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9. Characterization

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9.1. Necessity of Crystal Characterization

It is obvious that there are no ideal crystals in reality and all crystals grown by any technique contain some defects, impurities and inhomogeneities. Most of the physical properties are sensitive to the deviation from ideality, therefore generally the characterization of the grown crystals is a necessity. The results of a careful characterization should be published along with any crystal growth results and with any physical measurements on the crystals. However, in the words of Holtzberg (1970) "There are too many examples of very sophisticated measurements on poorly characterized materials, leading to complex and incorrect theoretical analyses". Schieber recently mentioned in a review talk on Trends in Materials Research that it will be up to our children and grandchildren to repeat a number of physical measurements we are doing now, but on highly characterized crystals. Several years ago Roy (1965) tried to draw attention to the characterization problem, but still nowadays papers on measurements of physical properties of solid-state materials are published which are of little value because of the partial or complete absence of characterization.

Frequently in physical publications the only "characterization" given of the crystal used is its source (name of company or of the crystal grower), but this is insufficient except when reference can be given to a detailed published characterization of that crystal or of the corresponding batch of crystals.

A full characterization of a material or a crystal is very time-consuming and needs a large instrumental effort, which is why characterization by both crystal growers and crystal consumers is often left to the other party. Ideally characterization should be performed by a specialist group, but

such groups are available only in a very few universities and in a few large government and industrial research laboratories, since the instrumentation for the modern physical characterization techniques is very expensive.

The reliability, precision and speed of chemical, structural and defect characterization by physical techniques can be enhanced significantly by computer-based laboratory automation. For instance at IBM research laboratories at Yorktown Heights (New York) and San Jose (California) a medium-size computer controls on-line a number of characterization experiments (simultaneously with other physical measurements and with crystal-growth experiments), processes all data and presents the results as tables, plots or as graphs on display units.

Who is responsible for characterization? Reporting on a workshop discussion on magnetic materials, Wolf (1970) proposed that 75% of the responsibility for crystal characterization should be that of the "crystal chemist" and 25% that of the "consumer". This division of responsibility is perhaps too closely defined and the ratio should rather depend on whether it is the crystal grower or the consumer who most benefits from the crystal synthesis and who publishes results of either crystal growth or physical measurements.

Not only the physicist, but also the crystal grower should be most interested in characterization of the crystals grown. It is important to correlate the quality of the crystal with the growth technique and the growth parameters. The demand for crystals of the highest quality is increasing, and only systematic characterization enables the crystal grower to optimize the growth parameters in order to obtain better crystals.

A great stimulus to careful crystal growth and characterization work would be if the scientists responsible for these activities were to participate in some of the "physical" publications, since frequently the effort required to grow and characterize crystals is much larger than that for the physical measurements. In several research establishments joint publications of physicists, crystal growers and analysts have become routine, and this is to the benefit of all participants and of the results.

There are several definitions of "characterization",[†] but in the following discussion the definition is meant to include the full chemical and physical description of a material which is obtained from a whole spectrum of techniques. A single crystal may be characterized by a description of its chemical composition, of its structure, of its defects, and of the spatial distribution of these three features. A full characterization should also include determination of electronic and excited states of the chemical constituents of the material. In addition, the results of many physical measurements can assist in a full description of a specific crystal. However,

[†] Frequently the term "appraisal" or "evaluation" is used with a similar meaning.

physical properties alone of a given crystal cannot sufficiently characterize a crystal. Even a set of various physical properties will not allow the unequivocal identification of a material except for elements and some simple compounds. Chemical and crystallographic data are obviously preferable for the identification of a material.

An excellent review on characterization and on the potential, the sensitivity and the accuracy of the various characterization techniques has been compiled by a Committee on Characterization of Materials, Materials Advisory Board, National Academy of Sciences, Washington D.C., 1967 (Report AD 649 941). It is hoped that the recommendations in this report will be increasingly observed. On the other hand, a revised edition taking into account the more recent developments in characterization techniques would be beneficial if widely distributed.

A book on characterization of the semiconductor materials Ge, Si and III-V compounds has been written by Kane and Larrabee (1970), and many aspects of characterization are reviewed in Vol. 1 of *Treatise on Solid State Chemistry* edited by Hannay (1974).

In the following sections the factors necessary for a description of the chemical composition, structure and defects of crystals will be reviewed and the corresponding characterization techniques described. Further sections deal with the growth history as it can be deduced from characterization techniques, and with the determination and removal of inclusions. The final section is devoted to a proposal of a standard characterization procedure which, possibly in a modified form, could be taken as a requirement for experimental physics and crystal-growth papers to be accepted for publication in appropriate journals of high standard.

