

thickness. Despite appreciable cold working, the grain size after this treatment is approximately equal to that which was present before deformation. It is thought that this may be due to the fact that grain growth is greatly assisted by the similar orientation of the coagulating grains. In fact, a similar lattice orientation exists, after initial work recrystallization, in those parts of the specimen which have developed from a single grain.

With increasing plastic strain the nature of the original grain becomes less significant for the structure which develops after prolonged heat treatment. On the one hand, the deviation of originally parallel directions in an individual deformed grain becomes greater, whilst on the other, the differences between the orientations of neighbouring grains become smaller. Ultimately the grain-size relationship disappears entirely, leaving the size of the crystals which form after grain growth to depend on the plastic strain.

If, therefore, a rolled aluminium crystal is subjected to complete recrystallization, according to the plastic strain the following cases will arise (416). If deformation is slight, the number of crystals increases considerably with the strain; the grain being relatively coarse, grain growth cannot yet take place. At a certain plastic strain a single crystal appears suddenly—as a result of grain growth—and the number of new grains increases with the deformation.

No reliable picture can yet be given of the mechanism of grain growth [see (429) for numerous relevant observations]. All that can be said is that apparently it is not a question of growth from a nucleus but of the coagulation of similarly oriented grains (426). The relationship between the orientation of the final texture and that of the texture which preceded it is still obscure.

The presence of impurities greatly influences the progress of grain growth. It proceeds a thousand times more quickly with very pure aluminium than with technical aluminium [(416), (429)]. This means that, with very pure metal, it is still more difficult to distinguish between work recrystallization and grain growth, and that consequently the progress of recrystallization will be still more obscure. With increasing impurity content, especially if the impurities are precipitated as a new phase, the tendency for aluminium to form large crystals by grain growth is greatly reduced (430).

65. *Reversion to the Original Properties by Heat Treatment*

After the description of the textural change due to recrystallization we will now discuss briefly the changes in the lattice structure

and in the physical properties of cold-worked metal crystals produced by heat treatment. It might be expected that the changes in the properties would take place in three stages, corresponding to the three distinct processes of crystal recovery, work recrystallization and grain growth. It is impossible, however, to separate all three phases, since the corresponding processes overlap, work recrystallization being invariably attended by recovery, while grain growth can take place partly during work recrystallization.

Investigations into the *elimination* by heat treatment, of the *lattice disturbances* caused by cold working, have been carried out mainly on polycrystals. It was found with tungsten wires that recovery (revealed by a gradual reduction in strength) causes a definite resolution of the K_{α} doublet initially rendered diffuse by cold working. The temperature of the start of renewed resolution, determined by X-rays, is always somewhat higher than the temperature of incipient decrease in the strength of the wires even for solid solutions of tungsten with molybdenum and tantalum (431). The smoothing of the lattice becomes evident in the X-ray photograph after mechanical softening has set in; a similar observation was made when annealing extended aluminium crystals. Heating of a 15 per cent. extended crystal for half an hour at 400° C. resulted in a substantial decrease in the yield stress while the asterism in the Laue picture remained unchanged (432).

A quantitative study of the resolution of the K_{α} doublet during the recovery of tungsten wires revealed that the definition of the doublet tends towards a constant final value at each temperature with increasing length of the heating period; this value increases with increasing temperature of heat treatment (433). The definition was measured by the quotient of the maximum of intensity of the α_1 line and the minimum between the two lines. There is therefore a residue of lattice disturbance (stresses) in the polycrystalline tungsten wires investigated, at each temperature of recovery. These measurements cannot be extended into the region of incipient recrystallization owing to the spottiness of the Debye-Scherrer circles, which greatly interferes with the photometry. It is to be surmised, however, that upon conclusion of recrystallization the definition of the doublet will revert to that of the unworked material.

Reference has already been made in Sections 49 and 54 to the *changes* produced by recovery in the *mechanical properties* of deformed crystals. These changes are regular and gradual, and by suitable heat treatment they reproduce the initial values. In the case of recrystallization, on the other hand, the hardening of the

crystals consequent upon plastic deformation is discontinuously and completely eliminated. Table XXIII contains some figures for the yield point of tin crystals which, after the original extension, had again become single crystals by recrystallization. After heating, the yield-stress values come within the same order of magnitude as for unstressed original crystals; the appreciable plasticity (approximately 4–6-fold), which disappeared completely after deformation, has now returned. If work recrystallization leads to the formation of a polycrystal, the mechanical properties will depend largely upon the grain size of the resultant texture. The same applies

TABLE XXIII
*Softening of Extended Tin Crystals as a Result of
Recrystallization (404)*

Yield point in g./mm. ² .	
before	after
annealing (~10 min., at 140° C.).	
1700	156
1480	98
1630	443
2050	137
3740	260

naturally to the grain growth which follows work recrystallization, and which in certain circumstances may even lead back to the single crystal.

Owing to the technical importance of the subject a very great deal of research has been carried out on the changes produced by annealing in the mechanical and physical properties of cold-worked polycrystals. Attention has already been drawn to the reduction in the strength of tungsten wire within the range of recovery. It is not intended to examine in detail the numerous investigations relating to this matter; but we would draw attention to the comprehensive accounts in (415) and especially in (434) and (401). It can be said in general that the modification of a property by annealing proceeds approximately as shown in Fig. 173 for the tensile strength and elongation of a hard-drawn mild-steel wire. Following upon a range of temperature in which only slight changes occur, and in which the fibrous deformation texture is retained, at a certain

temperature a sudden change takes place in the properties. An increase in the temperature of annealing is not attended by any further appreciable change, provided that the temperature is neither too high nor the duration too long. The relationship with the three processes—recovery, work recrystallization and grain growth—is quite obvious. The region of minor changes in properties within the low-temperature range corresponds to recovery; the sudden reversion to the initial values of fine-grained unworked material,

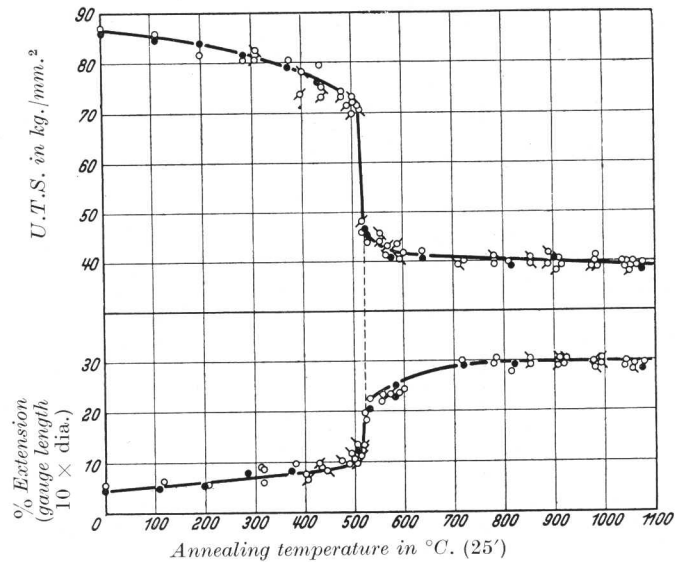


FIG. 173.—Change in the Tensile Strength and Elongation of Hard-drawn Ingot Iron (0.08% C.) with Increasing Temperature of Heat Treatment; Annealing Period 25 min. (435).

coinciding with the transformation of the texture, corresponds to work recrystallization; and the further irregular changes which occur if heating at high temperature is prolonged, and which usually have an adverse effect on the mechanical properties, are to be ascribed to the formation of a coarse grain size by grain growth.

A note must be added regarding recovery. It has been found with fine-grained materials that, as in the case of the lattice disturbances described above, a complete elimination of the changes in the properties due to cold working cannot be effected by recovery. Fig. 174 exemplifies this statement by means of the tensile strength and elongation of the mild-steel wire already referred to. It will be

seen that to each annealing temperature there corresponds a degree of softening which is not exceeded even if the heating period is greatly prolonged. The capacity for recovery of the deformed polycrystal therefore differs substantially from that of the freely extended crystal (cf. also Section 62). This difference becomes intelligible if it is remembered that the grains of the deformed polycrystal, which owing to mutual interference have become warped, cannot revert to a completely unobstructed state without the formation of a new texture.¹

Although the behaviour shown by the mechanical properties of steel wire is observed in general with other properties also, marked

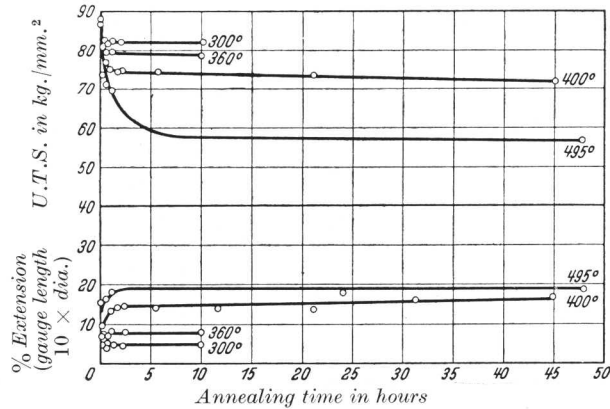


FIG. 174.—Effect of the Annealing Period at Various Temperatures (below 500° C.) on the Tensile Strength and Elongation of Drawn Ingot Iron (435).

differences arise for individual metals and alloys. It is particularly noticeable that the most rapid changes in various properties do not always occur within the same range of temperature. This happens with copper, silver and gold, but not with nickel and metals of the platinum group. With these metals the reversion to the original values takes place for different properties in different ranges of temperature [(436) to (439)].

In conclusion, reference must be made to the release of gas during the heat treatment leading to the recovery and recrystallization of worked metals (440). Recently alloys have been prepared with small

¹ Although according to this statement recovery does not restore the original properties of the technical polycrystal, this limited capacity for recovery nevertheless deserves closer attention than it has so far received [cf. also (414)].

amounts of radio-active elements; the progress of the heat treatment could be followed very accurately by measuring the emanations liberated (441).

As has already been mentioned in the case of cold working, when investigating the changes in properties caused by heat treatment special attention must be paid on the one hand to trivial causes, and on the other to the formation of preferred orientations. Among the former must be included the formation of cavities which are observed in grain growth at the point of contact of several grains [cf. for instance (442)]. In sections 78 and 82 particulars will be found of the regular texture which frequently results from work recrystallization, and which, owing to the marked anisotropy of many properties of metal crystals, may be attended by very pronounced changes in properties as a result of the preferred orientation of the crystals.

