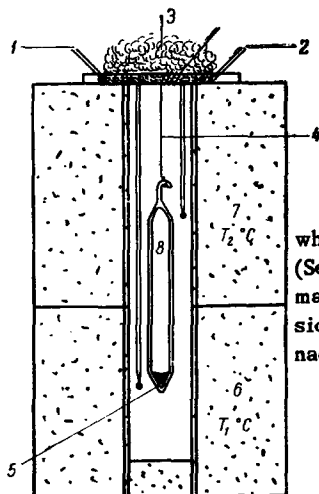


FIG. 7. Apparatus for producing whiskers by vapor condensation (Sears): 1, 2) thermocouples; 3) thermal insulation; 4) wire for suspension of vessel; 5) crystal; 6, 7) furnaces; 8) condensation vessel.

must be thoroughly degassed in advance and the metal must be at least triply distilled. A Pyrex vessel was used to grow cadmium and zinc whiskers, while a quartz vessel was used for silver and cadmium sulfide. After all of the metal is distilled at one end of the vessel, the latter is placed in the

temperature-gradient furnaces with the metal in the hotter region.

The degree of metal vapor supersaturation which is most favorable for crystal growth at a given temperature gradient was found to vary with the metal. The temperatures and supersaturations for whisker growth are given in Table II, from which it appears that the required degree of supersaturation is not very high. Bulk crystals grow at large supersaturation.

TABLE II

Metal	$T_1, ^{\circ}\text{C}$	$T_2, ^{\circ}\text{C}$	Degree of supersaturation, $P/P_0$
Zn	375	350	3
Cd	330	250	20
Ag	940	850	10
CdS	810	800	$\sim 2$

The influence of an inert gas (helium) on the growth of zinc whiskers was studied in reference 10. Growth took place at pressures 10 – 600 mm Hg and temperature gradients from 4 to 12 deg/cm. During growth lasting about 15 hours the largest quantity and greatest length of whiskers were produced at temperatures from the melting point to  $80^{\circ}\text{C}$  below. At pressures below 10 mm only large crystals grow, as a rule; with increasing pressure the crystal diameter was reduced, to about  $0.1\mu$  at 600 mm. The presence of the inert gas promotes whisker growth; lengths up to 17 mm were attained in the gas, whereas in a vacuum<sup>11</sup> the length was about 1 mm. With increasing purity of the inert gas and of the growth vessel the whiskers become longer and smoother and have a cleaner surface. Silver and cadmium whiskers, in addition to those of zinc, were grown from their gaseous state. It must be noted that the production of whiskers by vapor condensation is the best method with respect to the uniformity and reproducibility of the results as well as because of the small quantity of impurities which might otherwise seriously affect their properties. Thus in copper whiskers grown from  $\text{CuI}$  the relative impurity content was determined chemically to be  $3 \times 10^{-5}$ ;<sup>41</sup> a similar result was indicated by preliminary measurements of residual resistance in whiskers of Cu, Ag, Zn and Cd.<sup>42</sup>

c) Other techniques for producing metal whiskers. The growth of whiskers on cadmium-plated steel plates was recorded by Cobb in 1946.<sup>12</sup> A detailed investigation was later made of whisker growth on metal plates and on thin layers produced by electroplating or other techniques under differ-

ent (not very high) temperature and humidity conditions.<sup>13</sup> Whiskers were grown on layers of Cd, Zn, and Sn under natural conditions for two years. A slight temperature rise or the reduction of electroplating thickness (from 10 to 1  $\mu$ ) accelerated the growth; for example, whiskers grew on tin-plated steel at 70°C in two weeks although 3–6 months are usually required. Similar results were not obtained with metal plates; examination under an electron microscope<sup>47</sup> showed that in the latter case a crystal grows at its base (Fig. 8), whereas a crystal produced from the gaseous phase grows at its tip (Fig. 9). The photographs of a spontaneously growing whisker (in Fig. 8) which were taken over a period of two weeks,



FIG. 8. Successive stages in the growth of a tin whisker at its base. The configuration of the tip does not change during growth (Koonce and Arnold) ( $\times 12750$ ).

show that the tip remains unchanged, whereas Fig. 9, which illustrates growth from the gaseous phase, shows the changes at the tip.

Figure 10 shows Sn whiskers growing on a steel plate thinly coated with tin.<sup>13</sup> The rate of growth is evidently accelerated when residual stresses are present in the substrate or plating; this is confirmed by the fact that the growth rate of whiskers on tin-plated steel is sharply increased (by a factor of about  $10^4$ ) under compression<sup>14,15</sup> or rapidly repeated flexing.<sup>16</sup> No growth is observed during a certain time interval after the stress is applied; growth then begins at an approximately constant rate (proportional to the stress) up to a certain length (usually 1 or 2 mm), after which growth is slowed down or ceases. Growth occurs at certain fixed points ("active growth regions"); after the whiskers are removed growth begins again at the same points, and this can be repeated up to 10 times. After this secondary growth is terminated due to "exhaustion" of the active regions, grinding of the surface layer to a depth of a few dozen microns restimulates growth. Higher temperatures (up to 190°C) result in longer crystals of large diameter. Growth terminates at still higher temperatures. Alloys of Sn, Pb, Zn, and Cd with less plastic metals are just as efficient as electroplatings in growing

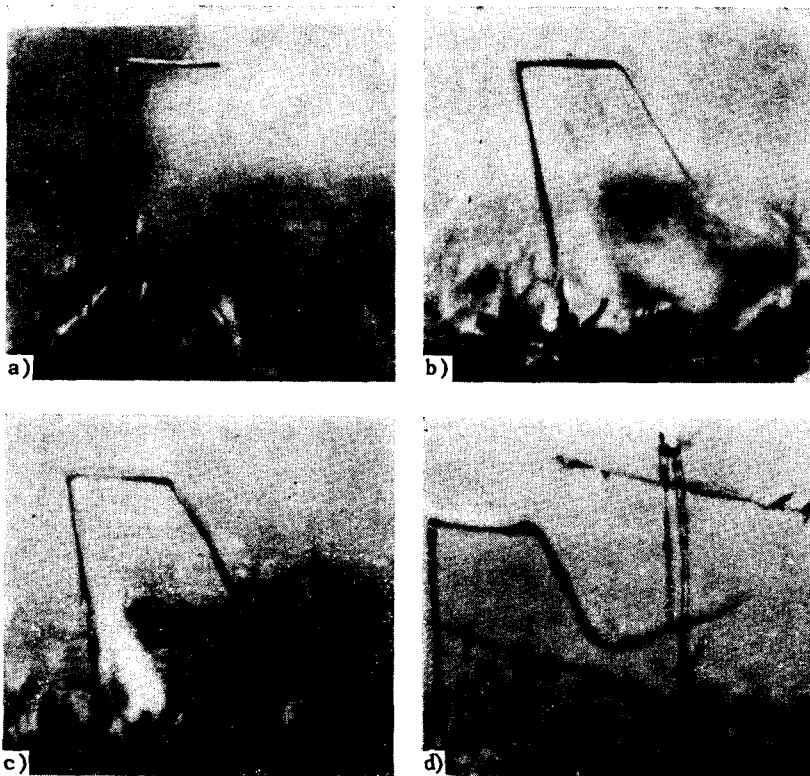


FIG. 9. Successive stages in the growth of a bent copper whisker produced by the reduction process.

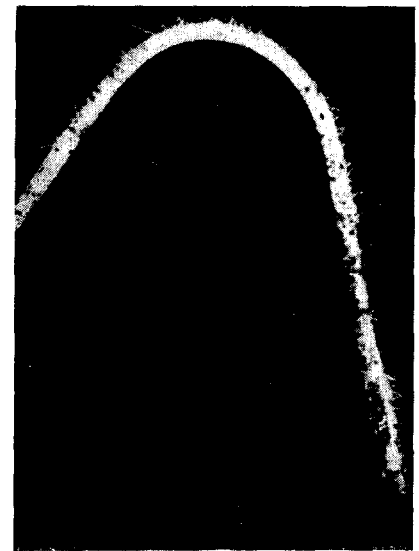


FIG. 10. Tin whiskers growing on a tin-coated steel plate.

whiskers under stress or spontaneously. For example, the compression of alloys of Sn with Al at room temperature and of Pb with Cu at 200°C results in whisker growth within 24 hours.<sup>15</sup> Whiskers were observed on most metals at higher temperatures (200–700°C) without external stress.<sup>17</sup> However, the latter whiskers were so short (1–2 μ) that their growth could only be observed with an electron microscope, and it still remains uncertain whether the observed crystals were oxides or not.

Whisker growth through the electrolysis of metallic salts usually occurs in the presence of various organic impurities. The growing of silver and copper whiskers in this manner has been reported in references 18, 19, 20, and 21. The parameters of silver whisker growth were investigated especially thoroughly by Gorbunov and Zhukov,<sup>19</sup> who observed how different concentrations of oleic acid, gelatin, and other organic materials affected the growth rate and limiting values of the currents required to initiate filamentary crystallization (cessation of growth due to the absence of silver ions) and to terminate it (transformation into dendrites). The transformation of an ordinary crystal into a whisker through electro-deposition is evidently accounted for by the difference in the number of impurity molecules adsorbed on different faces. After growth begins the few adsorbed molecules on a growing face will be covered by deposited silver atoms, whereas the denser adsorbed layer of molecules on lateral (non-growing) faces will prevent crystal growth in this direction.

The computation of growth rate and current limits on this model in reference 21 agrees with the experimental data of reference 19. However, the presence of impurities results in different properties (structure, mechanical properties and resistance) for whiskers grown in this manner compared with those grown through the reduction of halide salts, for example.<sup>21</sup>

Microcrystals with large length-to-diameter ratios have recently been produced by the anodic dissolution technique which is widely known in alloy metallurgy, and which is used with electrolytes under conditions that insure dissolving of the alloy matrix and passivation of crystals of the desired phase. Crystals of iron carbide, chromium nitride, chromium oxide, and chromium have been produced in this manner.<sup>22</sup> The production of sufficiently long crystals requires special preliminary heat treatment or selection of alloys that would yield the desired crystal sizes upon crystallization. For example, iron carbide crystals were produced

from carbon steel containing 1.3% carbon after annealing at 1120°C for 170 hours. Chromium crystals were produced from a eutectic copper-chromium alloy. The crystals obtained in these instances had diameters from 1 to 3 μ and lengths of 1 to 2 mm.

d) Production of nonmetallic whiskers. Numerous examples can be given of whisker production from salts through chemical reactions, crystallization and precipitation; some of these have been described by Buckley.<sup>23</sup>

Ionic crystals can be grown by crystallization through a porous wall; this technique was first proposed by Gyulai<sup>24</sup> for growing NaCl crystals. Porcelain, tiles etc. were used as the porous medium; in a few weeks crystals grew up to a length of 10–13 mm with diameters from 0.5 to 10 μ.

A simplification of this technique has recently been proposed.<sup>25</sup> NaCl, KCl, and KBr crystals were grown in a small bag of thin cellophane containing a slightly undersaturated solution. In a few days crystals had grown on the outside of the bag up to 10 mm in length with diameters from 1 to 10 μ. This procedure can evidently be used for the crystal growth of many highly soluble substances.

Sears<sup>26</sup> has observed the growth of LiF whiskers up to 2 mm from a supersaturated LiF solution containing a small concentration of FeF<sub>3</sub>, on the surface of freshly cleaved and etched LiF crystals.

Kato<sup>27</sup> has reported the growth of whiskers on large NaClO<sub>3</sub> single crystals from a saturated solution when the still wet parent crystal was placed in a desiccator. Growth occurred by deposition at the tip but only at temperatures from 10 to 60°C.

Gordon<sup>28</sup> grew whiskers of organic substances (hydroquinone, quinone, and resorcinol) by evaporating drops of an aqueous solution on a microscope slide. Crystallization began with the appearance of very thin filaments from 0.1 to 1.0 μ in diameter; these filaments then began to thicken, showing visible degrees of growth. In 1957 Bacon described a technique for growing graphite whiskers,<sup>29</sup> which was subsequently improved.<sup>30</sup> Growth took place very rapidly in a high-pressure arc, resulting in crystals as long as 30 mm with diameters ranging from 1 to 10 μ.