In this chapter we mention well-known techniques only briefly since they are described in many textbooks, and concentrate on new techniques and on recent developments in classical methods as well as on a few potentially important characterization techniques. This chapter is relatively long but we believe a detailed treatment is justified by the great importance of the (so often neglected) characterization.

9.2. Chemical Composition and Homogeneity

The determination of the chemical composition of a (single-phase) crystal may be separated into three problems, which may require different techniques. The first is a measurement of the concentration of the major constituents, with an accuracy which is sufficiently high to permit any significant departure from stoichiometry to be detected. Secondly, any minor impurities which are present in "trace" quantities must be detected and their concentration measured. The third problem is the determination of any inhomogeneities or striations of the major constituents or of the

traces. Frequently the determination of the valence state of the ions in polar compounds might be of interest and represents a further problem particularly when elements with multiple valence states, such as many transition and rare earth elements, are involved.

Another approach to the classification of characterization techniques is by the sample preparation necessary. Table 9.1 lists the various techniques,

TABLE 9.1. Characterization of Chemical Composition

Sample preparation	Analytical technique
MATERIAL (CRYSTAL)→	<i>Nondestructive methods</i>
↓ Sampling, grinding, mixing, surface cleaning	electron probe microanalysis X-ray fluorescence analysis neutron activation analysis optical emission spectroscopy with laser excitation (nearly nondestructive)
↓ SAMPLE POWDER→	<i>Direct methods (powders)</i>
↓ Dissolving in acids or fused salts, preparation of defined solution	optical arc and spark emission spectroscopy spark source mass spectrometry (for traces only)
↓ SAMPLE SOLUTION →	<i>Direct methods (solutions)</i>
↓	flame emission spectroscopy atomic absorption colorimetry titrimetry gravimetry coulometry polarography } if no interference by other constituents
↓ Separation of constituents	
↓ SOLUTIONS OF MAJOR→ CONSTITUENTS	<i>Determination of major constituents</i>
↓ Separation (and enrichment, pre- concentrating) of minor constituents or traces	colorimetry titrimetry gravimetry coulometry polarography
↓ PRECIPITATES OR SOLUTIONS→ OF TRACES	<i>Trace determination</i>
	colorimetry titrimetry polarography coulometry

INCREASING COST OF APPARATUS (general trend)

separated into classes of non-destructive, direct and non-direct methods. Non-destructive and direct methods generally require less time per analysis than the non-direct methods, whereas the cost of the instrumentation for nondestructive and direct methods is generally very high.

The various chemical and physical techniques for the determination of composition and of inhomogeneities are reviewed in the Committee on Characterization Report (1967). Further general information on this subject may be obtained from the books of Kolthoff and Elving (1959-1972), Wilson and Wilson (1959-1971), Berl (1960), Wainerdi and Uken (1971) and Maxwell (1968).

The most important techniques which may be applied in chemical analysis are listed in Table 9.2, together with the normal limits of sensitivity and average precision. The lower limit of quantitative analysis by several techniques is higher by one or two orders of magnitude than the sensitivity, because a barely detectable signal cannot be measured with the necessary precision. The values quoted in Table 9.2 are approximate and can vary with the element to be detected, and they often depend strongly on the other major elements present in the crystal. The sensitivity and accuracy of most analytical techniques are dependent on the type of instrument and on the analyst, as was found by test analyses of standard samples sent for analysis to various laboratories. A reliable analytical service is obviously a necessity when the characterization is to be correlated with the physical properties of a given crystal or material.

9.2.1. Analysis for major constituents

The nature and the concentration of the major constituents have to be determined when new crystalline phases are synthesized or when solid solutions are grown. In most cases, however, the major constituents and their ratio are fixed by the structure type of the material and by the requirement of electrical neutrality in the crystal. Also the stoichiometry of many crystals grown from high temperature solutions is very good since the growth temperature is relatively low and does not vary much (relative to the melting point). Many crystals of the spinel, garnet, perovskite, etc., type are often stoichiometric or show very little deviation from stoichiometry. In these cases, when no novel phases are to be expected, identification by X-ray techniques and often by the habit is sufficient, unless solid solutions are grown and unless the distribution of the cations on the various sites and the distribution of their valency states (e.g. in spinels and in garnets) is not clear. From the many analytical techniques only those which have a precision of better than about 1% are of interest for analysis of the major constituents. Nevertheless less accurate techniques are frequently used.