PLASTICITY AND STRENGTH OF IONIC CRYSTALS

Hitherto we have examined the phenomena of the plasticity and strength of crystals with reference to experimental data obtained from metal crystals. It has already been emphasized more than once that such crystals yield very satisfactory experimental material, owing to the ease with which they can be produced and deformed. But it has also been mentioned that the processes of gliding and mechanical twinning which underlie the plastic deformation of crystals were originally discovered, and closely studied, long ago in ionic crystals. The mechanisms of deformation appear to be substantially independent of the type of force by which the lattice is held together, which in the case of ionic crystals are mainly electrostatic forces between heteropolar ions, while in the case of metals they arise from positively charged atomic cores in a degenerate electronic gas.

The mechanical investigations into the structure of ionic crystals which form the subject of this section were restricted initially, in the main, to a determination of the crystallographic indices of their cleavage and fracture planes, and their glide and twinning elements. Numerical data about mechanical properties were obtained for the "hardness" of various crystal faces, determined by numerous different methods. Over a long period systematic investigations into the forces necessary to initiate plastic deformation, cleavage and fracture were carried out only occasionally, and it was not until recent years that a substantial body of experimental data referring mainly to sodium-chloride crystals became available.

66. Gliding and Twinning Elements

In what follows no complete account can be given of the great number of observations on the mechanism of deformation in ionic crystals; for fuller details the reader is referred to (443). Table XXIV contains particulars of the cleavage or fracture planes, and of the glide and twin elements of only the more important lattice types. In the case of ionic crystals, too, planes and directions of low indices are the most important. The significance of the lattice structure in determining the deformation elements is apparent from the table. As with metal crystals, it is still not clear by what factors the glide elements are determined. In the case of ionic

crystals the sign of the ionic charges is certainly a contributory factor. In connection with the gliding of sodium chloride it has been

TABLE XXIV
The Cleavage Planes, Glide and Twin Elements of Ionic Crystals [from (443)]

Material.	Lattice-type crystal class.	Cleavage or rupture planes.	Glide elements.		Twin elements.			
			T .	t .	K_1 .	K_2 .	s .	
Sodium fluoride, NaF Rock salt, NaCl Sylvite, KCl Potassium bromide, KBr Potassium iodide, KI Rubidium chloride, RbCl Ammonium iodide, NH ₄ I Periclase, MgO Lead sulphide, PbS Ammonium chloride, NH ₄ Cl Ammonium bromide, NH ₄ Br Fluorspar, CaF ₂ Nantokite, CuCl Marshite, CuI Zinc blende, α -ZnS	Cubic	(001)	(110)	[110]	—	—	—	
			(001), (111)? (001)	(001)	[110], [100]	—	—	—
	Caesium chloride, NH ₄ Cl Ammonium bromide, NH ₄ Br	Rock salt, O_h	(001)	(110)	[001]	—	—	—
				(111)	(001)	[110]	—	—
	Zinc blende, T_d	Fluorspar, O_h	(110)	—	—	—	—	—
				(111)	[112]?	—	—	—
	Rutile, TiO ₂	Tetragonal Rutile, D_{2h}	(110), (100)	—	—	{(101) (101)}	($\bar{1}$ 01) (301)	0.908 0.190
	Beryllia, BeO Red zinc ore, ZnO Wurzite, β -ZnS Greenockite, α -CdS Jodargyrite, α -AgI Millerite, NiS	Hexagonal	(1010), (0001)? (0001), (1010)	—	—	—	—	—
				—	—	—	—	—
		Wurzite, C_{6v}	(1010), (0001) (0001)	—	—	—	—	—
—				—	($\bar{1}$ 012)	1010	0.380	
Brucite, Mg(OH) ₂ Corundum, Al ₂ O ₃ Magnesite, MgCO ₃ Calc-spar, CaCO ₃ Manganese spar, MnCO ₃ Chalybite, FeCO ₃ Zinc spar, ZnCO ₃ Sodium nitrate, NaNO ₃	Rhomboidal Brucite, D_{3d}	(111)	(111)?	—	—	—	—	
			—	—	{(111) (100)? (011)?	(111) (011) (100)	0.635 0.202 0.799	
	Corundum, D_{3d}	(100)	(111), (111)?	[011]	—	(011)	(100)	0.694
			(111)	[011]	(011)?	(100)	0.781	
	Calc-spar, D_3	(100)	—	—	(011)	(100)	0.753	
			—	—	(011)	(100)	0.753	

pointed out (444) that ions of the same sign never approach each other during glide, since this would lead to repulsion forces perpendicular to the glide plane. It is true, of course, that this selective

principle, which apparently does not conflict with results obtained with other ionic crystals, is in itself inadequate. An infinite number of pairs of T and t satisfy this requirement (445).

As with the metal crystals so, too, in the case of ionic crystals an increase in temperature or pressure does not cause the disappearance of glide elements which operate under normal conditions of temperature and pressure; at elevated temperatures, on the other hand, new glide planes have been observed. For instance, in sodium chloride at elevated temperatures, in addition to the dodecahedral system which is normally operative, glide occurs also in the (111) plane (446); an increase in the number of glide planes with rising temperature also takes place with rhombic crystals of baryte (BaSO_4), celestine (SrSO_4) and anglesite (PbSO_4) (447). Glide in cube planes was observed with sodium chloride [(448), (449); cf. also (450)], particularly in the case of wetted crystals with certain special orientations relative to the direction of tension (451); here, too, the glide direction is the face diagonal.

Owing to the importance of *dodecahedral glide* in crystals of the sodium-chloride type, some particulars should be given of the *lattice rotation* by which it is accompanied in tension (452). First it is observed that for all orientations the same shear stress occurs in at least two glide systems, since t and the normals to T are interchangeable. Geometrically considered, therefore, single glide cannot be expected for any initial orientation of the crystal. The cube edges are found to be stable final positions; the face diagonals represent unstable positions: tensile or compressive stress parallel to the body diagonals cannot lead to dodecahedral glide, since a force acting in this direction cannot produce a non-vanishing resolved shear stress in any such glide system [three (110) planes lie parallel to the direction of force; in the remaining three the glide directions are transverse to it].

It should be emphasized in regard to *mechanical twinning* (which we do not propose to discuss further), that in many cases the movement of all lattice points is not a simple shear. Polyatomic compounds rarely exhibit a straight line movement for all atoms. It is observed, however, that centres of gravity of polyatomic ions or molecules frequently move according to a simple shear (445). As regards the dynamics of twinning, an observation concerning the magnitude of the elastic shear strain parallel to the twin elements at the moment of twinning may be mentioned. Measurements carried out on rectangular parallelepipeds of calcite revealed, for two different directions of the compressive force, elastic shear

strains of $2.4 \cdot 10^{-3}$ and $3.5 \cdot 10^{-3}$ (453). Thus, as with metal crystals (see Section 51), the elastic shear at the start of twinning is only a small fraction of the strain due to twinning. In this case, too, the exact conditions of twinning could not be determined.

Although the *cleavability* of crystals has long been known, the principle by which the cleavage planes in the lattice are determined still remains obscure. Here again the geometrical properties of the lattice are certainly not the only relevant factors; the distribution of the electric charge is also important. A view which was originally

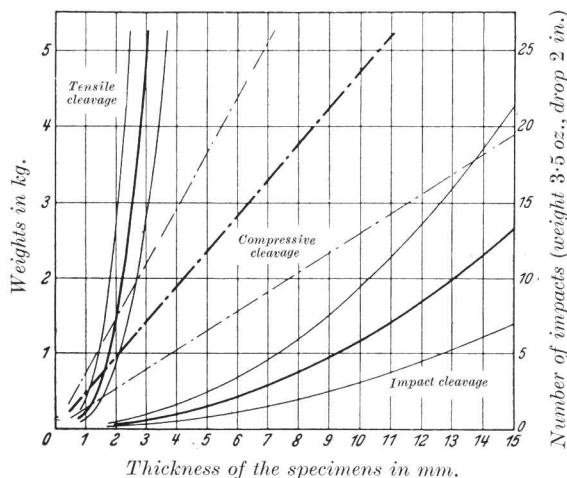


FIG. 175.—Cleavage of NaCl Crystals under Tensile, Compressive and Impact Stress (456).

expressed with reference to the cubic cleavage of sodium chloride (444) now appears to apply to many other cases also; as a result of the shear which precedes cleavage, ions of the same sign are moved so as to face each other; this produces forces of repulsion which lead to disintegration. However, like the analogous discussion in the case of glide, this condition is insufficient to explain cleavage.

A quantitative measure of cleavability with respect to a given plane is not available; qualitatively it is described as being very perfect, perfect, distinct and imperfect. In any case, cohesion perpendicular to the cleavage planes is very slight, and it is this circumstance which determines the appearance of these planes as planes of fracture. The absence of a quantitative measure of cleavability is due to the complex stress systems which arise in the

usual methods of cleaving. In recent years attempts have been made to facilitate the quantitative determination of cleavability by standardizing the methods of testing (454). According to the type of test employed a distinction is made between tensile cleavage, in which the compressed portion of the crystal is hollow so that the crack appears on the underside subjected to maximum extension, compression cleavage and impact cleavage [cf. also (455)]; the relations between the necessary forces or energies and the dimensions of the crystal are then examined. A graph showing the results obtained with the three types of cleavage, using the NaCl crystal, is given in Fig. 175, which shows the influence of the thickness of the specimen and also indicates the scatter of the measurements. Similar relationships between the work of cleavage and the thickness of the specimen were also found for lead sulphide (457) and anhydrite (458).

The cleavage of NaCl crystals along a (110) plane indicates that this is only an apparent plane built up stepwise from cubic or (110) vicinal planes [(455), (459)]. It is surprising that impact cleavage along this plane should require less energy than along a cubic plane (460). This illustrates well the complexity of cleavage phenomena.

Unlike the cleavage test, the tensile and compression tests are characterized by very simple states of stress. In this type of test quantitative relationships corresponding to those described for metallic crystals are found to apply, at least for glide.