## 2. Shape, Structure and Orientation of Whiskers

The shapes, sizes and surface states of crystals vary greatly, depending on the technique and conditions of growth. As a rule visibly smooth and straight crystals are selected for the study of

their properties. When grown by the reduction of metal halide salts<sup>6</sup> or vapor condensation<sup>10</sup> under optimum conditions the majority of the whiskers are smooth and straight with diameters 1–20  $\mu$ . Figure 11 is the silhouette of a copper

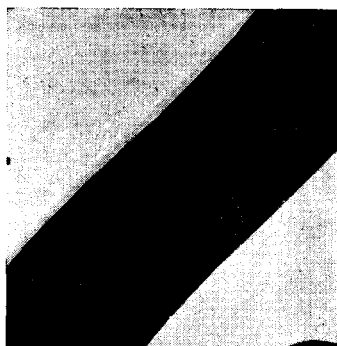


FIG. 11. Surface of a whisker enlarged 40 000 times (Brenner).

crystal grown from CuI magnified 40,000 times, which would have revealed roughness of the order of 25 Å. The fact that the surfaces of whiskers may be atomically smooth is indicated qualitatively by experiments on the electrodeposition of copper on copper whiskers from a  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$  solution.<sup>44</sup> While ordinary copper crystals require an excess voltage of 5–15  $\mu\text{V}$  for uniform copper deposition, thin crystals of about 3  $\mu$  diameter require excess voltages above 100  $\mu\text{V}$  and deposition occurs only at separate surface sites, forming "lumps". In addition to relatively straight whiskers much more complicated shapes are observed such as spirals, twists, beads, tangles, platelets etc., a few of which are shown in Figs. 12–14.

Smooth straight crystals are almost never grown from a thin layer of tin under tension.<sup>14</sup> A detailed electron-microscopic study of the shapes and surface structure of such crystals using carbon replicas<sup>31</sup> revealed that crystals with very little surface structure or almost none

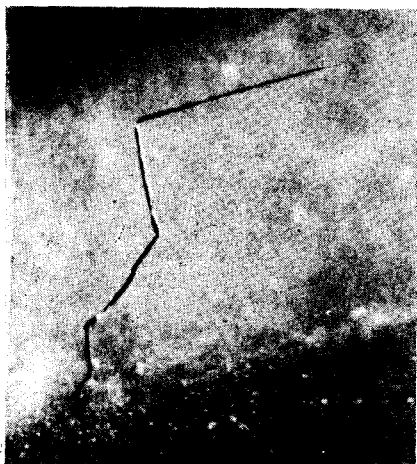


FIG. 12. Bent copper whisker (Brenner) ( $\times 13.3$ ).

FIG. 13. Silver whisker produced by reduction of a mixture of AgCl and AgI at 660°C (Brenner) ( $\times 60$ ).

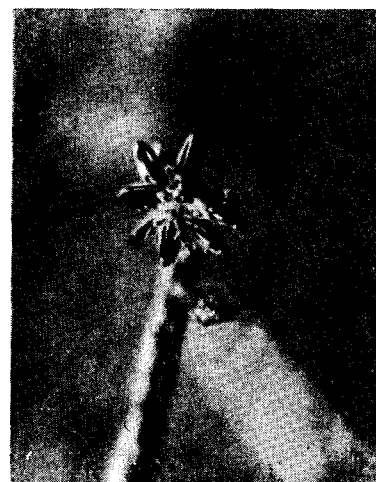


FIG. 14. Copper whisker (Brenner). Reduction at 610°C ( $\times 3500$ ).



and crystals with a regular constant cross section are seldom encountered; cylindrical crystals with diameters under 0.25  $\mu$  are more frequently formed. The given growth conditions most frequently produced bands of about 1  $\mu$  width and thickness of the order 1000 Å (Fig. 15) with easily visible surface structure resembling a bundle of thin crystals. Stellate shapes were frequently observed or complicated cross sections with well developed ridges (Fig. 16).

An electron-microscopic study<sup>32</sup> of ionic whiskers (NaCl) revealed round crystals with irregular cross sections and no crystal faces in the case of small diameters (under 0.5 or 1  $\mu$ ). Further growth occurs through thickening in layers, and crystal face structure begins with two parallel (100) planes while other surfaces remain irregular.

X-ray and electron-diffraction studies of whiskers show that the great majority of them, even when they contain fractures, kinks, and spirals, are single crystals.

No final conclusions have yet been reached regarding the departure of whiskers from ideal perfection, one cause of which following from the theory of their growth (Ch. II) may be the presence of



FIG. 15

FIG. 15. Tin whiskers in the shape of bands  $0.1\ \mu$  thick ( $\times 9000$ ).

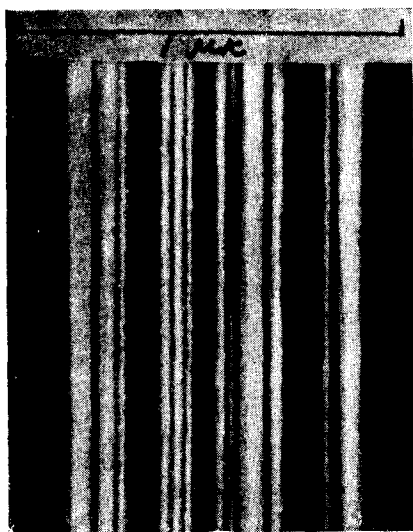


FIG. 16

FIG. 16. Tin whisker with well developed ridges.

a screw dislocation with its Burgers vector parallel to the crystal axis. Eshelby<sup>33,34</sup> showed that in this case the lattice must be twisted about its axis through an angle which for small whisker diameters (of the order  $1\ \mu$ ) must be large enough to permit measurement by means of a Weissenberg goniometer<sup>35</sup> or from the tilt of equatorial Laue spots.<sup>36</sup> The Burgers vector in the axial direction can be computed from the angle of twist. This technique was used to investigate crystals of Sn,<sup>35,37</sup> Zn, Cu, Ni, Fe, Mn, Pd, Ag,  $\text{Al}_2\text{O}_3$ ,<sup>36</sup> and  $\text{Hg}^{78}$ , of which only the last two revealed axial screw dislocations while the other exhibited no perceptible axial twist. Ag, Pd, and Cu crystals when found in the form of twisted prisms and spirals exhibited twisting corresponding to screw dislocations with Burgers vectors equal to an integral multiple of the lattice constant in the  $\langle 0001 \rangle$  growth direction.

Some techniques of whisker growth promote structural imperfections. Thus it was shown in reference 38 that tin whiskers appearing in an Sn-Zn alloy after a few months are not perfectly ideal although more nearly perfect than ordinary single crystals. X-ray reflection intensities gave a structural factor, corrected for extinction, which was comparable with the computed value. Crystals with diameters of  $5.5$  and  $10\ \mu$  were found to contain blocks of  $1.5$  and  $2.7\ \mu$  respectively, which agrees with electron-microscopic results.<sup>31</sup> Laue spots of silver crystals produced by electrodeposition<sup>21</sup> were very diffuse, showing disorientation of a few degrees. On the other hand, Kikuchi lines were found in electron diffraction patterns of  $\text{NaCl}$ <sup>32</sup>

indicating a possibility of perfection.

As we know, crystal dislocations may be revealed by etch pits located where dislocations emerge at the crystal surface.<sup>39</sup> An investigation<sup>40</sup> of iron whiskers with diameters greater than  $10\ \mu$  showed that etch pits are usually not found on lateral  $\{100\}$  faces after growth. Pits appear after plastic deformation begins and increase in number after the deformation but independently of the etching time. The orientation of whiskers is usually determined from oscillating-crystal x-ray diffraction patterns or by means of a Weissenberg goniometer.<sup>43</sup> Crystal axes are usually parallel to simple crystallographic directions, but their orientation may depend on the growth technique. The axes of spontaneously growing whiskers (Zn, Cd, Sn, and Pb)<sup>43</sup> coincide with slip directions, with the exception of one tin orientation. Growth from vapor or by means of chemical reduction frequently results in other directions in addition to the slip direction.

Table III lists data on whiskers of a number of substances and their orientations.

## II. ON THE MECHANISM OF WHISKER GROWTH

Although the growth of crystals containing screw dislocations has been analyzed in great detail<sup>45</sup> and although we have very extensive experimental information concerning the growth of whiskers the quantitative theory of whisker growth is still far from complete.

In accounting for the growth of mercury whiskers<sup>9</sup> Sears used Franks' ideas about the growth of real crystals by the deposition of matter around the emergence sites of screw dislocations on the faces of growing crystals instead of deposition around two-dimensional nucleation centers according to classical theories of crystal growth. He postulated first, that the nucleus of a whisker contains a screw dislocation with its axis parallel to a definite crystallographic direction and, secondly, that the supersaturation of the vapor in this type of growth is lower than the supersaturation required for two-dimensional nucleation on lateral crystal faces, which are in consequence atomically smooth.

The rate  $W$  of mass accretion of atoms from the gaseous phase on a growing crystal tip of radius  $r$  is given by

$$W = \pi P r^2 \left( \frac{m}{2\pi kT} \right)^{3/2} \quad (1)$$

Here  $P$  is the vapor pressure above the growing crystal and  $m$  is the atomic weight.

From the experimentally observed bending of crystals as a result of Brownian motion Sears<sup>9</sup> estimated that the lower limit for the radius of

TABLE III

No.	Material	Characteristics of Growth		Mechanical properties				References
		Growth technique	Growth direction	Type of deformation	$\epsilon_{max}$ , %	$\sigma_{max}$ , kg/mm <sup>2</sup>	d, microns	
1	Sn	Spontaneous	[100], [110], [111]	Bending	1.0—2.0	—	1.8	13, 57, 43
2	Pb	"	[110]	—	—	—	—	43
3	Zn	"	[11 $\bar{2}$ 0]	—	—	—	—	13, 43
4	Zn	Vapor deposition	[11 $\bar{2}$ 3]	Elongation	1.0	50	1.0÷5.6	11, 58
5	Cd	Spontaneous	[11 $\bar{2}$ 0]	—	—	—	—	13, 43
6	Cd	Vapor deposition	[11 $\bar{2}$ 3]	Elongation	1.0	52	3.0	58, 11
7	Cu	Reduction of halide	[100], [110], [111]	"	2.8	300	1.25	6, 55
8	Ag	" "	[100], [110]	"	4.0	176	3.8	6, 55
9	Fe	" "	[100], [110], [111]	"	4.9	1340	1.6	6, 55
10	Ni	" "	—	"	1.8	—	—	6
11	Co	" "	—	—	—	—	—	6
12	Pt	" "	—	—	—	—	—	6
13	Au	" "	—	—	—	—	—	6
14	Hg	Vapor deposition	[100]	In electric field gradient	—	100	0.01	9, 59
15	Mn	Reduction of halide	—	Bending	1.5	310*	1.7	22
16	Cr	Precipitation from solid phase	—	"	3.8	800*	1.6	22
17	Si	Reduction of halide	[111]	Elongation	2.0	390	—	60
18	Si	Vapor deposition	[111]	Bending	2.6	500	16÷28	54
19	Ge	Reduction of halide	[111], [11 $\bar{2}$ ]	"	—	30	20	54, 43
20	ZnO	Synthesis of zinc, oxygen and hydrogen	{0001}	"	1.5	150*	21	51
21	Zn	Vapor deposition	{0001}	"	1.5	105*	up to 50	61
22	CdS	" "	—	"	2.4	—	—	11, 65
23	Mn <sub>3</sub> Si <sub>3</sub>	Reduction of halide	—	"	2.7	—	—	22
24	Si <sub>3</sub> N <sub>4</sub>	Nitriding of silicon	—	"	4.0	320*	2.8	22
25	Al <sub>2</sub> O <sub>3</sub>	Oxidation in gaseous phase	{0001}	"	2.3	1200*	3	22
26	Cr <sub>3</sub> O <sub>4</sub>	Precipitation from solid phase	—	"	0.3	67**)	4.1	22
27	Cr <sub>2</sub> N	" " " "	—	"	5.8	—	2.2	22
28	Fe <sub>3</sub> C	" " " "	—	"	4.1	800*	1.9	22
29	C	In high-pressure arc	—	—	2.0	2100	5.0	30
30	NaCl	Evaporation through porous material	[100], [110]	Elongation	2.3*)	110	1.0	24, 32
31	KCl	" "	[110]	—	—	—	—	32
32	LiF	From supersaturated solution	[100]	Bending	1.2	—	4.5	26
33	Hydroquinone	" " "	—	"	6.0÷8.0	—	up to 5	28