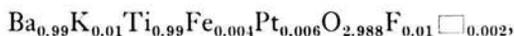
TABLE 9.2. Comparison of Chemical Analytical Methods with respect to Sensitivity and Precision

Method	Detection limit (p.p.m.)	Precision %	Elements detected	Destructive or Non-destructive	Standards†	Min. sample weight mg.	Determination of sample weight necessary
Colorimetry	10^{-2} – 10^2	0.1–10	most	D	a	10(0.1)	yes
Titrimetry	~ 10 – 10^3	0.01–1.0	many	D	c	10(0.1)	yes
Gravimetry	10^3 – 10^5	0.01–1.0	many	D	c	100(10)	yes
Coulometry	major phase	0.001–0.005	most	D	c	10	yes
Polarography	10^{-2} – 10^2	0.1–10	most	D	a	10	yes
Opt. emission spectroscopy	10^{-2} – 10^2	1–10	most	D	b	10	yes
Atomic absorption	10^{-2} – 10^2	1–10	most	D	a	10	yes
X-ray fluorescence	10 – $2 \cdot 10^2$	0.1–2	} Atomic No. > 5 – 11	N	b	100(10)	no
Electron microprobe	10^3 – 10^4	0.5–5		N	b	10^{-3}	no
Mass spectrometry	10^{-2} –1	> 5	all	D	a, b	10(0.1)	yes
Neutron activation	10^{-3} – 10^{-1}	2–10	many	N	b (c)	10(0.1)	yes
Radioactive tracer	10^{-3} – 10^{-1}	~ 1	many	N	b (c)	10(0.1)	no

† a. standard solutions necessary, b. internal standards or standard samples necessary, c. no standards necessary (but of advantage for checking).

Of the methods used for the determination of the major constituents, the classical method of *wet chemistry* is still the most widely used, although its importance has declined rapidly as new physical techniques have been developed. Wet analysis involves the dissolution of the crystal (or its powder) in acids, fused salts or in conventional fused salt mixtures†, separation when necessary of the various chemical constituents, and the quantitative determination of the elements by gravimetric, titrimetric or colorimetric methods (see for instance Kolthoff and Elving, 1961, 1959–1972; Ringbom, 1963; Gordon *et al.*, 1959; Vogel, 1966; Seel, 1970; Sandell, 1959; Boltz, 1958; Schwarzenbach, 1957 and Kodama, 1963). The results of wet chemical analysis are sometimes unreliable, when interfering elements are present. Some elements, such as boron and oxygen, are difficult or impossible to determine by this method. Apart from problems of interference by other elements, the main disadvantage of wet chemical analysis is the amount of time required for a quantitative determination. Except for simple routine analyses, the complexity of wet analysis is such that considerable experience is required before reliable results are obtained. Perhaps for this reason, relatively few examples of complete chemical analyses of HTS-grown crystals have been reported, although there are many examples of results of trace analysis or analysis of a single component.

The value of careful chemical analysis in HTS growth has been demonstrated by investigations such as that of Arend and Novak (1966) and of Arend *et al.* (1969) on barium titanate crystals of the butterfly twin morphology. In one example, the composition of a crystal of nominal formula BaTiO_3 was found to be



where \square denotes an anion vacancy. Of particular significance are the rather high concentration of vacancy from the crucible material and the replacement of an appreciable amount of O^{2-} by F^- from the KF flux. That the fluorine ions are present substitutionally rather than in inclusions is indicated by the changes in properties of the crystals with time at ambient temperature, due to hydrolysis. The observation of F^- substituted for O^{2-} is of considerable importance since fluoride solvents are often used for crystal growth of oxides. The probability of fluorine substitution will

† Rapid and complete decomposition of a variety of oxide components is achieved according to Biskupski (1965) by fusing the powdered sample at 850 °C in a platinum crucible with 2 g B_2O_3 and 3 g LiF, and by dissolving the product in H_2SO_4 . According to Thilo *et al.* (1955) alumina and ruby powder dissolve rapidly in a fused mixture of Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$ and KClO_3 in the weight ratio 5 : 4 : 1. Fusion techniques in chemical analysis have been reviewed by Bock (1972) and by Dolezal *et al.* (1968), and pre-molten fluxes of high purity are commercially available.

depend critically on the presence of charge compensating ions which can enter the lattice simultaneously.

Coulometry (Lingane, 1958; Taylor *et al.*, 1965; Stock, 1965, is a very precise analytical technique for major and minor constituents. It is essentially titration with electrons and therefore replaces the classical titrimetric methods. In this quantitative electrolytic technique a constant electrolysis current is applied, which is very convenient, or the electrolysis potential is controlled very precisely, the latter technique being more selective. The sensitivity of coulometric techniques approaches the p.p.m. range, and the precision is of the order of 0.001 to 0.005%. Its disadvantage is that solutions have to be prepared as in the wet chemical techniques, and the necessary steps are time-consuming and might reduce the accuracy if impurities are introduced.