67. *Initiation of Glide. Shear Stress Law*

The behaviour of ionic crystals under tension at room temperature differs substantially from that of the metallic crystals in the amount of extension that can be achieved. With numerous metallic crystals extensions of many hundreds per cent. are possible, as against not more than a few per cent. for ionic crystals. Systematic investigation of the latter therefore demands much more sensitive instruments. Owing to the brittleness of the material great care must be taken, in the tensile tests, to avoid bending due to eccentric application of the load. Even a slight eccentricity may reduce the strength by 50 per cent. and more (461). Pivoting of the grips into which the crystal specimen is usually cemented in universal joints or on needle points is therefore recommended. In order to ensure a uniform increase of the load, free from vibration, the tensile force is applied usually by floaters, often with additional lever transmission; the buoyancy of the floater is reduced by lowering the water level. The extension is measured, with the upper grips at rest, either

directly by microscopic observation of the displacement of the lower grips, or by means of a mirror apparatus which, at very high magnifications, can at the same time be used for photographic recording [for particulars of the technique of tension and compression tests see (462), (463), (452), (464)]. The methods developed in recent years for growing large crystals have greatly facilitated the systematic testing of ionic crystals (cf. Sections 13 and 14).

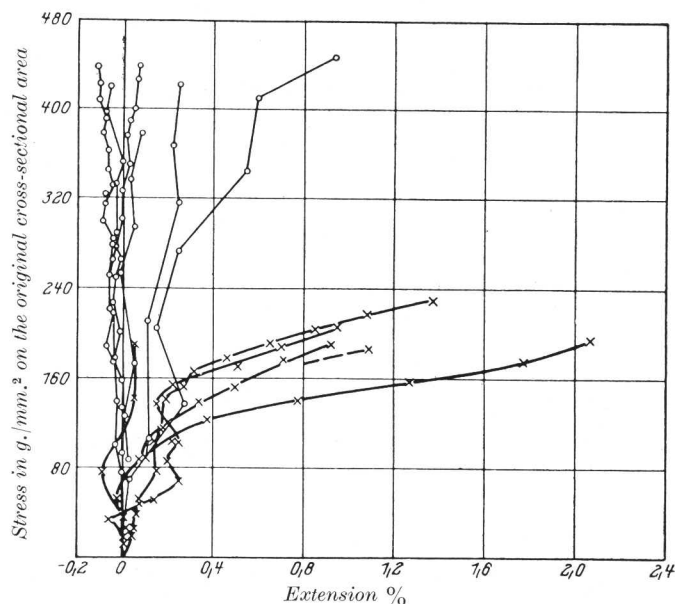
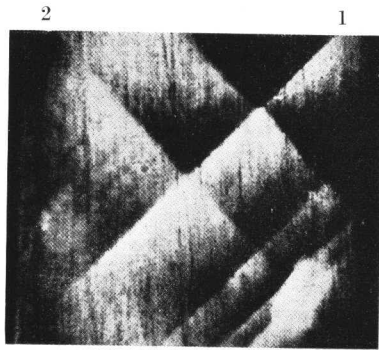
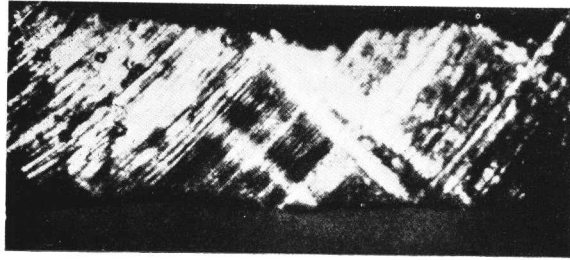


FIG. 176.—Stress-Strain Curves of Natural NaCl Crystals (452).
X = annealed for 3 days at about 600° C.; O = unannealed.

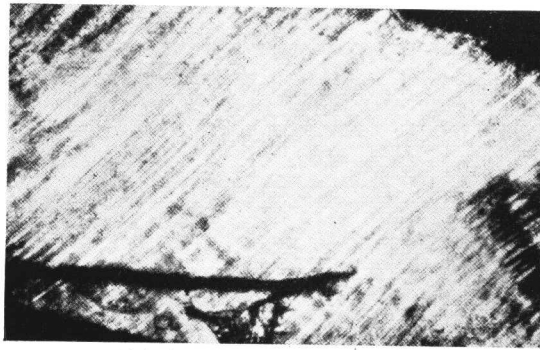
A few stress-strain curves obtained on small cylindrical bars of rock salt oriented parallel to the cube edge are shown in Fig. 176. It is seen that this material, which in the initial state breaks in a brittle manner, exhibits marked elongations after annealing at 600° C. Although in this instance the curves are not very accurate, the tests nevertheless reveal the existence of a definite *yield point*. In other ways, too, a stress value is observed beyond which the deformation increases rapidly. From this point onwards, for instance, glide bands appear on the surface of the crystals. The extension can be followed very closely in transmitted polarized light, owing to the double refraction which results from the residual



(a) Determination of the start of glide (463).



(b) Bent crystal (465).



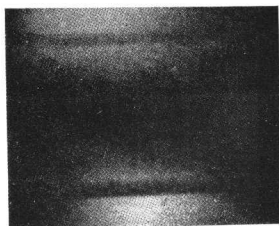
(c) Compressed crystal (465).

FIG. 177 (a)-(c).—Glide Bands in Deformed NaCl Crystals, Rendered Visible by Stress Birefringence.

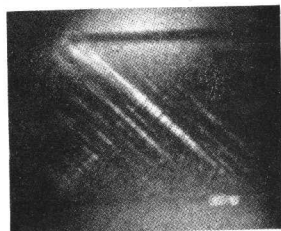
stresses. Fig. 177*a* shows the first glides in a tempered crystal of sodium chloride. No change was observed up to a stress of

78 g./mm.². After this stress had been maintained for 20 seconds,

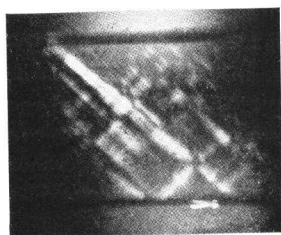
*Un-
stressed*



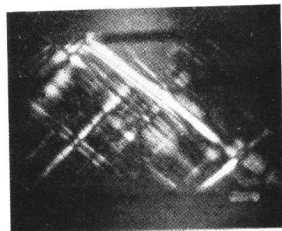
95.5
g./mm.² :
start of
flow



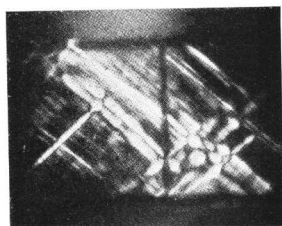
154.5
g./mm.²



206
g./mm.²



*Fractured
at 254
g./mm.²*



the bands shown as 1 and 2 appeared suddenly. The other bands also appeared suddenly after varying intervals, without the load being increased ("jerky deformation by glide"). Crystals with glide planes packed very closely together are shown in Fig. 177, *b* and *c*.

Investigation of potassium halide crystals by means of polarized light clearly revealed various stages of deformation in crystals (466). With increasing tensile stress local glide processes occur in the interior of crystals of KCl, KBr and KI (at a stress of about 50 g./mm.²), followed by the first passage of a glide plane through the entire cross-section. As the stress increases so the glide planes multiply, until finally there is a more or less sudden increase in the intensity of all the glide zones present (yielding). Continued increase of the stress gives rise from time to time to thicker packets of glide zones. By way of example, Fig. 178 illustrates the double refraction along the glide planes of a KCl crystal grown from the melt. The stage of deformation which corresponds to yielding coincides with the appearance of visible glide bands.

An X-ray determination of the onset of plasticity is based on the appearance of distorted Laue interferences [asterism (462)]. However, the stress limit which is thus defined does not coincide with that revealed by the stress-strain curve; it corresponds with permanent deformations which are already clearly per-

FIG. 178.—Stress Birefringence in a KCl Crystal which has been Extended by Various Amounts (466).

ceptible (467). The start of plastic deformation can also be determined photo-chemically. Unlike the X-ray method, the change in colour gives very low values, which probably coincide approximately with the stresses corresponding to the first deformations revealed by polarized light (468).

The *shear stress law* which was established for metallic crystals applies also to the yield point of alkali halide crystals, as revealed by the appearance of visible glide bands [for NaCl (469), for KCl, KBr and KI (470); for wetted NaCl crystals see Section 72]. The dependence of the tensile yield point on the orientation according to the shear stress law would be represented by the *yield surface* shown

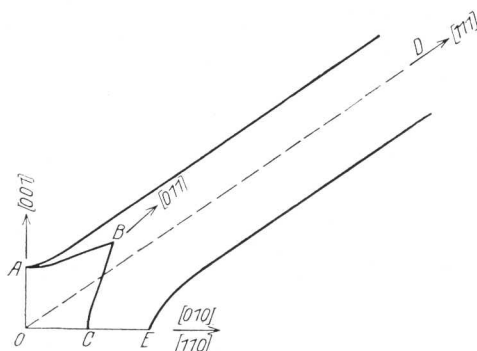


FIG. 179.—Section through the Yield Surface of Alkali Halide Crystals Assuming Dodecahedral Glide (452). $OABCO$ Intersects with (100) , $OADEO$ Intersects with (110) .

in section in Fig. 179 if dodecahedral glide alone is assumed. Crystals exhibit minimum resistance to flow parallel to the cube edges; the yield stress of rods parallel to the body diagonal is infinitely high, and directions near to this are distinguished by extremely high values.

Figures for the yield point of ionic crystals can be given only with some reserve. The critical shear stress of glide systems is, indeed, a typical example of the "structure-sensitive" properties of crystals (cf. Section 60). The tensile yield point values for natural rock salt crystals therefore vary within wide limits according to their place of occurrence and previous history [70–500 g./mm.² (464)]. In order to avoid the differences existing between natural crystals, recent plasticity investigations have been carried out with synthetically produced crystals of uniform quality. From the above values, *elastic shear* strains of magnitude 10^{-4} are obtained

(471). Therefore the same statement is true for the limit of stability of the dodecahedral plane in the [101] direction as for the glide planes of metallic crystals and twin planes: namely, that the elastic shear strain at the start of plastic yielding is only a small fraction of the displacement which occurs in the ensuing glide.