Remarks: \*Estimated from elastic constants of ordinary single crystals.  
 \*\*Not the maximum; still under investigation.<sup>22</sup>

a whisker which is capable of stable growth is given by

$$r_{min} = 0.01 \mu.$$

It is assumed that each atom deposited on the tip of the growing whisker where a screw dislocation emerges is attached to a solid mercury lattice and that the crystal radius remains constant. Then, if

$\rho$  is the mercury density and  $\dot{l}$  is the linear growth rate of the crystal tip in its axial direction, we have

$$W = \pi r^2 \rho \dot{l} \tag{2}$$

and

$$\dot{l} = \frac{P}{\rho} \left( \frac{m}{2\pi kT} \right)^{1/2} \tag{3}$$



At  $-30^\circ\text{C}$  with a mercury pressure of  $7 \times 10^{-6}$  mm this formula gives  $\bar{l}$  equal to  $3 \times 10^{-8}$  cm/sec. At the given temperature and pressure an experiment on mercury whisker growth yielded  $\bar{l}_{\text{exp}} = 1.5 \times 10^{-4}$  cm/sec, which is  $5 \times 10^3$  times greater than the computed rate. Sears accounts for the discrepancy by assuming that atoms which strike the lateral surface of the growing crystal or the glass diffuse along the surface to the tip of the growing crystal, where they join the lattice. Let us assume that growth is aided by atoms that strike the lateral surface at a distance from the growing end not greater than  $\lambda_x$ , which we shall now estimate. It follows from the foregoing hypothesis that

$$2\pi r\lambda_x + \pi r^2 = 5 \cdot 10^3 \pi r^2 \quad (4)$$

or (since  $\lambda_x \gg r$ )  $\lambda_x = 2500r$ ; assuming  $r = 0.01 \mu$ , we obtain  $\lambda_x = 0.025$  mm. With this altered concept of the growth mechanism the expression for the axial rate of growth now becomes

$$\bar{l} = \frac{2\lambda_x}{r} \frac{P}{\rho} \left( \frac{m}{2\pi kT} \right)^{1/2} \quad (5)$$

The value of  $\lambda_x$  as a diffusion length can be obtained theoretically according to reference 45 from the formula

$$\lambda_x = a \exp \left\{ \frac{w - u}{2kT} \right\}, \quad (6)$$

where  $a$  is the atomic separation,  $w$  is the energy of evaporation from the surface,  $u$  is the activation energy of a transition to an adjacent equilibrium position on the surface. Using the results given in reference 46, we may assume  $u = 10\%w$  and

$$\lambda_x = a \exp \left\{ \frac{0.9w}{2kT} \right\}, \quad (7)$$

and the required result  $\lambda_x = 2.5 \times 10^{-3}$  cm is obtained by using very reasonable values for the other quantities in (7).

Sears also showed<sup>9</sup> that evaporation from the surface of a growing crystal can be neglected because of its small effect on the growth rate. An attempt to calculate the axial growth rate from classical ideas of two-dimensional nucleation results in a value which is different from experiment by twenty orders of magnitude.

To account for the radial growth of a whisker which results in its thickening, since growth in the direction of the lateral surface is excluded, Sears suggests that new layers may be nucleated at the base and grow in the axial direction, thus thickening the crystal. No quantitative estimates of radial growth are available.

When  $\lambda_x \approx r$ , which occurs in the growth of zinc crystals<sup>10</sup> in an inert gas, and when  $r \approx 1 \mu$  instead of (5) for the axial rate of growth we obtain

$$\bar{l} = \left( 1 + \frac{\lambda_x}{r} \right) \left( \frac{P - P_0}{\rho} \right) \left( \frac{m}{2\pi kT} \right)^{1/2}, \quad (8)$$

where  $P_0$  is the equilibrium vapor pressure of the condensed phase. The assumption  $\lambda_x \approx r$  will make the rate of growth 300 times smaller than the experimental rate. Taking into account the diffusion of the condensing vapor through the inert gas and the fact that the mean free path cannot be greater than the radius  $R_0$  of the tube, we arrive at an upper limit for the possible rate of growth:

$$\bar{l}_{\text{max}} = \frac{4.1(P - P_0)mR_0D}{r^2\rho RT}, \quad (9)$$

where  $D$  is the diffusion coefficient of the vapor in the inert gas. Since in these experiments Zn whiskers grew without overgrowths, it may be postulated that the supersaturation was not greater than that required for two-dimensional nucleation, so that  $P - P_0$  can be estimated. It was shown previously in reference 11 that  $P/P_0 \approx 5$  for two-dimensional nucleation of Zn; at  $T = 680^\circ\text{K}$ ,  $P = 1 \times 10^{-1}$  mm Hg; the remaining quantities are:  $r = 10^{-4}$  cm,  $R_0 = 1$  cm,  $D = 0.1$  cm/sec<sup>2</sup>. From (9) we thus obtain

$$\bar{l}_{\text{max}} \approx 3 \text{ cm/sec}$$

From (5) we obtain

$$\bar{l}_{\text{max}} \approx 10^{-3} \text{ cm/sec}$$

These estimates provide a qualitative explanation of the high rate of whisker growth that is observed experimentally.

The foregoing calculations were based on the assumption that the crystal grows along its axis, inheriting its screw dislocation from a devitrified crystal grain in the Pyrex surface.

It is sometimes suggested that a crystal can obtain the screw dislocation required for axial growth from the growth of an impurity particle. This mechanism for the generation of a screw dislocation in the growth of foreign particles is described in reference 49.

It is not clear from the above why, with the relatively large supersaturation used experimentally for growing whiskers, ordinary smooth crystal growth does not take place by the Franks spiral mechanism despite the fact that the surface of the containing vessel is assumed to possess a sufficient number of the emerging screw dislocations which are required for growth by the Franks mech-

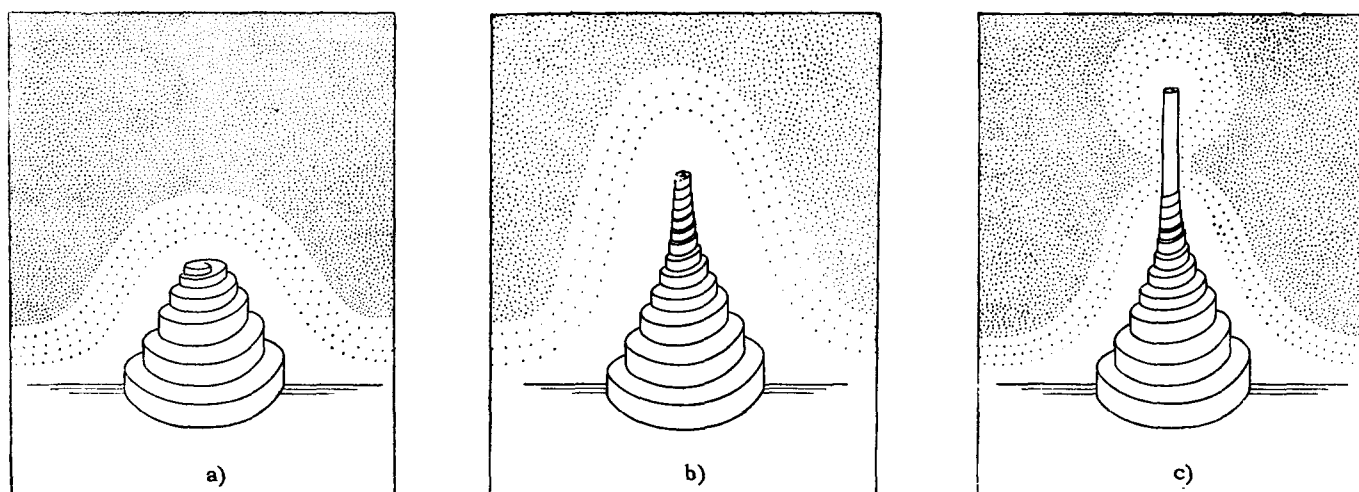


FIG. 17. Successive stages of a growth cone (Sears and Brenner).

anism. Sears and Brenner<sup>50</sup> have attempted to supply an answer by proposing a third growth mechanism which takes into account the conditions for diffusion and heat transfer in the gaseous phase. It is also postulated that any real surface has screw dislocations and therefore serves as a deposition site under low supersaturation.

When a face of such an imperfect crystal is immersed in its own sufficiently saturated vapor, deposition will take place on the steps of screw dislocations and the entire surface will grow smoothly by the Franks mechanism. The concentration and temperature gradients near the growing surface will vary. Individual spirals which are sufficiently distant from their nearest neighbors will produce growth cones. As the apex of a cone rises above a smoothly growing surface the conditions of vapor atom diffusion to the former are changed. The tip begins to deprive the steps below it of their share of the diffusing atoms, and grows at an increasing rate with the departure from linear diffusion and approach to spherical diffusion. The process is self-accelerating. Figure 17 shows three successive stages of whisker formation from the apex of a cone; the diffusion path to the tip is evidently shorter than the distance between steps.

After the tip is greatly elongated away from the growing surface and has reached a stage of constant cross section it will grow at a constant rate. At the same time the crystal will thicken as layers grow from its base, which will thus push upward and be converted from a cone to a cylinder. The maximum whisker cross section will be a function of the supersaturation and of the rates of gaseous and surface diffusion.

The initial critical supersaturation  $\sigma$  required for the growth of a whisker from a screw disloca-

tion depends on its minimum distance  $R$  from neighboring dislocations. As  $R$  decreases the critical supersaturation required for whisker growth at the same site increases. It is observed experimentally that higher initial supersaturation results in more closely placed crystals, although there is an upper limit of supersaturation under which whiskers can grow. Screw dislocation which are too closely placed or under too high supersaturation cannot produce growth cones and result in continuous growth of the entire surface.

It has been stated in Ch. I that the necessary presence, according to Sears, of one axial screw dislocation has not received final experimental confirmation, except for the growth of  $\text{Al}_2\text{O}_3$  and mercury whiskers. The negative result of direct x-ray investigations can be regarded either as refuting Sears hypothesis or a result of the fact that during the growth process the dislocation has emerged on the crystal surface. It was shown by Hirth<sup>48</sup> that in thin whiskers with smaller than critical radius an axial screw dislocation can emerge on the surface as a result of thermal activation; this is also a possible mechanism for the termination of crystal growth. However, mechanical tests (Ch. II) indicate that a crystal may lack even a single dislocation.

Sears<sup>3</sup> second hypothesis is evidently confirmed by experimental data on the degree of supersaturation for the growth of Hg, Zn, Cd, Ag, and CdS crystal from their vapors<sup>41</sup> (Table II). In any event, the mechanism of whisker growth by deposition from a vapor is not entirely clear and internally consistent.

The theory of whisker growth by other means has been developed even less fully than the mechanism of growth from a vapor. Growth through the reduction of metal halides is superficially similar

to deposition from a vapor in a gaseous medium if it is assumed that after hydrogen reduction of the halide vapor the resulting metal vapor diffuses through the gaseous phase to the surface of the growing crystal. Brenner<sup>6</sup> showed that a very high supersaturation of  $10^4$  is required for this process. However, a study of the reduction kinetics and a determination of the activity in these reactions (equivalent to the supersaturation for reaction in a gaseous mixture) showed that growth obviously does not occur through direct metal condensation. The low metal vapor pressure, which is below  $10^{-7}$  atmos, shows that reduction does not take place in the gaseous phase, because such a relatively small quantity of metal cannot account for the observed growth rate. Instead, the metal halide vapor, under much higher pressure (from  $10^{-5}$  to  $10^{-1}$  atmos), diffuses to the crystal surface and is reduced either while diffusing along the lateral surface to the growth site at the crystal tip or after diffusion to the tip. The low activity shows that growth occurs under much lower supersaturation of the metal vapor. This may also account for the smooth surface facets of whiskers.