Polarography (Kolthoff and Lingane, 1952; Breyer and Bauer, 1963; Neeb, 1969) is used for the determination of most elements in solution when an electrolytic oxidation or reduction process can be used. Several elements in minor or major concentration can be measured simultaneously, and sensitivities are often below the p.p.m. range. The precision of this technique for traces is of the order of 20%, whereas for favourable concentration ranges it can be better than 1%. A disadvantage of polarography is that the sample has to be dissolved prior to analysis, and the same is true for optical (flame) emission and atomic absorption spectrometry discussed in the following section.

Optical emission spectrometry is used mainly for trace analysis but can be used for major constituents. Excitation of the spectrum is achieved by various techniques according to the nature of the specimen. The flame (Mavrodineanu and Boiteux, 1965) and d.c. arc were used in most early experiments and the book of Ahrens and Taylor (1961) is based exclusively on the d.c. arc. More recently the a.c. arc, a.c. spark (with a higher voltage) and combinations of arc and spark have been used as sources, and lasers have been used to initiate combustion of insulating samples. The important criterion for accurate quantitative analysis is that combustion of the specimen must be complete and spark sources are normally considered more satisfactory, especially for metallic samples (Harrison *et al.*, 1963; Harvey, 1964; Nachtrieb, 1950). The main advantage of lasers over conventional methods of excitation is that a small volume of a crystal can be vaporized selectively and the spectrum of the resulting vapour excited by means of an auxiliary spark source. The region examined may be smaller than 50μ in diameter and 25μ deep. By this means the distribution of major constituents and of trace elements can be determined without slicing up the crystals (Moenke and Moenke, 1966; Snetsinger and Keil, 1967; Blackburn *et al.*, 1968).

Dispersion of the emitted radiation is achieved by prisms or gratings. The requirements of sensitivity and resolution are diametrically opposed and Cooper *et al.* (1969) describe the simultaneous use of three types of spectrograph, each receiving radiation from an arc. Medium- and large-prism spectrographs were used for elements having lines well resolved from those of other elements present, while a grating spectrograph was used for transition elements and the actinides because of their complex spectra.

The spectra are recorded either photographically or with photoelectric counting systems. Photographic emulsions require careful calibration and their relative inconvenience has led to gradual replacement by direct-recording techniques. For the highest accuracy it is necessary to compare the spectra for the sample under test with that of a standard material.

The limit of detection of optical emission spectroscopy varies between 0.3% for potassium and 0.4 p.p.m. for magnesium, but for many elements lies between 1 and 100 p.p.m. Optical emission spectroscopy is the subject of books by Herzberg (1944), Ahrens and Taylor (1961), Clark (1960), Harrison *et al.* (1963) and Slavin (1971). The emission spectra can be evaluated with the help of computers (Thompson *et al.*, 1969; Helz *et al.*, 1969).

Atomic absorption spectrometry is a related but newer method which permits the concentration of a large number of elements to be determined using relatively simple and inexpensive apparatus. The precision depends upon the element considered but can be as high as $\pm 0.5\%$. The principle relies upon the absorption of light at a characteristic wavelength by atoms in a vapour produced from the sample. The sample is normally dissolved and the resulting solution vaporized by spraying through an aerosol into a flame or heated graphite tube. A spectrometer selects the wavelength corresponding to the strongest spectral line of the element and the decrease in intensity on passing through the vapour is measured.

The absorption is related to the concentration n of the element in the vapour by the usual law

$$\ln \frac{I}{I_0} = \mu nl,$$

where I_0 and I are the intensity of the radiation before and after passing through the flame respectively, l the path length and μ the absorption coefficient. The latter parameter is normally found by calibration using solutions of known concentration.

A number of light sources are required to cover a wide range of elements. As with emission spectroscopy, the accuracy is expected to be higher for elements with relatively simple spectra. The accuracy may be affected by

interference from other elements present, and possible causes of interference must be considered in the interpretation of analytical data. A detailed account of the advantages and limitations of atomic absorption spectrometry has been given by Slavin (1968), and other books on the topic have been written by Ramirez-Munoz (1968) and Angino and Billings (1967).