For thin crystals, a definite dependence of yield point upon the diameter was observed (472). The various sections were produced

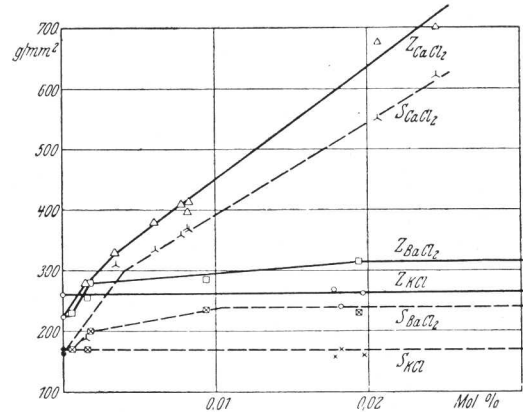


FIG. 180.—Effect of Admixtures on the Yield Point (S) and Tensile Strength (Z) of NaCl Crystals (475).

by dissolving rods of sodium chloride in their own melt. The yield point (σ_s) increases as the initial cross-section is reduced, the observed results being well expressed by the curve

$$\sigma_s(\text{kg./mm.}^2) = \frac{0.330}{d_0} + 0.020(d_0 = \text{initial diameter in mm.})$$

The effect of admixtures was exhaustively investigated on sodium-chloride crystals grown from the melt. Shear hardening is very pronounced so long as the formation of a solid solution can be assumed; in this respect the addition of bivalent cations is much more effective than that of monovalent cations (473). Where precipitation is ultra-microscopically observable, the effect is either nil or only very slight. Very definite hardening results from the addition of PbCl_2 , which in a concentration of about 10^{-3} mol.-per cent. (one molecule of PbCl_2 to about 100,000 molecules of NaCl) increases the yield point three-fold (474). The effect of additions of CaCl_2 , BaCl_2 and KCl is seen in Fig. 180; SrCl_2 behaves in the same way as CaCl_2 ; MgCl_2 in amounts up to 0.1 mol.-per cent. has no

effect. If two compounds which cannot be detected ultra-microscopically are added simultaneously, their hardening effect is additive, as with metals (cf. Section 45); this corresponds to the independent insertion of the impurities into the lattice (476). Unlike the result when the yield point is determined from the appearance of glide bands, the photochemically determined onset of plasticity of NaCl crystals is not affected by additions of SrCl_2 (476a).

Attention has been drawn repeatedly to the importance of a previous *heat treatment*. Fig. 176 shows the very great influence on plasticity of annealing for several days. The yield point, which had in most cases previously exceeded the strength, was reduced to about 100 g./mm.² Systematic investigation of the effect of annealing at various temperatures showed that the individual differences between sodium chloride crystals of different origin are prone to disappear as the temperature of annealing rises, and tend to a common minimum value after treatment at 600° C. Still further increase of the temperature of annealing causes the yield point to rise again (464). Annealing was also found to reduce the yield point of natural sylvine. Pure crystals of KCl and KBr, grown from the melt and from solution, showed no effect, as was to be expected from their method of production (470).

The softening which results from annealing must be regarded as a recovery effect. This is seen mainly from the fact that, in the polarization microscope, heat treatment is revealed by the elimination of the stresses which are always present in natural crystals as a result of plastic deformation (by earth pressure). How far the renewed increase in strength at high temperatures results from a temperature dependence of the solubility of the admixture cannot yet be decided. In any case, initially different crystals can be brought to a comparable state by suitable annealing. Natural crystals of rock salt of the most diverse origin give a value of about 40 g./mm.² for the critical shear stress of the dodecahedral glide system after annealing at 600° C. for 6 hours. In Table XXV are given the values obtained with crystals grown from the melt under specially controlled conditions (De Haen material of maximum purity; the unglazed porcelain crucible was used for a single melt only).

Specially noteworthy is the value for crystals of rock salt grown from the melt. It is almost twice that of the annealed natural crystals, and it cannot be substantially reduced by a similar anneal.

Investigation of the dependence of the yield point upon temperature showed a very pronounced decrease at high testing temperatures [(446), (477)]. At temperatures of about 100° C., however, there

seems to be a range of slight dependence upon temperature. For the stress limit determined by X-rays which, as already mentioned, greatly exceeds the yield point, the values for sodium chloride were

TABLE XXV

Critical Shear Stresses of the Dodecahedral Glide Systems of Alkali Halide Crystals Grown from the Melt

Salt.	Total of impurities, weight, %.	Critical shear stress of the dodecahedral glide system, g./mm. ² .	Literature.
NaCl . .	0.030	75	(476)
KCl . .	0.016	50	(466)
KBr . .	0.030	80	
KI . .	0.020	70	

found to fall to zero at the melting point both in tensile and compressive tests (462). This behaviour differs characteristically from that of metallic crystals (Section 47).

A comparison of the critical shear stresses of the glide systems obtained in tension or compression with those obtained with other types of loading is possible as yet only for torsion (478). The dependence upon orientation of the torsional yield point of rock salt crystals drawn from the melt is also governed in general by the shear stress law (minimum yield point for orientations close to the [101] direction); rods parallel to the cube edge cannot be twisted by dodecahedral glide. The critical shear stress was found to be 111 g./mm.². If we accept the condition for torsional yielding as discussed in Section

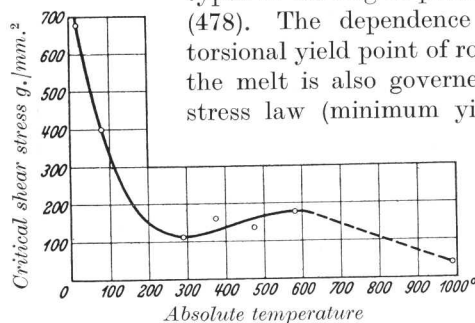


FIG. 181.—The Critical Shear Stress, under Torsion, as a Function of Temperature. NaCl Crystals (478).

41, according to which the whole section of the crystal has to be deformed, we obtain a value of 70 g./mm.², which agrees sufficiently with the value determined in tension. The influence of temperature on the critical shear stress as revealed by torsion tests is shown in Fig. 181. If the temperature is reduced

from room temperature to -253°C . it increases about eightfold, but even when the temperature is raised, a slight increase in yield point is observed in the neighbourhood of 300°C . Investigations into the bending of rods of cubic orientation are discussed in [(479) to (481) and (467)].

68. *Further Course of the Glide Process*

The further course of the glide process in ionic crystals has received far less attention than the start of glide. The establishment of quantitative criteria, such as work-hardening curves, has been hampered by the fact that instead of glide taking place in one glide system only, several equivalent and intersecting systems participate in the deformation. However, the extension of sodium- and potassium-halide crystals oriented parallel to the cube edge, for example, does not proceed by the same amounts of glide along the four geometrically equivalent systems. Usually only two related dodecahedral systems become active (they belong to the same (100) zone), and it frequently happens that one of these is specially preferred. This means that the orientation of the crystal does not usually remain unchanged, as would correspond to the stable initial position; instead, where extension is large, lattice rotations up to approximately 30° occur.

It is clear from the shape of the stress-strain curves which show a rise in stress with increasing extension, that here, too, the deformation is accompanied by a *shear hardening* of the operative glide systems (cf. Fig. 176). Such an increase in stress always points to an increase in the critical shear strength of the operative system (Section 43).

The amount of extension which can be achieved under tension at room temperature does not usually exceed more than a few per cent. Extensions of more than 50 per cent. have, however, been reported for very thin annealed rods of rock salt. The increase in extension with reduction in cross-section, like the similar increase in yield point, starts at initial diameters of about 0.6 mm., at which it is very marked (472). Even when rods of sodium chloride are loaded parallel to the body diagonals, a perceptible though small extension precedes fracture. It is clear from the orientation relationship discussed above that this extension cannot result from dodecahedral glide; instead, glide occurs here on the cube planes, as is shown in (451).

As the temperature rises and the yield point falls, there is substantial increase in the amount of plastic deformation that can be

obtained. Crystals of rock salt can be easily bent and twisted by hand in a flame of alcohol (482). At temperatures above 400° C. there is obvious necking which may produce local extensions of up to thirty times (462). The reduction of the yield stress with increasing temperature corresponding to varying amounts of strain is seen clearly from Fig. 182, in which the initial portions of the stress-strain curves of melt-grown crystals of rock salt are represented.

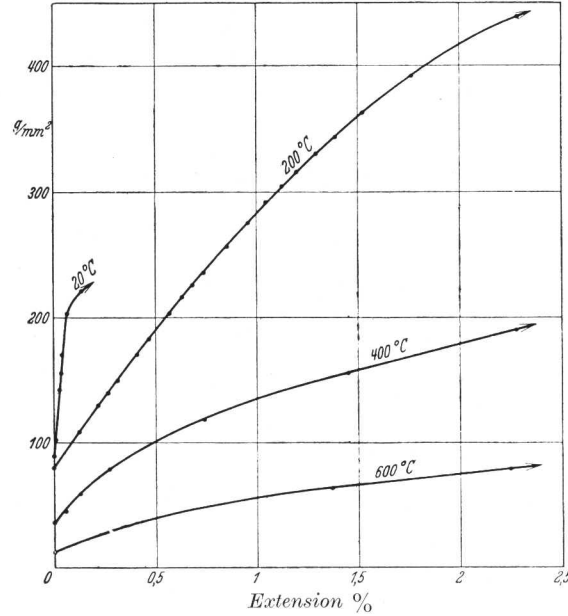


FIG. 182.—The Stress-Strain Curves of NaCl Crystals as a Function of Temperature (477).

The increase of plasticity due to increasing temperature was measured by torsion tests in (483) and (478).

Measurement of the compression of square cleaved specimens of alkali halide crystals (down to 1/10 of the original height) has led to the discovery of a very simple relationship. If s is the compressive strain referred to the final height ($s = \frac{h_0 - h}{h}$), λ the "slenderness" of the specimens ($\lambda = h_0/d$; d = length of edge of the square section), then for not too low pressures p (from about 2000 kg./cm.² upwards) $s = b\lambda p$, where b represents a characteristic constant of the material. Table XXVI, which contains the values

which have so far been determined for b , reveals a relationship between these and the lattice constants. Where the cation is the same, b increases approximately linearly with the lattice constant. At the high pressures employed, the origin and previous history of the crystals are no longer found to exert an important influence [(484), (485), (486)].