An essentially different mechanism evidently accounts for spontaneous growth and growth under stress. Unlike the preceding forms, growth now occurs from the base. To account for all experimental facts Franks<sup>15</sup> suggested that growth occurs on a free metal surface under external or internal stress when the stress is higher than that required for free extrusion but that general "extrusion" is inhibited (as in SnAl alloys, for example), and the temperature is high enough to insure diffusion. For example, the self-diffusion coefficient of tin is high enough at room temperature (about  $10^{-12}$  cm<sup>2</sup>/sec), while lead requires about 200°C to reach the same value. Dislocation loops reaching the surface through slip raise the surface by steps which are multiples of the Burgers vector; whisker growth takes place through diffusion to these nucleation centers. Several mechanisms have been suggested for the formation of dislocation loops and their motion to the surface,<sup>15,51,52</sup> but we at present have no experimental basis for selecting the most probable of these.

The more highly diversified growth of nonmetallic whiskers has been investigated much less than that of metallic whiskers. Therefore the theory of their growth is almost entirely undeveloped and it has still not been established whether growth occurs at the tip, as Gyulai<sup>24</sup> and Kato<sup>27</sup> believe, or at the base as observed by Amelinckx.<sup>25</sup>

Sears<sup>53</sup> used an analysis of Kato's<sup>27</sup> data as a basis for a theory of NaClO<sub>3</sub> whisker growth. He suggested that an aqueous solution of the material produces a hydrodynamic flow in the surface film of the solution on the crystal surface, in the direction of the tip. Evaporation of water from the tip raises the concentration and produces a concentration gradient, which in turn induces a surface tension gradient that is the driving force of the flow in the surface film. Matter is deposited on the tip by a dislocation mechanism.

The growth of ionic crystals through a porous wall can also be accounted for qualitatively by deposition on the base of a nucleating crystal (on the outer surface of the porous wall) containing an axial screw dislocation.<sup>25</sup> The rate of growth is determined by the supply and supersaturation conditions in the capillary layer between the nucleus and porous wall.

Thus the theories of whisker growth contain a number of inconsistencies, so that we can neither regard these theories as well developed nor consider their fundamental hypotheses confirmed.

### III. MECHANICAL PROPERTIES OF WHISKERS

#### 1. Testing Methods

The mechanical properties of whiskers are usually tested by bending or tensile straining. The strains can be measured more accurately in bending than in stretching tests. The maximum bending strain is the ratio of the sample radius to the bending radius; the latter is easily determined from the formula  $R = L/\theta$ , where  $L$  is the length of the bent part of the crystal and  $\theta$  is the bending angle. However, in bend tests the stresses are complicated and are not uniformly distributed with respect to either the cross section or length of the sample.

Figure 18 is a schematic drawing of the apparatus

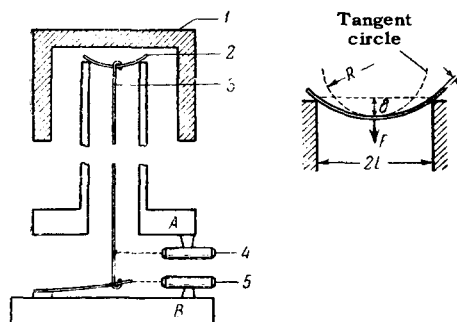


FIG. 18. Apparatus for bend tests of whiskers (Pearson, Read and Feldman): 1) furnace; 2) whisker; 3) quartz hook; 4) microscope for measuring crystal deflection; 5) microscope for measuring deflection of spring; A - quartz holder; B - base.

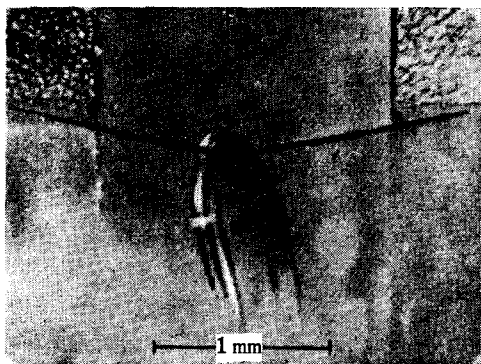


FIG. 19. Plastic bending of silicon whisker. The quartz hook is seen (Pearson, Read, and Feldman).

ratus for bend tests of whiskers.<sup>54</sup> The sample is mounted in a quartz holder A. The stress is transmitted to the middle of the crystal through a hook made of a quartz filament with 150 – 250  $\mu$  diameter (Fig. 19). The lower end of the hook is held by a calibrated spring attached to the base B. The holder A can move with respect to the base B. Two microscopes are used to observe the displacement of the quartz hook (strain variation) and the displacement of the spring (stress variation).

Elastic strains and stresses are computed from the formulas  $\epsilon = \frac{\delta}{l^3/3r}$  and  $\sigma = \frac{F}{\pi r^3/2l}$ , where  $\delta$  is the deflection,  $F$  is the stress,  $l$  is the distance between the supports and  $r$  is the radius of the sample. From Hook's law  $\sigma = E\epsilon$  and the formula

$$\frac{F}{8} = \frac{3\pi r^4}{2l^3} E$$

the elastic modulus can be computed or, if the modulus is given, the radius of the sample can be computed. Figure 19 shows the plastic bending of a silicon whisker.

Figure 20 represents the apparatus for tensile tests of whiskers.<sup>55</sup> This apparatus was used to test crystals of 1.2 – 15  $\mu$  diameter and 1 – 4 mm length; it consists of an ordinary system of levers,

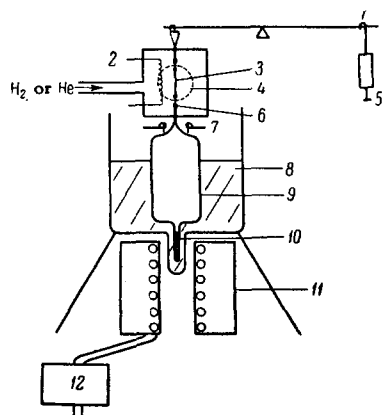


FIG. 20. Diagram of apparatus for tensile tests of whiskers (Brenner): 1) scale; 2) heater; 3) crystal; 4) microscope lens; 5) counter weight; 6) glue; 7) guide; 8) mineral oil; 9) float; 10) magnet; 11) coil; 12) recording instrument.

for which a laboratory microbalance can be used. For more precise and smooth loading a float (in oil) is used, the end of which is drawn into the magnetic field of a coil at a rate varying from 0.2 to 1 mm/min. The test crystal was attached to mounts by means of a special glue.

In bend and tensile tests of silicon whiskers<sup>55</sup> rupture occurred at about the same stress. However, the character of the stressed state can greatly affect the strength; thus tin whiskers growing on electroplating may possess great bending strength but small tensile strength.<sup>56</sup> This may be accounted for by internal spatial defects in such crystals.<sup>38</sup>

In testing the mechanical properties of whiskers experimentally the strain is usually measured, after which the elastic limit is computed from the appropriate modulus. But because of the special nature of whiskers it must be remembered that the normal elastic modulus of ordinary crystals may differ from that of whiskers. However, it will be shown below that in the case of a number of metals the normal elastic moduli for whiskers and ordinary crystals are of the same order of magnitude. We are therefore fully justified in using the moduli for ordinary crystals to estimate the elastic properties of whiskers.

## 2. Comparison of Experimental Deformation Data for Whiskers and Ordinary Crystals

Data are now available for the yield point (tensile strength) of whiskers of many materials. Ordinary single crystals yield below 0.01% while whiskers withstand an elastic deformation of the order of 1 or 2%. Table III contains presently available data on whiskers, including their orientations and elastic properties (maximum stresses and corresponding strains, measured or computed from the elastic moduli of ordinary single crystals). In the table the mechanical properties of some materials pertain to the strongest individual samples. The number and spread of values depend on the growth technique; there is less spread in the case of deposition from vapors. On the whole whiskers can actually only withstand stresses several times smaller than those given in the table but still much greater than for ordinary single crystals; as the diameter is increased up to 25 – 50  $\mu$  the strength decreases and approaches that of ordinary single crystals.

We shall now consider a few experimental investigations in greater detail. Herring and Galt<sup>57</sup> were the first to observe the extraordinary mechanical properties of whiskers. Investigating

TABLE IV

Material	Whiskers			Ordinary crystals		$\frac{\sigma_{\max}}{\sigma_{\text{str}}}$	$\frac{\tau_{\max}}{\tau_{\text{str}}}$
	Diameter, $\mu$	$\sigma_{\max}$ , kg/mm <sup>2</sup>	$\tau_{\max}$ , kg/mm <sup>2</sup>	$t_{\text{cr}}$ , kg/mm <sup>2</sup>	Strength ( $\sigma_{\text{str}}$ ), kg/mm <sup>2</sup>		
Fe	1.60	1340	364	4.5	16—23 <sup>62</sup>	84—57	81
Cu	1.25	300	82	0.10 <sup>62</sup>	12.9—35.0 <sup>62</sup>	23—8.6	820
Ag	3.80	176	72	0.06 <sup>62</sup>	—	—	1200

the bending of tin whiskers with  $1.8\mu$  diameter which had grown spontaneously on a layer of tin,<sup>13</sup> they observed that the crystals are elastic up to deformations of the order 1 or 2%. Plastic deformation in bending begins only with surface deformation or about 2 or 3%. In tensile tests of ordinary tin crystals plastic flow is observed after a deformation of about 0.01%.

Similar high elastic limits are observed in tensile tests of whiskers; an elastic deformation of 1 or 2% was observed in zinc and cadmium whiskers<sup>58</sup> with diameters ranging from 1 to  $10\mu$ . This gave an elastic limit of 28 kg/mm<sup>2</sup> for cadmium, whereas according to Schmid and Boas,<sup>62</sup> the yield point of cadmium single crystals depending on the angle between the slip plane and direction of tensile stress varies in the range 0.099—0.159 kg/mm<sup>2</sup>.

Brenner<sup>55</sup> has made a thorough study of the tensile properties of iron, copper and silver whiskers. Table IV gives the maximum strengths ( $\sigma_{\max}$ ) of more than 70 tested whiskers, calculated from the maximum load preceding rupture and from the microscopically measured areas of the samples.<sup>63</sup> The possible error of  $\sigma_{\max}$  was estimated to be  $\pm 10\%$ .

A study of the crystallographic orientations of the samples together with data on the crystallography of slip permitted an estimate of the maximum tangential stresses ( $\tau_{\max}$ ), which are also given in Table IV. The table also lists the critical tangential stresses and strengths of ordinary single crystals of the same metals taken from reference 62. The tensile strength of whiskers is greater by a factor of 8—80 and the yield point by a factor of 80—1200 than for ordinary crystals.

A recent investigation of bending strength in the case of brittle single crystals of some materials and their compounds,<sup>22</sup> produced by chemical reactions (Mn, Mn<sub>5</sub>Si<sub>3</sub>, Si<sub>3</sub>N<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>) or by precipitation from alloys (Cr, Cr<sub>2</sub>N, iron carbide), showed that the greatest deformation which any of these microcrystals can endure without rupture or plastic deformation may amount to a few percent (Si<sub>3</sub>N<sub>4</sub>:  $\epsilon_{\max} = 4.0\%$ ; Cr<sub>2</sub>N:  $\epsilon_{\max} =$

5.8%; Fe<sub>3</sub>C:  $\epsilon_{\max} = 4.7\%$ ), whereas ordinary single crystals of the same materials experience brittle fracture after very small deformations.\*

Reference 52 reports an extensive investigation of silicon whisker bending as a function of the test temperature and crystal diameter. The maximum stress was 500 kg/mm<sup>2</sup>, with a mean of the order 200 kg/mm<sup>2</sup>, whereas for an ordinary silicon single crystal the breaking point is 35 kg/mm<sup>2</sup>.

The tensile strength of NaCl whiskers was observed<sup>24</sup> to rise steeply with decreasing diameter to 100 kg/mm<sup>2</sup> for a diameter of the order of  $1\mu$ . For LiF whiskers Sears observed elastic deformation up to 1.2% in a bend test and 0.38% in a tensile test.<sup>26</sup>

The highest breaking strength, 2100 kg/mm<sup>2</sup>, was reported by Bacon<sup>30</sup> for graphite whiskers with the sheets of the graphite layer structure parallel to the whisker axis. Gordon<sup>28</sup> observed during the growth of whiskers of certain organic and inorganic compounds (such as hydroquinone) that as thin bent crystals thickened internal stresses arose which sometimes led to rupture, after which the crystal straightened out elastically. From the radius of curvature the deformation was estimated to be of the order 6—8  $\mu$  for crystals 2—4  $\mu$  thick.