Perhaps the best example of the use of atomic absorption spectrometry in the appraisal of HFS-grown crystals is the study of the lead concentration in various rare-earth orthoferrites by Remeika and Kometani (1968). Their analyses for Pb were considered to be accurate to within 2% of the amount present, which varied from 0.08% to 13.4% by weight of the material. The high concentration of lead in the heavier rare-earth orthoferrites would have a major effect on the properties of these materials if it were incorporated in the lattice (see Chapter 3).

X-ray fluorescence analysis has been used increasingly as an alternative analytical method and has advantages of directness and convenience over wet chemistry. As may be seen from Table 9.2, it is one of relatively few analytical methods which may be non-destructive, so that analysis can be performed on the actual crystal or crystalline layer used for a subsequent experiment. The crystal is placed in a strong beam of "white" X-rays produced by a heavy-metal anode, and each excitable element in the crystal will emit X-rays of its characteristic wavelengths. This fluorescent radiation is analysed by a counter spectrometer employing a crystal such as sodium chloride, and the intensity of radiation at a characteristic wavelength is proportional to the concentration of the particular element. The precision which can be obtained in a single analysis is of the order of 5 to 10%, but by routine procedures it may be reduced to about 0.5%. Such precision can be achieved by forming a composite sample containing some standard material in addition to that analysed so that errors due to a difference in density between the sample and the calibration standard can be eliminated. X-ray fluorescence is often carried out with non-dispersive systems, usually attached to a scanning electron microscope. Reviews of X-ray fluorescence spectroscopy have been given by Birks (1969), Adler (1966), Jenkins and De Vries (1967), and Müller (1972).

Electron probe microanalysis (EPMA) has been increasingly used, particularly to study variations in the concentration of an element in the region near the surface of a crystal. It is probably the most powerful method for the investigation of compositional gradients and striations, although optical methods may be preferable if the crystal contains only atoms of low atomic number. As in X-ray fluorescence, the analysis depends upon the emission by an element of its characteristic X-ray spectrum, but the excitation in EPMA is produced by a beam of electrons. The great

advantage of electron excitation is that the beam can be focused, and a spatial resolution of less than $1\ \mu\text{m}$ is possible with EPMA compared with $>50\ \mu\text{m}$ for X-ray fluorescence.

A schematic diagram of an electron probe microanalyser is shown in Fig. 9.1. The idea was patented by Hillier (1947) but the first instrument was constructed by Castaing (1951). The specimen is mounted on a stage which can be displaced or rotated, and is observed through a microscope so that it can be continuously viewed in order to select a particular region for analysis. An area of the specimen is usually scanned and an image is simultaneously observed at a number of wavelengths corresponding to the constituent elements. The instrument is particularly powerful if combined with a scanning electron microscope and commercial instruments with both facilities are available.

As with X-ray fluorescence analysis, the range of elements which can be detected depends upon the X-ray spectrometer and detector, which are difficult to build for very long wavelengths. The range of elements which can be detected is slowly increasing and instruments could be built to detect all the elements except possibly helium and hydrogen, but in current commercial instruments the limit is at atomic number 5 (boron).

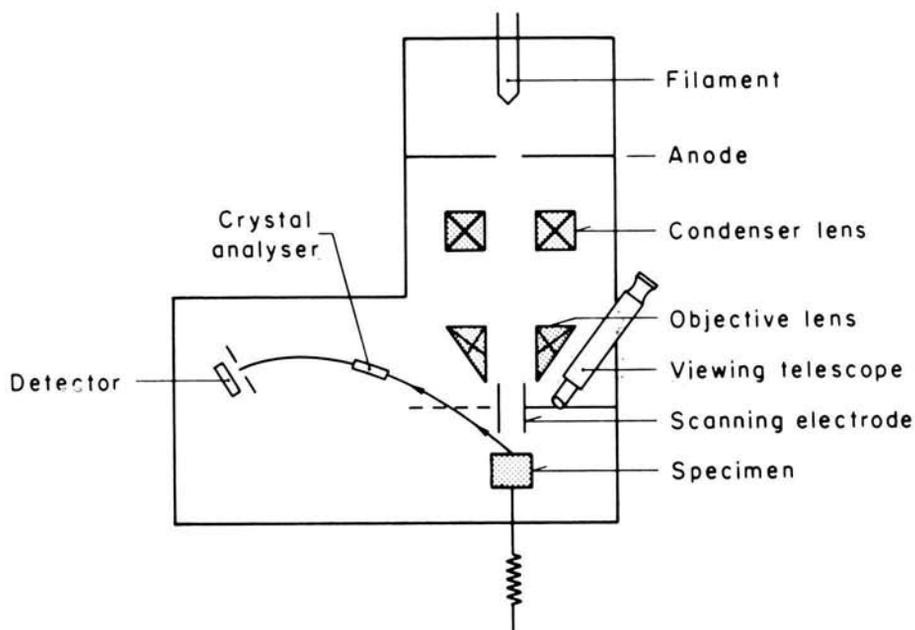


FIG. 9.1. Electron microprobe analyzer (diagrammatic).