TABLE XXVI
Compression of Alkali Halide Crystals (486)

Material.	b , cm. ² /kg.	Lattice constant, Å.
NaCl	0.0020	5.628
NaBr	0.0052	5.96 ₂
NaI	0.0086	6.46 ₂
KCl	0.0044	6.27 ₇
KBr	0.0070	6.58 ₆
KI	0.0094	7.05 ₂

Mention may finally be made of experiments with load reversal. It was observed long ago that the hardening of rock salt crystals in bending tests is directional (487). *Inhomogeneously* stressed crystals therefore show the phenomenon which came to be known later as the *Bauschinger effect* [cf. also (488)]. Similarly, *hysteresis* and *after-effect* occur in plastically bent crystals. The cause of this behaviour should be sought in the internal stresses stored in the crystal as a result of the inhomogeneous stressing, the existence of which stresses can be made directly visible by the movements which occur after removal of the surface layers by partial dissolution (481).

69. *Fracture of Crystals. Sohncke's Normal Stress Law*

As mentioned in Section 53, the first systematic investigations into the influence of the crystal orientation upon the tensile strength of sodium chloride crystals led to the formulation of the *Normal Stress Law* (489). For all orientations ([100], [110], [120] and [111]) of tensile direction that have been examined the cube plane appeared as fracture plane; as the angle between fracture plane and the direction of pull was reduced, the tensile strength of the specimen increased to an extent roughly consistent with the existence of a critical normal stress of the cube plane [equation (40/2)]. In view of subsequent investigations which revealed that the nature of the planes forming the surface of the specimen influences the magnitude of the tensile strength, the normal stress law was rejected (461), and

not until it had been rediscovered many years later on metal crystals was it also possible to demonstrate its validity for crystals of rock salt (490). It was found that the experiments which had led to the rejection of the law could also be regarded as its confirmation, provided there was one pair of surface planes common to the variously oriented rods. The use of cylindrical specimens avoids the surface effect, which can perhaps be regarded as an increase of the tensile strength due to the preparation of the specimen. Whereas theoretically the tensile strengths to be expected for the [100], [110] and [111] directions should be proportional to 1 : 2 : 3, the ratios actually observed are 1 : 2.24 : 3.32 when based on maximum values, and 1 : 2.22 : 3.51 for mean values. It is a striking fact, however, that the values for a [112] direction do not fit into this picture : instead of the (theoretically) expected factor of 1.5, an observed strength of about double that amount is obtained [(452); cf. also (469)]. These tests show that constancy either of the normal dilatation perpendicular to the cubic fracture plane, or of the elastic energy, is excluded as a condition of fracture [(491), (492)].

So far the normal stress law has not been confirmed for melt-grown crystals of KCl and KBr. The tensile strengths in this case are so widely scattered that the scatter range has been resolved into several maxima of frequency. Nevertheless, the values obtained for tensile directions lying in a cube plane do not appear to conflict with the assumption of a constant normal strength of the cube plane of fracture. No influence of the orientation of the surface planes was observed [(466), (470)].

A model showing the relationship between orientation and tensile strength of cubic crystals which fracture along the cube plane according to the normal stress law is illustrated in Fig. 183. The minimum strength corresponds to the direction of the edge of the cube; the maximum strength, which is three times as great, to the space diagonal.

The tensile strength values for the cube plane of rock salt crystals, like the values for the yield point, fluctuate within wide limits, usually between 200 and 600 g./mm.², according to origin and history. Sometimes values up to 1800 g./mm.² are obtained (464). For the *elastic dilatation* perpendicular to the cube plane at the moment of fracture the order of magnitude of 10^{-4} is again obtained; owing to the dependence of tensile strength and modulus of elasticity upon orientation, the normal dilatation in tension parallel to the space diagonal is about three times as high as in tension parallel to the edge of the cube.

The tensile strength of sodium chloride crystals, like the yield point and elongation, also shows dependence on the *cross-sectional area* of the specimen. This, too, becomes observable only from very small diameters (about 0.8 mm.) downwards; increases up to twenty times the normal strength have been determined (472). In the case of thin specimens produced by dissolution in water (493)

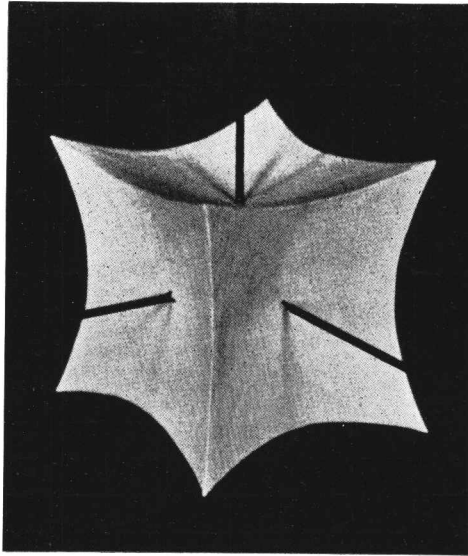


FIG. 183.—Model showing the Tensile Strength of Cubic Crystals which Fracture along the Cube Plane (452).

instead of in the melt, the objection could be raised that the water might exert a hardening effect [(480); cf. also Section 72].

The tensile strength of rock salt is influenced by *additions* in much the same way as the yield point. Tensile strengthening and shear hardening proceed along parallel lines, as is seen from Fig. 180. If two added constituents which form solid solutions are present simultaneously in small quantities, the strengthening effect of the single constituents becomes additive (476). Formally, therefore, the tensile strengthening caused by the additions can be expressed in the same way as the shear hardening caused by alloying (Section 45).

Annealing, too, affects tensile strength in the same way as has been

described above for the yield point. Fig. 184 shows the effects obtained with natural rock salt crystals of various origins. It will again be noted that the chief result of annealing for several hours at 600° C. is to equalize substantially the strength values, which originally differed very considerably. This common strength value (approx. 170 g./mm.²) represents a minimum which is reached after

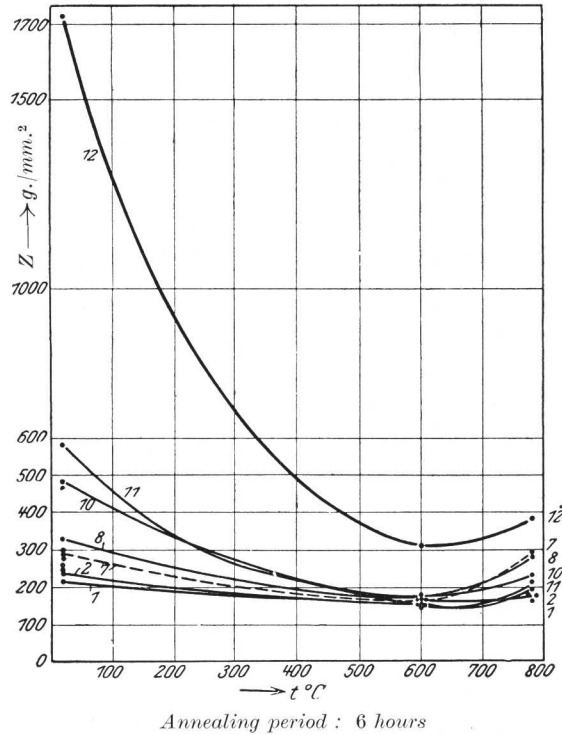


FIG. 184.—Effect of Annealing on the Tensile Strength of Natural NaCl Crystals of Various Origins (464).

the hardening arising from the previous history of the specimens has been eliminated. If the temperature of annealing is raised still further, there will be a slight increase in strength, no doubt owing to the presence of impurities.

Table XXVII summarizes the values for the normal strength of fracture planes of ionic crystals. It contains in the first place the values for melt-grown crystals of the NaCl type and produced from

De Haen preparations of maximum purity. Fluorspar was examined as a natural crystal, while strontium chloride, which also crystallizes in the fluorspar lattice, was investigated as a melt-grown crystal. Assuming the validity of the normal stress law, the extreme values for the tensile strength of *octahedral fracture planes* vary in the proportion of 3 : 1. Whereas for cube cleavage the strength maximum is found parallel to the space diagonal, and the minimum parallel to the edge of the cube, the exact opposite is true for octahedral cleavage.

It must be emphasized here that the low tensile strengths observed and their marked dependence on the orientation are closely related to the appearance of smooth fracture planes. If these are absent,

TABLE XXVII

Normal Strength Values of the Fracture Planes of Ionic Crystals

Salt.	Fracture plane.	Normal strength of fracture plane, g./mm. ² .	Reference.
NaCl . . .	} (100)	220	} (476)
KCl . . .		200	
KBr . . .		250	} (466)
KI . . .		240	
CaF ₂ . . .	} (111)	1550-2430 *	(495)
SrCl ₂ . . .		approx. 1100	(496)

* Cf. also (494), in which differences in strength in the proportion of 1 : 3 were observed on crystals of different origin.

or if the fracture proceeds more or less at random through the crystal, higher strength values and an appreciably lower anisotropy are obtained.

In regard to the *temperature dependence* of the tensile strength, most of the available results relate to rock salt crystals. It is necessary in this case to distinguish between static tests and those in which the load is increased rapidly. In the first case the crystal stretches considerably before it fractures, especially at high temperatures; in the second, plastic extension of the crystal is largely prevented by the rapid increase in load, with the result that the tensile strength can be determined without being affected by tensile strengthening. Natural crystals exhibited a virtually constant tensile strength of about 450 g./mm.² within the temperature range of -190° C. to +600° C.; the scatter was of the order of only 5-10 per cent. (462).

If, on the other hand, the load is increased so slowly that marked plastic deformation can occur, appreciable tensile strengthening takes place corresponding to the extent of the deformation; this strengthening can amount to thirty times the tensile strength value at room temperature. Fig. 185 shows the increase of the tensile strength of natural rock salt crystals as a function of the reduction of area during extension. The graph gives the results obtained at high temperatures (up to $600^{\circ}\text{C}.$) as well as after cooling the crystals down to room temperature. The fact that all experimental results could be expressed by a smooth curve is remarkable, since it indicates that the magnitude of the tensile strength is determined solely by

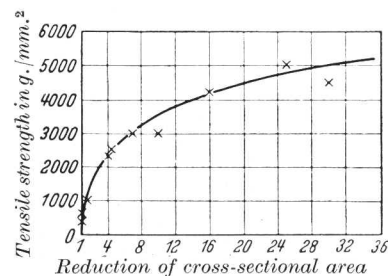


FIG. 185.—Tensile Strength of Rock Salt Crystals as a Function of Extension (Reduction of Cross-sectional Area) (462).