### 3. Fracture and Plastic Deformation of Whiskers

Whiskers can fracture in a brittle manner after a certain amount of plastic deformation.<sup>55,24</sup> However, it has been observed that iron whiskers<sup>55</sup> fracture without appreciable preliminary plastic deformation; sudden rupture is accompanied by twisting. A microscopic examination of the fracture site under high magnification sometimes re-

\*Tests of crystals separated from crystallized alloys are of great interest not only because of their special properties but also because the techniques for testing the mechanical properties of whiskers reveal a new procedure for investigating the microcomponents of alloys. This together with microchemical and microdiffraction analyses can furnish much valuable information for metallurgy and the physics of metals.

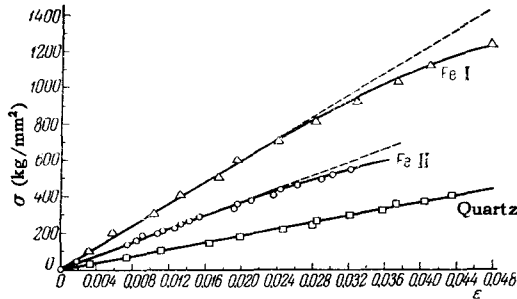


FIG. 21. Stress-strain curves for iron whiskers (Brenner): Fe I—1.6  $\mu$  dia.; Fe II—3.8  $\mu$  dia. Young's modulus for first crystal—30 000 kg/mm<sup>2</sup>; for second crystal—18 500 kg/mm<sup>2</sup>. Curve of quartz filament (4.3  $\mu$ ) is given for comparison. No departure from a linear relationship is observed.

veals a slight reduction of the cross section or a few cracks. Stress-strain curves for two iron whiskers are shown in Fig. 21. Both crystals were subjected to preliminary loading and unloading (I up to almost 1000 and II up to 300 kg/mm<sup>2</sup>), after which no evidence of plastic deformation was detected, so that the entire deformation was elastic. Hook's law is valid up to a 2% strain within the limits of experimental error; for greater strains the stress-strain relationship is no longer linear, although the deformation remains elastic and the curve is completely reversible during unloading. An elastic deformation of 4.8% was observed.

Young's modulus can be computed from the slopes of the straight portions of the curves. For ordinary single crystals of  $\alpha$ -iron Young's modulus is 13500 kg/mm<sup>2</sup> in the [100] direction and 29000 kg/mm<sup>2</sup> in the [111] direction. The given data show that whiskers and ordinary crystals possess the same elastic modulus. This provides full justification for determining the elastic limit of whiskers by measuring their elastic deformations.

The stress-strain curve for a cadmium whisker

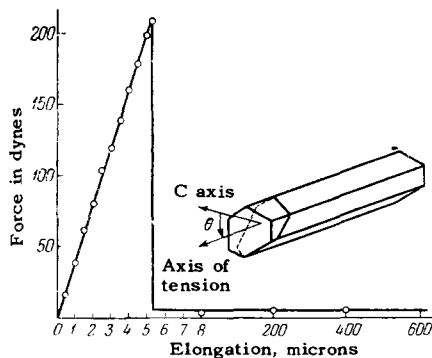


FIG. 22. Stress-strain curve of cadmium crystal (Coleman, Price, and Cabrera). Initial length 535  $\mu$ ; elastic deformation 1%; cross sectional area  $8.3 \times 10^{-8}$  cm<sup>2</sup>; yield point  $2.78 \times 10^9$  dynes/cm<sup>2</sup>; computed modulus  $2.78 \times 10^{11}$  dynes/cm<sup>2</sup>.

is given in Fig. 22.<sup>58</sup> In this case, too, the elastic modulus is of the same order as for ordinary single crystals.

Copper whiskers sometimes rupture in the same manner as iron whiskers, but at other times plastic deformation is observed. In the latter cases shortly before the rupture evidence of slip is easily observed at one or more places.

All of the investigated silver whiskers exhibited considerable plastic deformation before fracture.

The stresses which produce plastic deformation are always below those at which flow began. The clear appearance of a yield point for stretched whiskers and its absence on the stress-strain curves of iron shown above suggest that the strength measured by Brenner<sup>55</sup> pertains to an elastic interval.

Brenner<sup>41</sup> has made a thorough study of plastic deformation in copper and silver whisker with diameters ranging from 5 to 25  $\mu$  and length of about 2 mm. When the load is not quickly reduced after the elastic limit is passed flow, when it does occur, is so rapid that study of the deformation is practically prevented. The apparatus for the study of plastic flow therefore had to be improved; specifically, some arresting device was needed to interrupt the deformation after the elastic limit is reached. After such artificial slowing down of plastic flow the crystal is loaded again with a considerably smaller load.

The stress-strain diagram of a silver whisker is shown in Fig. 23. An extremely sharp elastic limit and extended region of "easy glide" are followed by a work-hardened region. Similar curves were obtained for copper whiskers (Fig. 24) with an elastic limit approximately 80 times greater than the flow stress. At the highest stress, corresponding to the elastic limit, a local slip band was formed. The "easy glide" region represents the propagation of the slip band along the crystal. When the portion of a whisker which has exhibited slip is removed the remaining shorter whisker again possesses a high elastic limit which sometimes even exceeds that of the original crystal. This

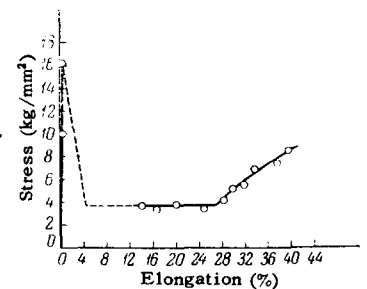


FIG. 23. Stress-strain diagram of a silver whisker. Axis in the [110] direction (Brenner).

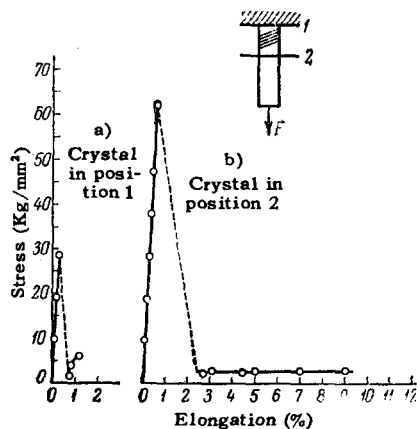


FIG. 24. Stress-strain diagram of copper whisker. a – initial state; b – after removing part of crystal in which slip occurred (Brenner).

effect is evidently associated with the reduced length of the sample and will be considered below.

Stress-strain curves are often complicated (Fig. 25). The observed alternation of flow and work hardening must be associated with the overcoming of obstacles to slip, the nature of which is unknown.

The tensile stresses required for the flow of copper whiskers with different orientations range from 1.2 to 4.7 kg/mm<sup>2</sup>. The shearing stresses at the elastic limit, calculated for different orientations, range from 6.1 to 38.6 kg/mm<sup>2</sup>, while the shearing stress at the beginning of flow ranges from 0.50 to 1.74 kg/mm<sup>2</sup>. The flow stresses in all instances are higher than the critical cleavage stresses for ordinary copper single crystals (0.1 kg/mm<sup>2</sup>).

In the “easy glide” region of copper the elongation is 4 – 20%.

The existence of a “sawtooth” on the stress-strain curves of body-centered and face-centered

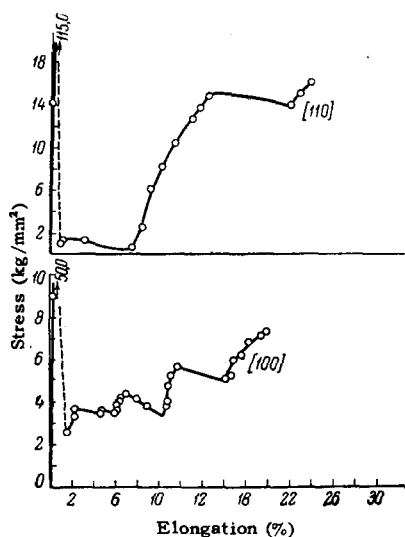


FIG. 25. Alternation of flow and work hardening in the stretching of copper whiskers (Brenner).

cubic crystals is well known and is usually attributed to impurities, being accounted for by the Cottrell “atmosphere”.<sup>64</sup> The relatively high purity of the investigated whiskers evidently eliminates this cause of a “sawtooth”.

The stress-strain diagram of cadmium whiskers<sup>58</sup> (Fig. 22) provides a clear example of a yield point. Elongation up to 1% is elastic. After the elastic limit is reached there is a sudden sharp drop of the stress and further elongation is produced by a relatively low and almost unchanging load (about 30 times smaller than the elastic limit). The region of the sample in which slip occurred could easily be detected by the slip bands; with further action of the load slip occurred throughout the sample and no longer required increase of the load. It is noted by the authors that the region in which slip begins does not change with further deformation, thus indicating a certain amount of work hardening.

It is very difficult to account for the existence of plastic deformation in whiskers. The formation of slip bands and the stress-strain diagrams such as Figs. 22 – 25 evidently indicate that whiskers may contain dislocations and other defects before deformation. Further evidence is provided by the dependence of whisker strength on their dimensions and temperature (see below).

#### 4. Creep in Whiskers

Only a few isolated measurements of creep in whiskers are available, but even this very meager information indicates that resistance to creep is much greater in whiskers than in ordinary crystals. When tin whiskers were bent<sup>57</sup> so that the relative deformation of their surface was  $6 \times 10^{-3}$  the creep rate under stresses of the order 10 kg/mm<sup>2</sup> was under  $5 \times 10^{-10}$  sec<sup>-1</sup>. The minimum creep rate of ordinary tin single crystals under stresses of 0.1 kg/mm<sup>2</sup> is  $2 \times 10^{-8}$  sec<sup>-1</sup>; thus with a load 100 times smaller the creep rate is 40 times greater.<sup>66</sup> It is interesting to note that the given tin whisker was under a bending stress for a week and straightened out completely after the load was removed.

Figure 26 is the creep curve of a silicon whisker<sup>54</sup> of 11.6 μ diameter at 800°C, tested under stresses comprising two thirds of the average yield point at 800°C. The creep rate falls off to zero after a few hours of testing, indicating work-hardening of the crystal during creep under constant stress.

Observations<sup>81</sup> of creep in Zn and Cd whiskers show that the initial creep rate increases under higher stresses. At a given stress the rate grad-

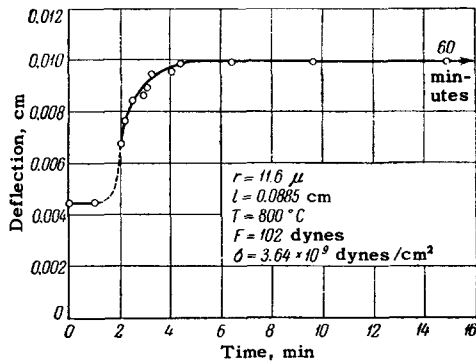


FIG. 26. Creep curve of silicon whisker at constant load and test temperature 800°C (Pearson, Read, and Feldman).

ually decreases and creep finally ceases. A change of the stress level after the termination of creep does not reinduce creep; this results from the pinning and ejection of dislocations in the original crystal. In the course of creep a crystal thus becomes more nearly perfect. A whisker which has been subjected to creep will flow again only at higher stresses; the magnitude of the elastic deformation is also increased. The pinning of dislocations may also be associated with impurities amounting to about  $10^{-4}$  per atom of the host crystal.

5. Influence of Test Temperature

Data concerning the influence of temperature have been published for copper,<sup>55</sup> cadmium,<sup>58</sup> zinc,<sup>58</sup> and silicon whiskers.<sup>54</sup> The copper crystals were bent in such a way that the surface stresses did not exceed the elastic limit even while sustaining a high temperature. Crystals with a diameter of  $5.4\mu$  were strained in this manner to 0.0025 (corresponding to 50 kg/mm<sup>2</sup> in the [111] direction) and were annealed for two hours at 900°C in a high vacuum. After the removal of the applied stress no trace of plastic deformation was detected.