The beam causes local heating of the sample which must therefore be stable in a vacuum at temperatures up to a few hundred degrees. This problem is encountered only with insulating samples and can be overcome by coating the surface with a thin layer of carbon or aluminium. This layer also serves to prevent charging of the sample and so stabilizes the electron beam.

X-ray intensities can be determined to better than 1% but corrections are necessary in order to achieve comparable accuracy in the concentration values. The principal corrections are for absorption of the X-rays and for excitation of fluorescent radiation from other elements in the specimen. In addition, the stopping power of electrons and the probability of back-scatter vary with the atomic number of the element and with the energy of the incident electrons. The theory and application of these corrections have been discussed in reviews by Castaing (1960) and Heinrich (1966, 1967). Generally the precision is not better than 5%.

Frazer *et al.* (1971) have proposed a procedure for quantitative analysis by microprobe in which two or more beam energies are employed and the intensities extrapolated to the values at the critical excitation potential. At this potential the absorption, fluorescence and back-scatter corrections become negligible and the resulting values require correction only for the electron retardation.

The use of EPMA in investigating the homogeneity of dopants has been reported for instance by Timofeeva *et al.* (1969a) (Cr and Nd in Al_2O_3). This method was also used by Sobon *et al.* (1967) to determine the Pb concentration in garnets. Monographs on electron probe microanalysis include those of Birks (1963), McKinley (1966), Reuter (1971), Heinrich (1968), Russ (1970) and Andersen (1973).

Electron spectroscopy has been developed to a valuable analytical technique by Siegbahn and coworkers (1967). Several terms are found in the literature, for example ESCA (electron spectroscopy for chemical analysis), IEE (induced electron emission), UPS (UV-photoemission spectroscopy), XPS (X-ray photoelectron spectroscopy), SXS (soft X-ray emission spectroscopy) and INS (ion neutralization spectroscopy).

Preisinger *et al.* (1971) proposed the classification of electron spectroscopical techniques according to the stimulating process:

Ion electron spectroscopy	IES
Electron electron spectroscopy	EES
X-ray electron spectroscopy	XES
UV electron spectroscopy	UVES

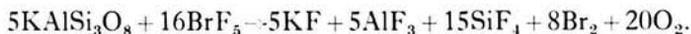
UV irradiation (3–50 eV) results in ionizing interactions with the bonding electrons whereas X-rays interact with the inner electron shells. The latter

process is therefore useful for chemical analysis whereas the former process gives information on the electronic structure of semiconductors, metals and recently also of insulators. Photons of uniform energy produce photoelectrons and Auger electrons simultaneously. Electron spectroscopy allows the determination of oxidation states of elements and also the analysis of elements in the surface layers (Chang, 1971; McDonald, 1970; Benninghoven, 1973) especially of the light elements (second period from Li to F).

Mass spectrometry is, with some exceptions such as the O₂ determination mentioned below, only valuable for analysis of minor elements (below 1%) because of its inaccuracy. Mass spectrometry relies on the variation with mass of the path of an ion in a magnetic field and/or an electric field. The major limitation is that it can be applied only to gaseous ions and so the material must be vaporized by a suitable ion source. At present the type of instrument most suitable for studies of solids is the spark-source mass spectrometer. Very small quantities of materials are required, and a large number of elements may be determined simultaneously. Monographs on mass spectrometry include those of Ahearn (1966), McDowell (1963), Kienitz (1968) and Roboz (1968).

The spark is produced by a potential of 20–100 kV at about 1 MHz and ionizes all elements with approximately the same sensitivity. The majority of ions are singly ionized, but doubly and triply ionized atoms are also produced. The major disadvantage is, however, that the ions have a wide range of energy and so the analysing system must separate and focus ions of different mass independent of their initial energy and direction. A suitable spectrometer is the double-focusing system of Mattauch and Herzog (1934), in which electric and magnetic fields of critical values are applied in series to the beam of ions. The spectra are recorded on photographic plates.