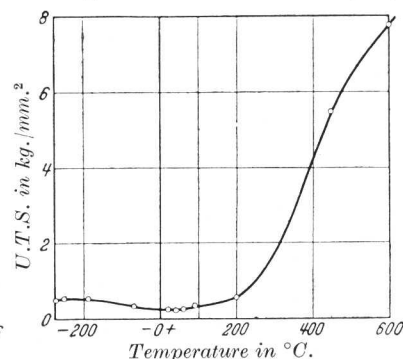


FIG. 186.—The Static Tensile Strength of Rock Salt Crystals as a Function of Temperature [(477), (497), (498), (499)].

the elongation, and not by the temperature at which the elongation takes place. At $600^{\circ}\text{C}.$ certain types of rock salt exhibit tensile strengths as high as $10,000\text{ g./mm.}^2$ (477). Fig. 186 shows the temperature dependence of the static tensile strength of melt-grown NaCl crystals (normal strength for the cubic fracture plane) within the range -269° to $600^{\circ}\text{C}.$ At the lowest temperatures (brittle fracture) it is roughly constant; it diminishes as the temperature rises, reaches a minimum at about $+40^{\circ}\text{C}.$ and increases rapidly at higher temperatures.

Very interesting observations have been made on the temperature dependence of the tensile strength of NaCl crystals containing various amounts of SrCl_2 . The results of the experiments are given in Fig. 187. At temperatures above $-100^{\circ}\text{C}.$ the strengthening effect of the added constituent (which is also indicated by the critical shear stress of the glide planes) becomes increasingly

apparent as the temperature of the test is raised. The position is reversed for temperatures below this value. In this case the strength of the contaminated crystal is always lower than that of the pure crystal, the difference increasing with the percentage of ingredient and with a reduction of the temperature.

It seems that both a determination of the dependence of the *strain-hardening* curve on temperature, and an investigation of the critical normal strength of the fracture plane as a function of the glide strain and the temperature, are necessary for a systematic study of the matter.

So far little is known about the mechanism of *tensile fracture*. Clearly it is a process that takes place at a finite speed. This fact is demonstrated by the deep cracks, parallel to the cubic cleavage plane, which are often found on tensile specimens of annealed NaCl crystals. With crystals of potassium halides between crossed Nicols it has sometimes been possible to observe the progress of fracture across the section of the specimen, starting from one side (466). Preliminary cinematographic tests to ascertain the duration

of the fracture of rock salt crystals led in three cases to times of 10^{-3} to 10^{-4} seconds (500).

Determinations of the *bending strength*, which for brittle fracture should coincide with the tensile strength, gave substantially different values for different orientations of NaCl crystals (501); it is remarkable, however, that these values were twice as high as the corresponding tensile strengths.¹ This discrepancy may be due partly to the unjustified use of the theory of elasticity. It is certain that at the moment of fracture, plastic deformations are already present in the outer parts of the bar, and that this causes appreciable deviation from the theoretical elastic stress distribution (502). Moreover,

¹ Compare with the analogous case that greater force is needed to produce tensile cleavage than compressive cleavage in the bent crystal (Fig. 175).

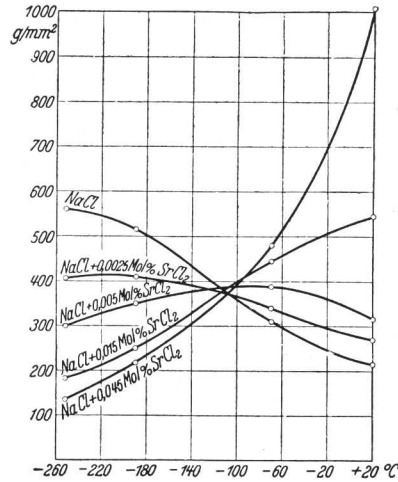


FIG. 187.—Tensile Strength of Rock Salt Crystals Containing Various Amounts of SrCl_2 as a Function of Temperature (498).

the plastic deformation of the outer zones may have already produced tensile strengthening there. Both factors may serve to explain the high *torsional strengths* which have been obtained experimentally [about 2700 g./mm.² (503)]. In this case the surface of fracture often consists of several planes. The cube plane, which is distinguished by the maximum value of the normal stress, is always very prominent in such experiments (478).

Owing to the fact that the normal stress law has so far been confirmed only for temperatures at which fracture is preceded by more or less marked deformation, this law has recently been regarded as originating from a law of strain strengthening from which no inference can be made about the behaviour of undeformed crystals (504). It is clear, in fact, from static tensile tests carried out with NaCl crystals at elevated temperatures that tensile strengthening can be very considerable. Nevertheless, in view of the extremely diverse gliding possibilities which are available in the various tensile directions (see above), it seems to us that the normal stress law, which was established at room temperature for crystals of the NaCl type, usually at small plastic deformations, should be regarded as analogous to the shear stress law, and should be applied to cases where no deformation has taken place.

70. *Hardness* (see 505)

Hardness, which is closely related to the plasticity and strength of crystals, is a property much more obscure than the critical shear stress of the glide systems or the normal strength of the fracture planes which have been discussed above. In reality the term embraces many properties which are distinguished according to the method by which the "hardness" is determined. As a characteristic property of materials, hardness is technically very important; a further advantage is the relative ease with which it can be measured.

The various methods for determining hardness can be summarized as follows (see 506):

I. The penetrating body moves along the surface of the test piece:

1. Comparison of hardness by mutual scratching.
2. Scratching with a hard point under a controlled load:
 - (a) measurement of the load at which the scratches become just visible;
 - (b) measurement of the load for a given width of scratch;
 - (c) measurement of the width of scratch at a given load.

3. Determination of the wear resistance of the test surface or of its resistance to penetration by a drill or a rotating disc.

II. The penetrating body moves vertically relative to the test surface :

1. Indentation tests (ball or cone indentation).

2. Impact test. A punch of a fixed shape is driven into the surface of the specimen with a given energy.

An intermediate position is taken up by a method which derives hardness from the damping of an oscillating pendulum which rests on a ball, knife edge or point on the test surface. Finally, mention should be made of a method which measures hardness from the magnitude of the rebound of a small drop-hammer.

From the above summary it is seen that, as mentioned above, hardness is not a uniquely defined quantity. Quantitative comparisons become possible only if the same test procedure is applied. To-day it is still impossible to express hardness values in terms of simple mechanical properties.

The following remarks relate to the various methods of testing and the hardness values obtained therewith.

The basis for the testing of hardness by mutual scratching is provided by Mohs' hardness scale, the standard minerals of which are shown in Table XXVIII.

TABLE XXVIII

Hardness Scale (Mohs)

1. Talc	Greasy to the touch	$\left. \begin{array}{l} \text{can be scratched} \\ \text{with the finger-} \\ \text{nail} \end{array} \right\}$	$\left. \begin{array}{l} \text{can be easily} \\ \text{scratched with} \\ \text{a knife} \end{array} \right\}$
2. Rock salt			
3. Calcite	$\left. \begin{array}{l} \text{Impossible to scratch} \\ \text{with a knife; they} \\ \text{will scratch plate} \\ \text{glass} \end{array} \right\}$	$\left. \begin{array}{l} \text{sparking occurs when} \\ \text{struck by steel} \end{array} \right\}$	
4. Fluorite			
5. Apatite			
6. Feldspar			
7. Quartz			
8. Topas			
9. Corundum			
10. Diamond			

A material that is not scratched by a mineral of hardness number n , but is scratched by a mineral of number $(n + 1)$, has a hardness which lies between these two numbers and is therefore designated by $(n + 1/2)$. Much finer differences than are discernible by this method can be obtained with the aid of the methods mentioned under I. 2. These more refined procedures for determining scratch-hardness make it possible to study anisotropy of hardness in various

directions on the same surface. A particularly convenient apparatus which operates on this principle is the Martens scratch-hardness testing machine (507). In Figs. 188 and 189 are shown the results of scratch-hardness determinations on the cube and octahedral planes of NaCl and fluorspar crystals, plotted in the form of curves (508). These are obtained by connecting the terminal points of lines which start from a point on the surface and whose length is proportional to the scratch-hardness measured in that direction.

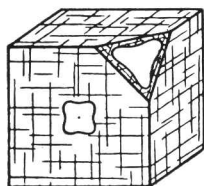


FIG. 188.—Scratch-hardness Patterns on (100) and (111) Planes of NaCl Crystals.

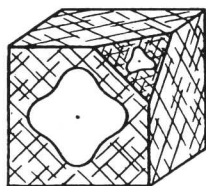


FIG. 189.—Scratch-hardness Patterns on (100) and (111) Planes of Fluorspar Crystals.

The relationship of the scratch-hardness to the crystal symmetry, and also to the cleavability as indicated in the figure, is seen clearly. It can be said in general that measurable differences in hardness appear especially in crystals that possess cleavability; if the surface under investigation is per-

pendicular to cleavage planes, the hardness parallel to the direction of cleavage is a minimum; if the surface is inclined to a cleavage plane, the hardness is usually different in opposite directions. Scratch-hardness measurements have also disclosed relationships between hardness, crystal structure and chemical constitution (506).

Drill-hardness tests serve only to determine surface hardness. The measure of drill-hardness is the number of revolutions which a drill or disc, under constant load, must perform in order to produce a hole of given depth. Hardness tests by grinding, too, yield as a rule only a measure of surface hardness. The work necessary under given conditions to grind away 1 cm.³ of the crystal parallel to the surface examined, serves as a measure of hardness. It was recently shown that this method is also sufficiently sensitive to detect anisotropy of hardness on the surfaces of crystals (509).

The indentation and impact methods, as well as the method of measuring hardness by rebound, are used mainly for metals. The Brinell Ball Hardness Number, in particular, is one of the most important technological data. This test has recently been systematically applied to alkali halide crystals. Table XXIX contains the values obtained in this way.

By means of such hardness measurements it was possible to follow

the work hardening of crystals by plastic compression and their softening by recrystallization. An investigation of the plasticity of ionic crystals by the *cone-indentation* method led to a formula

TABLE XXIX

Brinell Hardness of Alkali Halide Crystals [(485), (486)] (Based on the Diameter of the Indentation on the Cube Plane with a Load of 5 kg. and a Ball Diameter of 0.71 cm.)