The influence of low temperatures on cadmium and zinc whiskers was tested in greater detail.<sup>58</sup> The results, given in Table V, show that a temperature rise from 20 to 300°K reduces the elastic deformation and strength by about one-half and changes the type of fracture. Two modes of fracture are possible: (1) Preceded by flow with the propagation of slip bands after their formation at the critical shearing stress for slip  $\tau_{cr}$ , corresponding to the elastic limit (Fig. 22) (for Zn above 160°K and for Cd above 20°K); (2) below these temperatures — fracture along a cleavage plane (0001) without appreciable slip. The critical stresses inducing slip in cadmium and zinc are a few hundred times higher than in macroscopic crystals.

TABLE V

Test temperature, °K	$\epsilon^{elast. max.}$ %	Type of deformation	[0001]	[11 $\bar{2}$ 0]	$\sigma$ kg/mm <sup>2</sup>
<b>Cadmium</b>					
20	1.6	brittle fracture	1.3	1.4	26
77	1.2	slip	1.0	1.1	20
300	1.0	" "	0.9	0.9	15
<b>Zinc</b>					
77	1.9	brittle fracture	2.1	1.1	50
160	1.9	" "	2.1	1.2	50
300	1.0	slip	1.1	0.6	25

The influence of temperature on the behavior of silicon whiskers<sup>54</sup> has been studied with crystals of 16 – 28  $\mu$  diameter and 2 mm length (Fig. 27). Bending tests were used; in all cases the crystal axis was in the [111] direction. At room temperature the samples were elastic up to a 1% deformation; the maximum elastic deformation which could be observed under the given conditions was 2.6%. Brittle fracture took place in all cases; with a temperature rise to 600° before fracture, as a rule no signs of plastic deformation were detected. In the range 600 – 650°C the whiskers either ruptured in a brittle manner or began to flow; in some instances they ruptured after very little flow. Above 650°C the curves have a saw-tooth and considerable flow occurs.

Figure 28 shows the temperature dependences of the fracture stress, yield point and minimum stress at which flow occurs. All of these quantities are seen to decrease as the temperature is raised above 600°C.

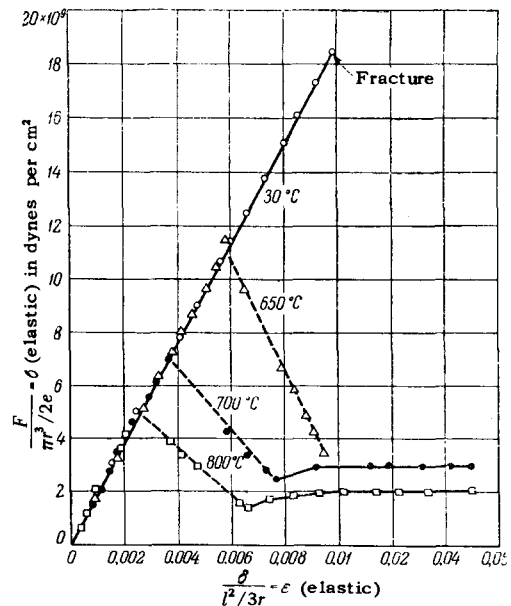


FIG. 27. Load-deflection curves for silicon whiskers at several temperature (Pearson, Read, and Feldman).



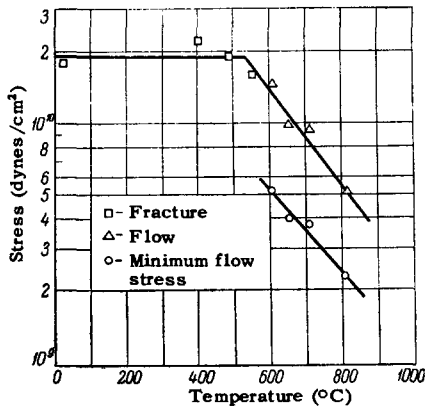


FIG. 28. Temperature dependence of fracture stress, yield point and minimum flow-inducing stress for silicon whiskers (Pearson, Read, and Feldman).

The dependence of the logarithm of the yield point on the logarithm of absolute temperature has a negative slope of about 5. In the opinion of the authors this indicates that whiskers are not perfect crystals and that under sufficiently high stresses thermal activation generates dislocations which result in plastic flow. The stresses required to produce dislocation loops in a perfect material are given by the relation  $\tau = \frac{Eb}{l}$ , where  $E$  is the elastic modulus,  $b$  is the Burgers vector and  $l$  is the length of the pinned dislocation segment. It is obvious that the temperature dependence of the stress is determined by the temperature dependence of the elastic modulus and will vary very little in the given temperature interval. The experimentally obtained temperature dependence of the stress indicates rather that the tested silicon whiskers already possessed a large number of dislocations.

The same investigators later obtained data<sup>37</sup> showing that the observed dependence of the yield point can be accounted for by the presence of very small amounts of oxygen interacting with dislocations.

**6. Influence of Whisker Dimensions on Their Strength**

Brenner<sup>6</sup> has studied the influence of whisker diameter on the strength of iron, copper and silver whiskers. The results for copper are shown in Fig. 29; although there is a considerable scatter of the data (which also occurs for iron whiskers), the influence of the diameter on the strength is obvious. The relationship between the mean strength for crystals with similar diameters and the value of  $\frac{1}{d}$  (Where  $d$  is the crystal diameter) is a straight line which can be expressed as follows:

$$\sigma_{\text{mean}} = \frac{410}{d} + 36 \text{ kg/mm}^2 \text{ for Cu}$$

$$\text{and } \sigma_{\text{mean}} = \frac{1630}{d} - 50 \text{ kg/mm}^2 \text{ for Fe.}$$

The relation obtained for iron is valid only in the range  $1 - 1.5 \mu$ . Even with  $d = 15 \mu$  iron and copper whiskers possess extraordinary elastic strength ( $65$  and  $38 \text{ kg/mm}^2$ , respectively). The results obtained by Gyulai<sup>24</sup> for NaCl whiskers also show the clear dependence of strength on size; with reduction of the diameter from approximately  $15 - 20 \mu$  to  $1 - 2 \mu$  the strength increased from  $2 - 4 \text{ kg/mm}^2$  to  $100 \text{ kg/mm}^2$ .

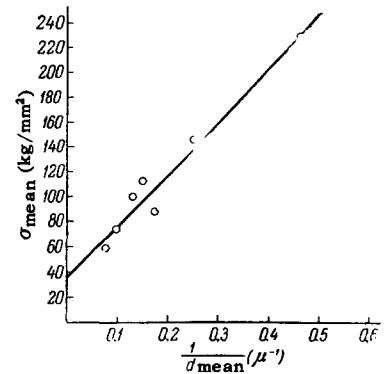


FIG. 29. Dependence of mean strength of copper whiskers on mean value of  $\frac{1}{d}$  ( $d$  is the crystal diameter) (Brenner).

The increase of crystal strength with diminishing diameter has been known for a long time. Taylor<sup>67</sup> produced very thin antimony crystals; with a  $30 \mu$  diameter the strength of such crystals was  $18 - 22 \text{ kg/mm}^2$  (which is close to the strength of steel). The strength of antimony crystals with a diameter of  $4 \text{ mm}$  is  $0.57 - 0.77 \text{ kg/mm}^2$ .<sup>55</sup>

According to reference 69 the critical shearing stress for cadmium crystals previously etched to a diameter of  $25 \mu$  is 14 times greater than that for crystals with diameters greater than  $500 \mu$ , and is  $15 \text{ kg/mm}^2$  for cadmium whiskers with diameters from  $1$  to  $10 \mu$ .

Figure 30 represents the results of very interesting parallel investigations of silicon whiskers

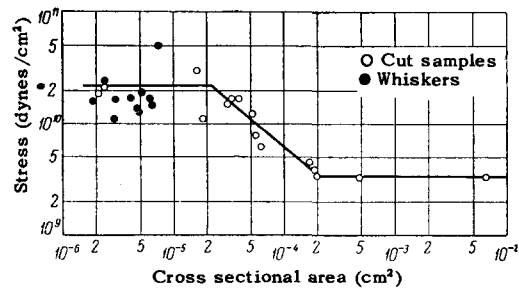


FIG. 30. Influence of size on the strength of whiskers and samples cut from large silicon crystals at room temperature (Pearson, Read, and Feldman).

and samples of the same sizes cut from large crystals.<sup>54</sup> Data for the whiskers are here represented by filled circles and data for the cut samples by open circles. The effect of size is obvious despite the scattering of the data, which increases as the size decreases. For cut samples with diameters greater than  $100\mu$  the fracture stress is independent of size and equals the strength of ordinary silicon crystals ( $\sim 35 \text{ kg/mm}^2$ ). Variation of the diameter from  $50$  to  $100\mu$  reduces the strength from  $220 \text{ kg/mm}^2$  to  $35 \text{ kg/mm}^2$ . The strength of cut samples with diameters from  $50$  to  $25\mu$  does not appreciably differ from that of whiskers with the same diameters. It should be noted here that in the case of silicon no linear relationship is observed between strength and the reciprocal of the diameter. It is also not known whether the properties of whiskers and ordinary crystals will remain identical when the diameter is reduced to  $10\mu$  and less. It is interesting that at  $800^\circ\text{C}$  the yield point of silicon crystals does not vary with the diameter; samples with diameters smaller than  $20\mu$  have the same yield point as ordinary single crystals. This indicates that the influence of defects which result in deformations depends on temperature.

A comparison of the strength of whiskers and crystals of the same size produced in a different manner, for metals as well as for silicon, is of special interest.

The strength of whiskers is also essentially dependent on their length, with the strength almost always increasing as the length decreases. This is illustrated very clearly by the following tests. An iron whisker of  $4.71\mu$  diameter and  $4 \text{ mm}$  length was fractured by a stress of  $99 \text{ kg/mm}^2$ . One part which was again subjected to tension exhibited considerably higher strength. After this half fractured a fourth part of the whisker was again tested; a further increase of strength resulted up to  $423 \text{ kg/mm}^2$ . The large spread in the strength of whiskers of different sizes indicates some statistical distribution of defects which can lead to fracture that may or may not be preceded by plastic deformation. The spread of the results could also result from some differences in the orientations of crystals with respect to external forces.

It may be presumed that defects arise accidentally during growth and do not necessarily appear in whiskers. Variation of the conditions for growth and of the purity of the materials may obviously affect the number and distribution of the defects. Indeed, the "purest" growth technique — deposition from a vapor in a temperature gra-

dient — yields a much less pronounced dependence of strength on diameter and a smaller spread of the results. With changing growth conditions (such as the reaction temperature in the reduction of halides<sup>71</sup>) whiskers may also be produced with little strength.

Defects which lower the strength may be found either on the surface or within crystals. The coarser surface defects are easily detected when light is reflected from the surface; in reference 55 nonuniform reflection from crystal surfaces was invariably associated with low strength. It is postulated that surface defects smaller than the resolving power of a light microscope can greatly reduce the strength of whiskers.

The internal imperfections can hardly be dislocation sources such as those proposed by Frank and Read. The tangential component of a stress required to activate a Frank-Read source is  $\tau = \frac{Eb}{l}$ . An estimate by means of this formula indicates that for any of the tested whiskers the length of dislocations sources in the most probable slip planes could not be greater than  $0.1\mu$ , which is only a small fraction of the whisker diameter. With the possible increase of the source length to the whisker diameter the stress would be very small.

A statistical analysis of presently available results from tests of whiskers would be extremely difficult because of the limited number of experiments and the absence of sufficient data on the nature, orientation and localisation of defects as well as on the orientations and sizes of the crystals.

The number of surface defects able to produce a certain effect must be proportional to the diameter  $d$ , while the strength is inversely proportional to  $d$ . In exactly the same way, given a certain number of internal dislocation sources, the length of the longest source will be proportional to  $d$  and the strength will be inversely proportional to  $d$ . Therefore the linear dependence of the mean strength on  $1/d$  does not affect the location of defects. If the reduction of strength results from the probability that a single internal dislocation source is formed during growth we may expect that strength will be inversely proportional to the cross sectional area of whiskers, i.e., to  $1/d^2$ .