Oxygen (in oxygen-containing compounds) is one of the most difficult elements to determine but can be analyzed by mass spectrometry if it is extracted from the material by (a) reaction with agents such as mercuric cyanide or silver cyanide to yield CO₂ (Anbar and Guttman, 1959; Shakhshiri and Gordon, 1966), (b) reduction with carbon at high temperatures to yield CO (Schwander, 1953; Dontsova, 1959) or (c) oxidation by fluorine or halogen fluorides to yield O₂. The latter oxygen extraction technique seems to be suitable for many oxides and oxide compounds and has been developed by Clayton and Mayeda (1963). 5 to 30 mg of the material is reacted for 12 hours at 450–700°C with bromine pentafluoride BrF₅, a colourless liquid at room temperature. As an example the reaction between orthoclase and BrF₅ may be written as



The extracted oxygen is separated by a liquid nitrogen trap and is

determined as such or after its transformation to CO_2 . The quantitative extraction of oxygen from a variety of materials and even from refractory oxides has been achieved at high temperatures with carbon as reducing agent by Kraus (1972) and by Paesold *et al.* (1967), and the latter were able to determine oxygen in a variety of oxides with a standard deviation of 1 to 1.5%. However, this precision and a high sensitivity were only possible by IR absorption analysis of the CO (formed during the extraction) with specialized apparatus.

The main problem in quantitative mass spectrometric analysis is to establish the correspondence between the elemental composition of the ion beam and that of the sample. Measurements may be made over different recording periods, the general principle being to compare the measured intensity with that of an added standard in the sample. With photographic recording techniques, the precision is usually worse than 10%. The main cause of error is variability of the spark source, and recent developments have been concentrated on improving the means of ion production. The best accuracy claimed is still in the region of 5%, and it is hoped that higher precision will be achieved in the near future.

The analysis of thin layers and of solids as a function of depth can be achieved by sputtering and the determination of the positive (or negative) ions in the very sensitive *ion microprobe* (Socha, 1971), by secondary ion mass spectrometry (SIM) described by Herzog and Viehböck (1949), Honig (1958), Benninghoven (1969), Benninghoven and Storp (1971), and Benninghoven (1973), or of the sputtered (by rf glow discharge) neutral particles by mass spectrometry (Coburn and Kay 1971). Lasers might be useful ionizing sources in the future (Fenner and Daly, 1968). Also the energy distribution of the back-scattered ions allows qualitative and quantitative analysis of the uppermost surface layer, and there is no interference from the continuum of ion energies associated with scattering from atoms beneath the surface. Thus the differentiation between the S- and the Cd-face of the polar CdS is possible (Smith, 1971).

9.2.2. Deviation from stoichiometry

Often crystals are nonstoichiometric and contain vacancies of either anions or cations, and the equilibrium number of such defects increases with temperature (see Section 9.5). The concentration of vacancies may also depend on the atmosphere employed during growth and on the nature of the solvent. Vacancies are also influenced by the kinetics of the growth process, and their concentration thus depends on the growth rate and on other growth parameters. Vacancies are often constituents of larger defects and their distribution can be random or they can be ordered, thus forming crystallographic superstructures (see Rabenau, 1970).

A crystal showing a deviation from stoichiometry can be regarded as a solid solution of the stoichiometric crystal with a compound of the next higher or lower valence state of the metal ion, or with a constituent element or with a constituent component without change of valence state. So CdS with sulphur vacancies can be regarded as a solid solution of CdS with Cd, and FeO with oxygen excess can be described as a solid solution of FeO with Fe_2O_3 . Many crystalline phases show a large range of composition at high temperatures (near the melting point), whereas at low temperatures the composition range of that phase can be small, even immeasurably small. For example, the width of the Ni_3S_2 phase is close to zero below 550°C and extends from $\text{Ni}_{2.56}\text{S}_2$ to $\text{Ni}_{3.68}\text{S}_2$ at 640°C (Huber and Liné, 1963).

Nonstoichiometry is a field of increasing importance and is treated in the books of Rabenau (1970), Wadsley (1964), Mandelkorn (1964), Brebrick (1969), Kröger (1964), Eyring and O'Keeffe (1970), and in several volumes of "Progress in Solid State Chemistry" (H. Reiss, editor).

Large deviations from stoichiometry (larger than 0.1–1%) are indicated in carefully determined phase diagrams and are determined by several of the more precise analytical methods described in the previous section. In the following discussion, methods will be described for the determination of small deviations from stoichiometry. This is possible by special chemical techniques, by thermogravimetry, by exact determination of density, lattice constants and other physical properties, or by determination of the abnormal valence state by physical techniques such as optical absorption, electron spin resonance, Mössbauer spectroscopy, X-ray spectroscopy and electron emission spectroscopy.