Material.	Hardness.	Material.	Hardness.	Material.	Hardness.
NaCl .	12.4	NaI	8.4	KBr	5.4
NaBr .	9.2	KCl	5.8	KI	3.2

containing five constants of the material, representing the cone-indentation hardness at different temperatures and for various periods of pressure (510). This shows clearly that hardness is by no means a simple basic property. On the idealizing assumption that the forces are transmitted to the crystal by the cone indenter (apex angle 90°) only in a direction perpendicular to the crystal face, the distribution of shear stresses in the dodecahedral glide systems in the tested surface has been calculated; it was found to agree qualitatively with the pressure figures which appear on the cubic, rhombic, dodecahedral and octahedral faces of rock salt (511). The pendulum hardness test, too, was for long restricted to polycrystalline

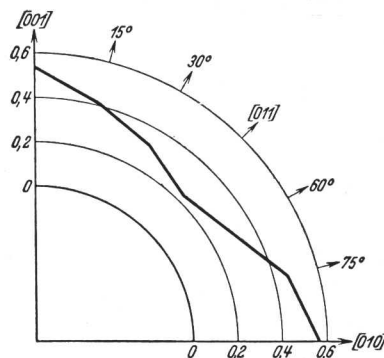


FIG. 190.—Anisotropy of the (001) Plane of NaCl Crystals as Determined by Pendulum-hardness Tests (514).

metals (512); recently, however, it has also been applied with success to the examination of ionic crystals [(513), (514)]. By way of example, Fig. 190 shows the anisotropy of hardness on the cube plane of rock salt, measured very accurately by this method.

In conclusion, it should be emphasized that we shall be unable to interpret so complicated a property as hardness until we have succeeded in relating the much simpler phenomena of crystal cleavage and deformation to the constitution and lattice structure of the

TABLE
Elasticity Coefficients (s_{ik}) of Ionic

Material.	Crystal.		s_{11} .	s_{12} .		
	Class.	System.				
Rock salt, NaCl	} O_h	cubic	24.3	— 5.26		
Sodium bromide, NaBr			23.0	— 5.0		
Sylvite, KCl			40.0	— 11.5		
Potassium bromide, KBr			27.4	— 1.38		
Potassium iodide, KI			29.4	— 5.3		
Fluorspar, CaF ₂			31.7	— 4.7		
Pyrites, FeS ₂			39.2	— 5.4		
Sodium chlorate, NaClO ₃			6.91	— 1.49		
			T_h		2.89	+ 0.44
			T'		24.6	+ 12.6
Beryl, Al ₂ Be ₃ (SiO ₃) ₆	D_{6h}	hexagonal	4.42	— 1.37		
Hæmatite, Fe ₂ O ₃	D_{3d}	rhomboidal	4.42	— 1.02		
Calc.-spar, CaCO ₃	D_3		11.3	— 3.74		
Quartz (rock crystal), SiO ₂	D_3		13.0	— 1.66		
Tourmaline	C_{3v}		3.99	— 1.03		
Topaz, (AlF ₂)SiO ₄	} V_h	rhombic	4.43	— 1.38		
Barytes, BaSO ₄			16.5	— 8.97		
Aragonite, CaCO ₃			6.96	— 3.04		

crystals. In addition, the quality of the surface will also need very careful consideration. Adsorption of polar molecules can cause, by the reduction of the cohesive forces near the surface by amounts corresponding to the energy of adsorption, very substantial reductions in hardness (more than 50 per cent.) (515).

71. *Effect of Cold Working on Various Properties. Recovery and Recrystallization*

We shall refrain from a detailed discussion of the anisotropy of the physical properties of ionic crystals, since the effect of cold working on these properties has not yet been studied quantitatively. We shall present only the elastic constants in Table XXX in so far as complete determinations were available.

As in the case of metal crystals, so, too, in that of the heteropolar crystals there is no evidence that *lattice dimensions* are influenced by deformation. The lattice constant of a plastically bent crystal of sylvine equals that of undeformed specimens within 0.5 per thousand. Diffusion of the K_α doublet was not observed (518). In agreement

XXX

Crystals (in dyn.-1/cm.² · 10⁻¹³)

s_{44}	s_{33}	s_{13}	s_{14}	s_{22}	s_{55}	s_{66}	s_{23}	Literature.
78.7	—	—	—	—	—	—	—	(516)
78.0	—	—	—	—	—	—	—	(517)
75.4	—	—	—	—	—	—	—	(517)
156.0	—	—	—	—	—	—	—	(516)
127.0	—	—	—	—	—	—	—	} (517)
161.0	—	—	—	—	—	—	—	
238.0	—	—	—	—	—	—	—	
29.6	—	—	—	—	—	—	—	
9.48	—	—	—	—	—	—	—	
83.6	—	—	—	—	—	—	—	
15.3	4.71	-0.86	—	—	—	—	—	
11.9	4.44	-0.23	+0.79 ₅	—	—	—	—	
40.3	17.5	-4.33	+9.15	—	—	—	—	
20.0 ₅	9.90	-1.52	-4.32	—	—	—	—	
15.1	6.15	-0.16	+0.58	—	—	—	—	
9.25	3.85	-0.86	—	3.53	7.53	7.64	-0.66	} (516)
84.0	10.7	-1.92	—	18.9	34.9	36.0	-2.51	
24.3	12.3	+0.43	—	13.2	39.0	23.5	-2.38	

with this *the changes in density* of NaCl crystals after deformation and heat treatment do not exceed 0.5 per cent. (519).

However, again in line with metal crystals, the virtual invariance of the lattice dimensions after cold working is by no means equivalent to complete intactness of the lattice. Attention has already been drawn in Section 67 to the stress birefringence which can be observed in polarized light after glide. An attempt to measure quantitatively the tensile (and compressive) stresses parallel to the operative (110) glide planes of NaCl crystals gave a value of about 2.3 kg./mm.² (463). The value of these local stresses exceeds considerably not only the yield point but also the tensile strength. Their determination is based on the proportionality within the elastic range between stress and birefringence. The distribution of the stresses corresponds to a bending of the glide packets. Very much higher stresses amounting to 60 kg./mm.² have been calculated from the asterism of the Laue photographs of bent NaCl crystals (520). Owing to the inhomogeneous distribution of these stresses along the operative glide planes there occurs in the vicinity a lattice distortion of not

more than 1° (521). As was observed with metal crystals (Section 59), reverse bending of the crystals is accompanied by a reversal of the bending of the lattice.

Attempts have also been made to determine the magnitude of internal stresses by measuring the absorption spectrum of deformed NaCl crystals (522). It has been found experimentally that the absorption maximum of coloured crystals (see below) which is at 4650 Å., is displaced after deformation by about 100 Å. towards the red. This indicates a reduction of the mean photo-electric work function for the most loosely held electron of the colour centres by $8 \cdot 10^{-14}$ erg per atom. If this energy were available as stored elastic energy in the ionic volume, it would imply local stresses of the order of 300 kg./mm.²

An attempt has been made to determine directly, on compressed crystals of synthetic KCl, the *lattice disturbances* which accompany deformation, by measuring the intensities of X-ray interferences and of the background scatter between the Debye-Scherrer circles [(518), (523)]. The disturbances accumulated in the vicinity of the operative glide planes do not merely reduce the absolute intensity in the directions of interference; they also modify the relative intensities of various reflexions. In accordance with their distribution they do not influence the width of the lines (524), but they increase the diffuse scattered radiation. The intensities of the various orders reflected from the cube plane, measured by means of an ionization spectrometer, do in fact show a reduction of the relative intensities of the higher orders in the compressed state compared with the undeformed state of the crystal. Based on this observation, an estimate of the lattice disturbances present after 3.8 per cent. compression indicates that about 2 per cent. of the lattice points are displaced from their normal positions with a maximum displacement of about 1/8 of the identity period in the direction of glide. Measurement of the intensity of the X-rays which had been diffusely scattered by a compressed KCl crystal (between the interference maxima) was carried out with a Geiger counter. It showed clearly the increase in scattered intensity resulting from lattice disturbances.

Changes in the *moduli of elasticity* as a result of plastic deformation have not so far been observed. Bending tests carried out on NaCl crystals showed that Hooke's Law was valid up to 97 per cent. of the fracture load (479).

The changes in the crystal lattice which accompany plastic deformation can be seen very clearly from their effect on the

phenomena of *coloration* which occur when the crystals are irradiated with ultra-violet light, X-rays or γ -rays. Crystals of NaCl, with which these investigations have been mainly carried out, become yellow by such irradiation. This is caused by the appearance of a selective absorption band, which at room temperature lies between 3500 and 5500 Å., with a definite maximum at 4650 Å. This absorption band is probably due to single sodium *atoms* which do not belong to the lattice and which absorb visible light; rock salt that has been coloured yellow by treatment with sodium vapour followed by sufficiently rapid cooling, shows exactly the same absorption spectrum (525). The free sodium atoms arise from the absorption of a quantum of radiation by a chlorine ion, by which process its extra electron is transferred to a sodium ion (526). The intensity of the colour increases with the intensity and duration of radiation, until finally a state of equilibrium is reached between the formation of atoms and the reverse formation of ions, so that the intensity of

the colour remains constant. In certain cases impurities dissolved in the lattice may undergo a sort of coagulation, and this may lead to a new coloration—the cause of which, however, is quite different (colours due to diffraction by submicroscopic particles).

There are two ways in which plastic deformation influences coloration [(527), (528)]. First, it diminishes the intensity of the existing colour as measured by the absorption coefficient in the maximum of the band, but without changing the spectral distribution; secondly, it increases the capacity for developing a colour by irradiation, *i.e.*, the absorption of crystals that are still uncoloured (cf. Figs. 191 and 192). In this way plastically deformed zones can be made visible to the eye by a simple device. Crystals grown from the melt or annealed crystals are more susceptible to colouring than natural crystals [(530), (531), (532)].

Although the greater part of the research into the effect of deformation upon colouring has been carried out on NaCl, particulars are also available for other crystals. A detailed discussion of the work which has been done in this field so far, together with particulars of experimental coloration tests, will be found in (533) and (528). It may be mentioned as an interesting fact that the twinned parts

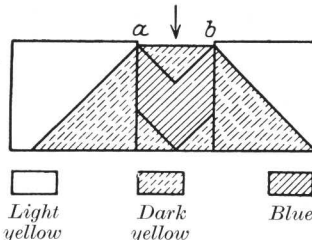


FIG. 191.—Coloration of a NaCl Crystal Compressed between *a* and *b* (529).

of calcite twins react to radiation in the same way as the original crystal.