The effect of length on the strength of whiskers indicates that rupture begins at single defects, which must be small in number and must be distributed irregularly.

We note in conclusion that although at room

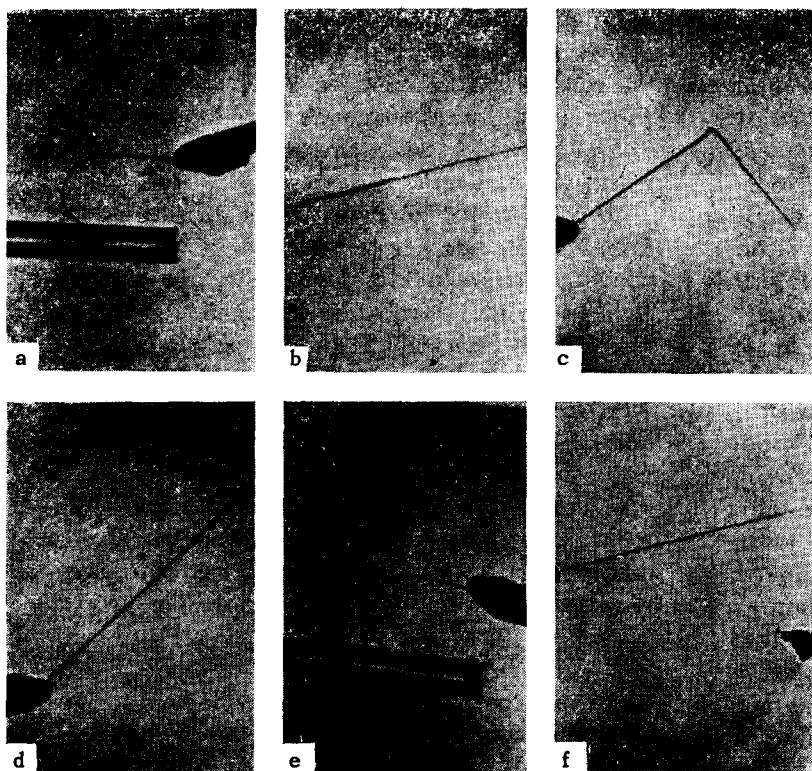


FIG. 31. Recovery of deformed copper whisker: a – deformation of about 0.3%; b – removal of load; c – break due to repeated loading; d – heating for ten minutes at 1015°C; e – repeated deformation to about 0.3%; f – removal of load. Crystal length  $2.5 \pm 0.5 \mu$ .  $\times 8.5$  (Brenner and Morelock).

temperature whiskers and crystals of the same size cut from single crystals possess the same mechanical properties (silicon), at 800°C the yield point of the former is five times higher than that of the latter. This indicates that the mechanical properties of whiskers are determined by some factors in addition to their small size.

### 7. The Influence of Surface Quality on Whisker Strength

During the growth of whiskers such defects as pits, overgrowths, spotty corrosion and occasional grain boundaries appear on their surfaces, and are, as a rule, associated with low strength.

Oxide films forming on the surfaces of ordinary crystals are known to raise their strength; in the case of cadmium crystals the critical cleavage stress is increased by about 150%. The strength-enancing effect increases as the film becomes thicker or the crystal diameter becomes smaller.

Continuous oxide films forming on whisker surfaces when heated in air (at 100 – 150°C) do not essentially affect their strength. However, it is noted in reference 55 that whiskers annealed in a vacuum were somewhat stronger than those annealed in air. On the other hand, it was established in the same experimental work that iron whiskers stored in air for a few days exhibited

lower strength, which was observed even before an appreciable oxide film was formed. In the opinion of the authors this indicates that edge dislocations may form during the oxidation of  $\alpha$ -Fe whiskers. The heating of silicon whiskers at 800°C followed by testing at room temperature resulted in no change of strength compared with unannealed crystals.<sup>54</sup>

We have at present too little data for any reliable judgment regarding the influence of surface films on the mechanical properties of whiskers.

It is very difficult to determine the effect of impurities on whisker strength. In any event, their great strength is not determined by impurities. The purity of whiskers is not especially high; for copper, for example, it may be estimated at 99.997% (p.284). Increased purity of the inert gas during the growth of Zn and Cd whiskers by vapor condensation<sup>58</sup> did not affect their strength.

Even the evidently large amount of impurities in silver whiskers grown by electrodeposition from electrolytes containing organic materials<sup>21</sup> does not reduce their strength to that of ordinary much purer silver single crystals. Such silver whiskers have a strength of 6 kg/mm<sup>2</sup> compared with 175 kg/mm<sup>2</sup> for the strongest silver whiskers grown from the chloride; the strength of ordinary pure silver single crystals is 0.21 kg/mm<sup>2</sup>.

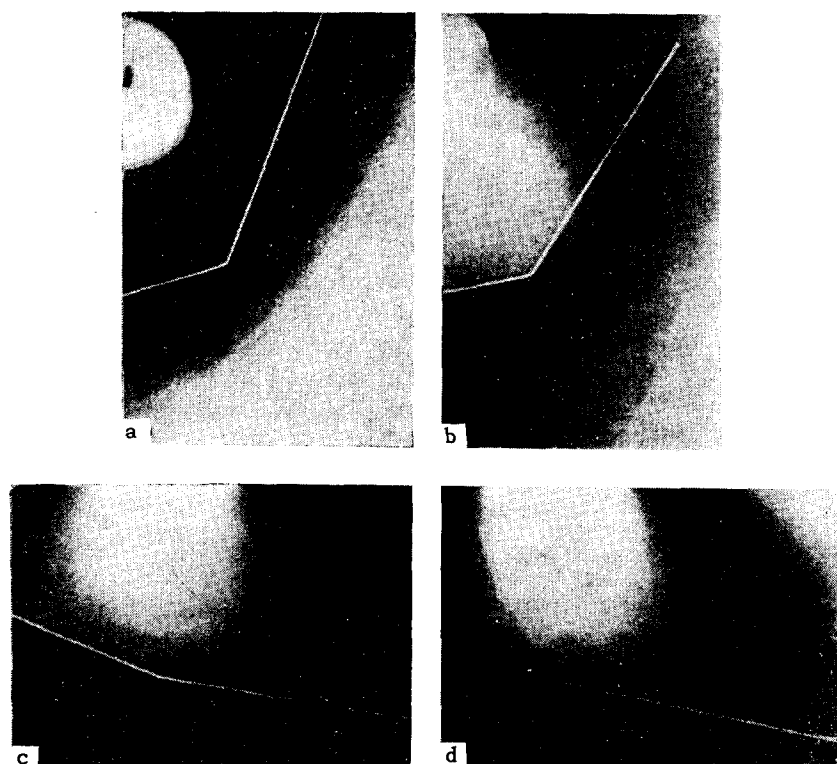


FIG. 32. Influence of heating time at 1015°C on recovery: a - 0 sec; b - 600 sec; c - 1460 sec; d - 2400 sec (Brenner and Morelock).

### 8. Recovery (Straightening) of Whiskers

The recovery of whiskers is described in reference 70. A highly elastic copper whisker about  $2.5\mu$  thick was plastically deformed and then heated in a hydrogen atmosphere at 1015°C for ten minutes, after which the crystal straightened out and exhibited its original high elastic strength. A photographed sequence of successive changes is shown in Fig. 31, while Fig. 32 shows the variation of the recovery picture with time. The recovery rate  $\frac{d\theta}{dt}$  (where  $d\theta$  is the variation of the whisker bending angle) is constant except for the initial and final stages; this is illustrated in Fig. 33. The oxide film formed at room temperature evidently does not delay recovery. A deformed whisker kept in air at room temperature for a few hours before being heated in helium recovered at the same rate as one heated in hydrogen.

Recovery experiments were also performed with silicon<sup>54</sup> and NaCl whiskers.<sup>24</sup> For silicon a linear relationship was established between the reduction of the bending angle and the logarithm of time. No direct relationship is indicated between the straightening rate and the initial angle.

Nabarro has considered a number of possible mechanisms for the straightening of whiskers<sup>37</sup> and has shown that the observed high rate of straightening must be associated with the re-

moval of dislocations from the interior of a crystal and their emergence on the surface.

The recovery of whisker properties as well as of their shape has been observed. The behavior of silicon whiskers above 650°C indicates that elastic deformation is followed by plastic deformation which proceeds without perceptible work hardening. An anneal of the plastically deformed crystal in the absence of stresses gradually restores the yield point. The time of restoration depends on temperature and on the very small content of impurities which are distributed throughout the volume and pin down dislocations. Special experiments<sup>37</sup> have shown that the impurity that pins dislocations in silicon is oxygen varying in amount from  $2 \times 10^{-7}$  to  $2 \times 10^{-5}\%$ .

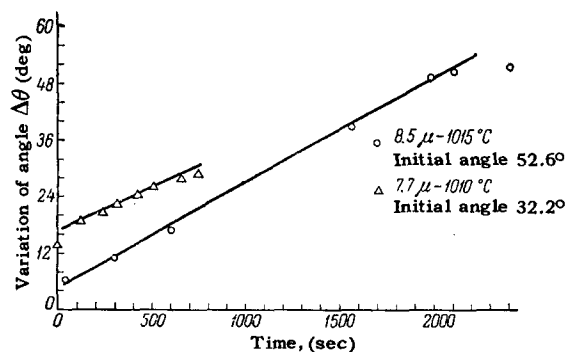


FIG. 33. Bending angle as a function of time in the recovery of copper whiskers (Brenner and Morelock).

#### IV. OTHER WHISKER PROPERTIES

If we assume that whiskers are crystals of a special character we may expect them to be marked by other properties besides their extremely high mechanical properties. Since, primarily, they are supposed to possess structural perfection we may expect differences of their structure-sensitive properties and of properties depending on the surface state. Direct experiments to determine the perfection of whiskers have thus far not yielded unambiguous results, and the investigation of certain other properties may be of help in this connection.

Up to the present time only a limited number of papers have been published on nonmechanical properties. Low-temperature conductivity is among the structure-sensitive electrical properties. The residual resistance of metals at temperatures close to absolute zero is determined by electron scattering from defects and impurities. At the temperature of liquid helium the electron mean free path is increased until it is comparable with whisker diameters, thus increasing electron scattering from the surface and making it more difficult to interpret the results. At present only preliminary results are available on residual resistance at 4.2°K of Cu and Ag whiskers grown by the chemical reduction of halides, and of Zn and Cd whiskers grown by vapor condensation.<sup>42</sup>

The residual resistance of Cu whiskers was found to vary from sample to sample, comprising from 10 to 30% of the resistance at 273°K; for Ag whiskers the residual resistance was less than 5% and for Zn and Cd whiskers it was less than 1% of the resistance at 273°K. These results may indicate the presence of impurities and defects.

Both the ordinary conductivity and the photoconductivity of semiconductors also depend on impurities and defects, which determine both the number of carriers and the traps which effect recombination. The decay of photoconductivity is determined mainly by traps; in ZnS whiskers the photocurrent decays 10–100 times more rapidly than in ordinary crystals.<sup>61</sup> In both instances the photocurrent was induced by illumination at 3650 Å. It has been remarked that this steep decay of the photocurrent indicates the great degree of whisker perfection. The optical properties of whiskers have been left almost uninvestigated. It has been noted in reference 65 that CdS whiskers do not exhibit the edge emission found in ordinary CdS crystals and ordinarily accounted for as the result of sulfur va-

cancies. Edge emission was induced in CdS whiskers by irradiation with protons of about 1 Mev energy, which is sufficient to produce both sulfur and cadmium vacancies.