Electrolytic conductivity is another property which can be substantially influenced by deformation. It is true that the experimental data available on this subject are still somewhat conflicting, owing mainly to the difficulty of carrying out reliable measurements. At low temperatures the currents are very small; at high temperatures the effect produced by deformation is small compared with the normal conductivity. Crystal recovery and recrystallization, too, interfere with the study of the effect of deformation. It is certain, however, that with NaCl crystals a sudden increase in conductivity accompanies each increase in load within the range of plastic deformation (534). The increased conductivity then diminishes

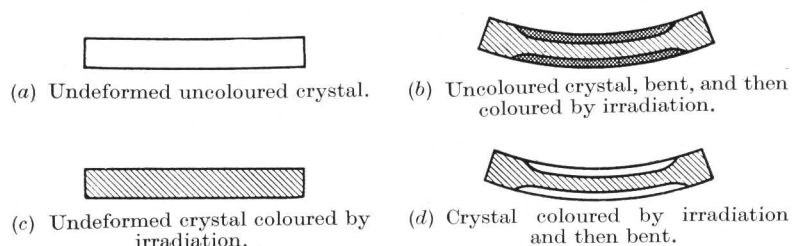


FIG. 192 (a)-(d).—Change in the Capacity of NaCl Crystals for Coloration as a Result of Bending (527).

with time, and it is not clear whether it continues to fall until the initial value is reached, or whether an effect of the plastic deformation remains [(535), (536)]. If crystals from which the load has been removed are loaded again, the jump in conductivity does not occur until the previous maximum load has been exceeded. This hardening effect is fairly permanent at 40–50° C.; even after 24 hours no softening effects are observed. With regard to the influence of deformation, the same contrast exists between ionic conductivity (heteropolar crystals) and electronic conductivity (metals) as in the dependence of conductivity on temperature. Whereas rising temperature and plastic deformation lead to an increase in *resistivity* where conduction is by electrons, they result in an increase in *conductivity* where conduction is by ions.¹

The *rate of solution* of deformed NaCl crystals is raised within areas of high internal stress (revealed by double diffraction) (519).

¹ Melt-grown crystals exhibit a conductivity which is many hundred times higher than that of the best solution crystals (532); impurities increase conductivity (537).

The changes which deformation produces in the properties of ionic crystals can be reversed by *crystal recovery* and *recrystallization*. These phenomena were observed even at room temperature in *compressed* crystals of NaCl and KCl, which formed the main subject of study [(538), (539)]. The most suitable method of investigation was found to be the coloration method, by means of which it was also possible to observe directly the shape of newly formed grains and their speed of growth. The grain boundaries are seen to be cube planes which push forward into the deformed material, along parallel lines, at a speed that often remains constant for days (about 0.1 mm. per day at room temperature). Sometimes the speed changes abruptly (540). The growth of a newly formed grain has been attractively demonstrated in a slow-motion film (541). The speed of recrystallization increases with the degree of deformation and the annealing temperature (542). A diagram, similar to the recrystallization diagram, showing the speed of recrystallization (reciprocal value of the time which elapses before coloured spots appear when irradiating compressed salt) as a function of the time of annealing and the percentage of reduction, is available for a certain type of rock salt (543).

This observed constancy of the rate of growth conflicts to some extent with the results of corresponding tests on metal crystals (Section 62), which revealed a reduction in speed as annealing continued. The explanation may be that recovery can be only slight in the compressed and microscopically distorted NaCl crystal.

Experiments with NaCl, KCl and KBr crystals showed that irradiation has a very marked retarding effect on the formation of recrystallization nuclei, but not on the rate of growth of the new grains. As a rough quantitative estimate it may be said that the neutralization of about 10^{-6} of the ions suffices to delay the recrystallization for many days [(543), (544)].

Detailed studies of the recovery of ionic crystals have not yet been carried out. That recovery actually takes place has already been concluded in (519) from the fact that flow occurs in bending tests at room temperature. A reduction of the rate of recrystallization of compressed crystals by a short intermediary annealing at high temperature (540) is probably also an effect of recovery.

72. *The Effect of a Solvent on the Mechanical Properties.*

Joffé Effect

The diversity of the plasticity and strength phenomena shown by ionic crystals increases greatly if the crystal is exposed to a solvent

while it is subjected to stressing. In recent years experiments of this type have been very numerous, owing to their importance for the theory of crystalline strength. The material used was generally rock salt.

The solvent has a twofold effect : it causes an appreciable increase not only of the plasticity but also of the strength.

It has long been known in salt mines that the normally brittle crystals can be bent and twisted in warm water. Systematic bending tests on rock salt prisms confirmed not only the increased plasticity of the crystals under water, but also showed that the maximum tensile stress in crystals deformed in the wet state can greatly exceed the bending strength of dry crystals (545). Since for ionic crystals, too, the dynamics of the glide process should be determined by the initial critical shear stress of the glide system, and by the work-hardening curve, the effect of the solvent must be described in terms of its influence on these properties. The following observations have been made of the start of plastic deformation in crystals which are being simultaneously dissolved. Initially there is a very perceptible increase in the rate of flow of wetted crystals in the bend test [(547), (549)]; the limits of plasticity, however, remain unchanged (550). Invariance of the yield point was observed under tensile stress also (552). In particular, the shear stress law still applied in cases where the crystals were dissolved as uniformly as possible, and the value of the critical shear stress agreed within the limits of error with the value obtained in the dry test (553). If the direction of tension is in the vicinity of a body diagonal, then, in view of the dependence of the yield point upon orientation, extension will take place by glide in a cube plane. The critical shear stress for this glide system amounts at room temperature to 238 g./mm.². That is more than three times the value for the principal (dodecahedral) system (554).

Unfortunately, it is still not possible to describe the effect of water in terms of its influence upon the strain hardening. We do not yet know the strain hardening curve appropriate even to the normal tensile test. The results so far indicate that if deformation and dissolution both take place at the same time, the increase in shear stress is much less than in the dry test. The shear hardening for a given deformation is greatly reduced by the solvent (550). Consequently, if a crystal under tension is wetted, its rate of flow is increased. It is also remarkable that if rock salt is subjected to a bending test, the (shear) softening influence of the water takes almost full effect if only the compressed side is wetted, but is almost

absent if dissolution occurs on the tensile side only (547). Since very high deformations can be achieved in water, the glide bands of square specimens which have been fractured under water can become visible by ordinary transmitted light (Fig. 193).

The effect of solution on the tensile strength of rock salt crystals was revealed by the Joffé experiment (546), in which crystals are subjected to a given load and then surrounded with water up to a certain level, the water being removed at the moment of fracture. The values obtained in this way, referred to the final cross-section, greatly exceed the normal strength of rock salt; they amount to as much as 160 kg./mm.². Although such exceptionally high values could not be obtained when the tests were repeated, it is certain that the strength can be increased up to 25 times of the value in the

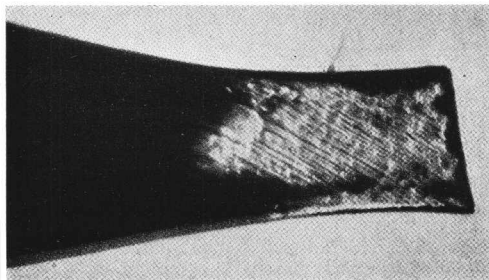


FIG. 193.—Glide Bands on a NaCl Crystal which has been Fractured under Water (552).

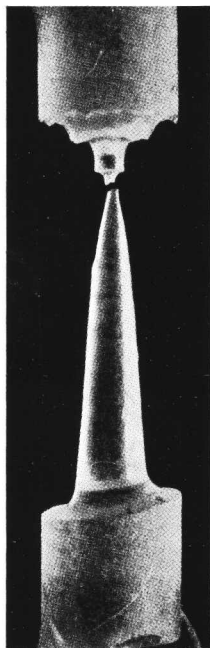
dry state (*i.e.*, to about 10 kg./mm.²). An element of uncertainty is introduced in these experiments by the circumstance that the tension could not have been uniaxial in the narrowest cross-section of the constricted specimen (see Fig. 194). When the conditions of solution were changed so as to reduce the cross-section along the whole crystal [periodic raising and lowering of the water level (555); rotation of the crystal placed horizontally in the solvent (553)], the tensile strength values could be noticeably increased, and fracture was preceded by elongations of up to 45 per cent.

The most important facts about the Joffé effect may be summarized as follows:

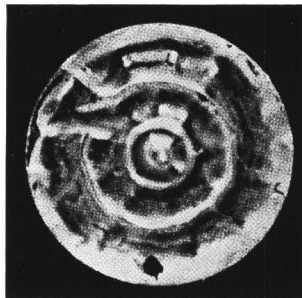
1. It is not absolutely essential for the attainment of higher strength that solution should take place while the specimen is loaded. Unloaded crystals which have been subjected to solvents and tested immediately after drying exhibit values which are just as high, providing solution has proceeded sufficiently far. In general, where

the initial cross-section was the same, the greater the degree of solution the higher the strength [(548), (551), 553)].

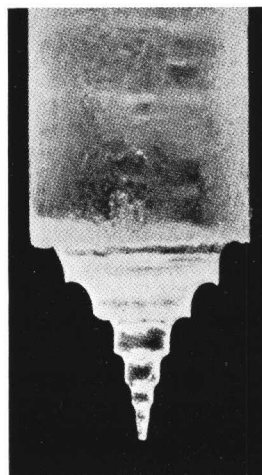
2. It was found that the orientation of the crystal had no influence. Those specimens in particular which were oriented parallel



(a) Full view.



(b) Appearance of the upper portion.



(c) Upper portion of a crystal dissolved in hot water.

FIG. 194 (a)-(c).—Shape of Cylindrical NaCl Bars after Fracturing under Water (551).

to a body diagonal (slight cubic glide in place of extensive dodecahedral glide; cf. Section 67) exhibited the effect to the same extent (551). Consequently, the normal stress law is valid also for wetted crystals (552).

3. Fracture in water is always preceded by plastic deformation.