Certain magnetic properties of Fe whiskers have been investigated to a greater extent. Domain structure is studied by means of a powder technique using a colloidal suspension.<sup>71,72,73</sup> Ferromagnetic domain patterns are observed on unmagnetized crystals and can always be interpreted directly because of the simple axis orientation and faces of whiskers (the axis being in the [100], [110] or [111] direction) and the small number of domains (sometimes only one). A change of the domain structure has been observed in Fe whiskers<sup>74</sup> as a result of magnetization or annealing. The motion of domain walls in Fe whiskers in an applied field was recently subjected to careful study.<sup>75</sup> The velocity of domain wall motion along the crystal axis may be close to 50 km/sec, which is 100 times faster than the usual velocity that is observed in a Ni-Fe wire, for example. The coercive force required to rotate the magnetization direction of a domain has been estimated theoretically to be about 500 oersteds for Fe, while in a Fe whisker it was 250 oersteds. These results, like previous experiments on Cu<sup>+</sup> ion deposition on Cu whiskers,<sup>44</sup> confirm the high perfection of whisker surfaces.

Sn whiskers have been used to study the effect of sample size on superconductivity.<sup>76,78</sup> The influence of a magnetic field on the temperature of transition to the superconducting state was observed as well as the hysteresis loop of the critical magnetic field below the transition temperature in zero field. A comparison of these results with those for bulk Sn crystals permitted a comparison of the Ginzburg-Landau and London-London theories for current penetration in superconductors. Much better agreement with the Ginzburg-Landau theory was found.

Still another unusual property has been observed in ZnS whiskers;<sup>61</sup> the hexagonal-to-cubic phase transition does not occur at 400°C as in ordinary ZnS crystals but at 750°C.

Thus the investigations of nonmechanical whisker properties, although incomplete and scanty, also indicate characteristics which can be accounted for by their special nature and difference from ordinary single crystals.

#### CONCLUSION

The unusual properties of whiskers of widely different materials (metals, semiconductors,

ionic crystals, organic crystals) are of great interest mainly for the theories of crystal growth and strength. The results obtained from studies of whiskers were first regarded as proofs of the dislocation theory of growth and the dislocation mechanism of deformation. Further study has shown that the situation is much more complicated.

The dislocation theory of growth, which is based on the hypothesis of an axial screw dislocation, is not confirmed by direct methods of observing the axial dislocation in the majority of whiskers. The extraordinary mechanical properties of whiskers result in even greater complications. We still have no experimental information that provides a clear explanation of the great strength of whiskers. Several explanations have been advanced:

1. Whiskers, because of the peculiar manner in which they grow, are structurally perfect (lacking edge defects) with the exception of a single axial screw dislocation. However, some data show that whiskers may contain dislocations or some other type of defect.

2. Whiskers, because of the manner in which they grow, possess a perfect surface, thus excluding the most harmful surface defects. There are still no results which can disprove this hypothesis, except in the case of tin whiskers.

3. The great strength of whiskers results from their small dimensions rather than from the mode of growth. This leads either to a smaller probability of finding defects (the "scale factor"<sup>67,79</sup>) or to a change in the relationship between growth and the stresses that determine the stages of shear (fracture) nucleation.<sup>80</sup> It is conceivable that each of these possibilities is realized in whiskers to some degree. Much more experimental work is needed, not only on mechanical properties but on others, especially structure-sensitive properties.

An understanding of the unusual properties of whiskers is of great scientific importance in accounting for the nature of strength and plasticity, and for the testing of the basic theories.

<sup>1</sup> C. Winkler, *Chem. Z.* **12**, 44, 721 (1888).

<sup>2</sup> V. Kohlschütter, *Kolloid Z.* **50** 1 (1930).

<sup>3</sup> H. W. Kohlschütter, *Z. Elektrochem.* **38**, 345 (1932).

<sup>4</sup> W. O. Ostwald, *Kolloid Z.* **102**, 35 (1943).

<sup>5</sup> H. K. Hardy, *Progress in Metal Physics* **6** (1956).

<sup>6</sup> S. S. Brenner, *Acta Met.* **4**, 62 (1956).

<sup>7</sup> W. W. Webb and E. F. Riebling, *J. Chem. Phys.* **28**, 1242 (1958).

<sup>8</sup> M. Volmer and I. Estermann, *Z. Phys.* **7**, 13 (1921).

<sup>9</sup> G. W. Sears, *Acta Met.* **3**, 361 (1955).

<sup>10</sup> R. V. Coleman and G. W. Sears, *Acta Met.* **5**, 131 (1957).

<sup>11</sup> G. W. Sears, *Acta Met.* **3**, 367 (1955).

<sup>12</sup> Cobb, *Monthly Rev. Am. Electroplaters Soc.* **33**, 28 (1946).

<sup>13</sup> Compton, Mendizza, and Arnold, *Corrosion* **7**, 327 (1951).

<sup>14</sup> Fisher, Darken, and Carroll, *Acta Met.* **2**, 368 (1954).

<sup>15</sup> J. Franks, *Acta Met.* **6**, 103 (1958).

<sup>16</sup> S. C. Lawrence, *Bull. Am. Phys. Soc.* **3**, 328 (1958).

<sup>17</sup> S. M. Arnold and S. E. Koonce, *J. Appl. Phys.* **27**, 964 (1956).

<sup>18</sup> H. W. Kohlschütter, *Z. Elektrochem.* **38**, 213 (1949).

<sup>19</sup> K. M. Gorbunova and A. I. Zhukova, *J. Phys. Chem. (U.S.S.R.)* **23**, 605 (1949).

<sup>20</sup> Ovenston, Parker, and Robinson, *Trans. Electrochem. Soc.* **104**, 607 (1957).

<sup>21</sup> Prinse, Vermilyea, and Webb, *Acta Met.* **6**, 524 (1958).

<sup>22</sup> W. W. Webb and W. D. Forgeng, *Acta Met.* **6**, 462 (1958).

<sup>23</sup> Buckley, H. E., *Crystal Growth*, Wiley, New York, 1951; *Russ. Transl. IL, Moscow*, 1954.

<sup>24</sup> Z. Gyulai, *Z. Phys.* **138**, 317 (1954).

<sup>25</sup> S. Amelinckx, *Physica* **24**, 390 (1958).

<sup>26</sup> G. W. Sears, *Phys. and Chem. Solids* **6**, 300 (1958).

<sup>27</sup> N. Kato, *J. Phys. Soc. Japan* **10**, 1024 (1955).

<sup>28</sup> J. E. Gordon, *Nature* **179**, 1270 (1957).

<sup>29</sup> Bacon and Bonman, *Bull. Am. Phys. Soc.* **2**, (1957).

<sup>30</sup> R. Bacon, *Bull. Am. Phys. Soc.* **3**, 108 (1958).

<sup>31</sup> Bradley, Franks and Rush, *Proc. Phys. Soc. (London)* **70**, 13,889 (1957).

<sup>32</sup> P. E. Charsley and P. E. Rush, *Phil. Mag.* **3**, 508 (1958).

<sup>33</sup> J. D. Eshelby, *J. Appl. Phys.* **24**, 176 (1953).

<sup>34</sup> J. D. Eshelby, *Phil. Mag.* **3**, 440 (1958).

<sup>35</sup> R. G. Treuting, *Acta Met.* **5**, 173 (1957).

<sup>36</sup> Webb, Dragsdorf, and Forgeng, *Phys. Rev.* **108**, 498 (1957).

<sup>37</sup> *Dislocations and Mechanical Properties of Crystals*, Lake Placid Conference, 1957.

<sup>38</sup> H. G. Smith and R. E. Rundle, *J. Appl. Phys.* **29**, 679 (1958).

<sup>39</sup> J. J. Gilman and W. G. Johnston, *J. Appl. Phys.* **27**, 1018 (1956).

<sup>40</sup> R. V. Coleman, *Bull. Am. Phys. Soc.* **3**, 108 (1958).

<sup>41</sup> S. S. Brenner, *J. Appl. Phys.* **28**, 1023 (1957).

<sup>42</sup> H. H. Hobbs and E. P. Stillwell, *Rev. Sci. Instr.* **29**, 653 (1958).

- <sup>43</sup>R. G. Treuting and S. M. Arnold, *Acta. Met.* **5**, 598 (1957).
- <sup>44</sup>D. A. Vermilyea, *J. Chem. Phys.* **27**, 814 (1957).
- <sup>45</sup>Burton, Cabrera, and Frank, *Phil. Trans. Roy. Soc. (London)* **243**, 299 (1953).
- <sup>46</sup>A. E. MacKenzie, Thesis, University of Bristol, 1951.
- <sup>47</sup>S. E. Koonce and S. M. Arnold, *J. Appl. Phys.* **24**, 365 (1953).
- <sup>48</sup>G. P. Hirth, *Conf. on the Mechanical Properties of Whiskers and Thin Films*, Cambridge, 1958.
- <sup>49</sup>Fisher, Fullman, and Sears, *Acta Met.* **2**, 344 (1954).
- <sup>50</sup>G. W. Sears and S. S. Brenner, *Acta Met.* **4**, 268 (1956).
- <sup>51</sup>G. D. Eshelby, *Phys. Rev.* **91**, 755 (1953).
- <sup>52</sup>Amelinckx, Boutink, Dekeyser, and Seitz, *Phil. Mag.* **2**, 1 (1957).
- <sup>53</sup>G. W. Sears, *J. Chem. Phys.* **26**, 1549 (1958).
- <sup>54</sup>Pearson, Read, and Feldman, *Acta Met.* **5**, 181 (1957).
- <sup>55</sup>S. S. Brenner, *J. Appl. Phys.* **27**, 1484 (1956).
- <sup>56</sup>D. Tarnbull, (see reference 48).
- <sup>57</sup>C. Herring and J. K. Galt, *Phys. Rev.* **85**, 1060 (1952).
- <sup>58</sup>Coleman, Price, and Cabrera, *J. Appl. Phys.* **28**, 1360 (1957).
- <sup>59</sup>R. Gomer, *J. Chem. Phys.* **26**, 1333 (1957).
- <sup>60</sup>R. L. Eisner, *Acta Met.* **3**, 414 (1955).
- <sup>61</sup>W. W. Piper and W. L. Roth, *Phys. Rev.* **92**, 503 (1953).
- <sup>62</sup>E. Schmid and W. Boas, *Kristallplastizität, mit besonderer Berücksichtigung der Metalle*, Springer, Berlin, 1935; Russ. Transl. ONTI, 1938.
- <sup>63</sup>S. S. Brenner and C. R. Morelock, *Rev. Sci. Instr.* **28**, 652 (1957).
- <sup>64</sup>A. H. Cottrell, *Dislocations and Plastic Flow in Crystals*, Clarendon Press, Oxford, 1953; Russ. Transl., Metallurgizdat, 1957.
- <sup>65</sup>D. S. Reynolds and L. C. Greene, *Bull. Am. Phys. Soc.* **3**, 108 (1958).
- <sup>66</sup>B. Chalmers, *Proc. Roy. Soc. (London)* **A156**, 427 (1936).
- <sup>67</sup>G. F. Taylor, *Phys. Rev.* **23**, 655 (1924).
- <sup>68</sup>G. Wassermann, *Z. Krist.* **75**, 376 (1930).
- <sup>69</sup>E. N. Andrade, *J. Inst. Metals* **86**, 138 (1953).
- <sup>70</sup>S. S. Brenner and C. R. Morelock, *Acta Met.* **4** (1956).
- <sup>71</sup>R. V. Coleman and G. G. Scott, *Phys. Rev.* **107**, 1276 (1957).
- <sup>72</sup>G. G. Scott and R. V. Coleman, *J. Appl. Phys.* **28**, 1512 (1957).
- <sup>73</sup>R. W. DeBlois and C. D. Graham, *J. Appl. Phys.* **29**, 528 (1958).
- <sup>74</sup>R. V. Coleman and G. G. Scott, *J. Appl. Phys.* **29**, 526 (1958).
- <sup>75</sup>R. W. DeBlois, *J. Appl. Phys.* **29**, 459 (1958).
- <sup>76</sup>O. S. Lutes, *Phys. Rev.* **105**, 1451 (1957).
- <sup>77</sup>O. S. Lutes and E. Maxwell, *Phys. Rev.* **97**, 1718 (1955).
- <sup>78</sup>R. Gomer, *J. Chem. Phys.* **28**, 457 (1958).
- <sup>79</sup>A. P. Aleksandrov and S. N. Zhurkov, *Явления хрупкого разрыва (Brittle Fracture)*, ONTI, 1933.
- <sup>80</sup>A. V. Stepanov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **17**, 271 (1953).
- <sup>81</sup>G. E. Gordon and J. W. Menter, *Nature* **182**, 296 (1958).

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