The chemical determination of the concentration of ions of abnormal valence state can be achieved by an appropriate oxidation or reduction reaction, by titrimetry, or by colorimetry. As examples, excess metal in ZnO and BaO is analysed by dissolving the materials in acids and by measuring the hydrogen formed (Berdennikova, 1932; Libowitz, 1953).

Metal excess can also be analyzed by oxidizing the metal and by titrating back the excess of the oxidizing agent (Alsopp and Roberts, 1957) and by similar methods (Novak and Arend, 1964; Kleinert and Funke, 1960), or by coulometric titration (Engell, 1956). Hildisch (1968) developed a technique which allows determination of 1 p.p.m. excess metal in a sample of 10–20 mg CdS by evolution of hydrogen and its determination by gas chromatography. Gruehn (1966) has developed a micro-technique for the quantitative determination of low oxidation states of metals. The oxides (or other compounds) are dissolved in molten KOH and thereby oxidized to the normal valence state and, according to the concentration of metal of low valence state, hydrogen is produced according to



This reaction is quantitative, and the hydrogen can be determined. The precision of the measured x values for the case of $\text{Nb}_2\text{O}_{5-x}$ was ± 0.002 .

Thermogravimetry (Duval, 1963; Garn, 1965) is a useful method for analyzing nonstoichiometry. The change of weight of a heated sample during oxidation or reduction reactions to a definite state (stoichiometric oxide of normal valency, for example) is a measure of the deviation from stoichiometry. Another approach by TGA (thermogravimetric analysis) is to produce controlled (by weight) nonstoichiometric compounds under given temperature and atmospheric conditions, check the chemical composition by chemical analysis (or TGA) and identify these compounds by X-ray data. Bartholomew and White (1970) crystallized several "nonstoichiometric" titanium oxides from solution and most probably identified them by X-ray data (comparison with earlier studies). Thermogravimetry has become quite popular since high precision instrumentation has become available and it has, for example, been of value in proving the existence of a variety of nonstoichiometric oxides of the rare earths (Wiedemann, 1964) and in analysis of the oxidation states and defect structure of ferrites (Reijnen, 1970).

Several properties are sensitive to deviations from stoichiometry, and especially the density often varies considerably with the composition. Nonstoichiometry can often be studied by precision lattice parameter measurements as was shown with gallium arsenide by Willoughby *et al.* (1971). The correlation of physical properties such as resistivity, thermoelectric power or Hall effect with the deviation from stoichiometry is often possible, and these properties may be extremely sensitive, but the effect of other defects, of trace impurities and compensation must not be overlooked in these cases.

Nonstoichiometry in lithium niobate LiNbO_3 could be correlated with the ^{93}Nb NMR linewidth and to the Curie temperature by Carruthers *et al.* (1971), whereas Scott and Burns (1972) used measured Raman linewidths and frequencies to determine nonstoichiometry in LiNbO_3 and LiTaO_3 . These techniques allowed determination of the subsolidus of the corresponding phase diagrams. Various models have been proposed in order to understand these deviations from stoichiometry (Nassau and Lines, 1970).

Specific physical techniques can be used in several cases to determine abnormal valance states. Many oxides (e.g. TiO_2) and oxide compounds (titanates, niobates, tantalates, molybdates, tungstates) which show little absorption in the visible are deeply coloured (blue, brown, black) in oxygen-deficient states and so can be examined by *absorption spectroscopy*.

Electron paramagnetic resonance (EPR, or ESR for the equivalent term electron spin resonance) can give details of the presence of certain transition-metal ions (with unfilled shells) and of the local structure but generally the paramagnetic ions have to be in very dilute concentrations in diamagnetic host crystals for ESR absorption to be detectable (Ayscough, 1967). As an example, Ti^{3+} has been studied in TiO_2 by Chester (1961). A useful technique for the determination of unusual valence states is *Mössbauer spectroscopy* (see Greenwood in Rabenau, 1970). For example, Mullen (1963) detected Fe^+ and Fe^{2+} in NaCl, Gallagher *et al.* (1964) studied the oxidation of $SrFeO_{2.5}$ to the perovskite $SrFeO_3$ containing Fe^{4+} , and Hannaford *et al.* (1965) investigated Sn^{2+} defects in neutron-radiation damaged $Mg_2Sn^{4+}O_4$ by chemical isomer shift. The application of the Mössbauer technique is somewhat restricted since, from the 70 isotopes of 40 elements which fulfill the conditions for recoilless emission of γ -rays, only ^{57}Fe and ^{119}Sn have been widely studied. A few publications mention ^{121}Sb , ^{125}Te , ^{151}Eu , ^{166}Er , ^{170}Yb and ^{197}Au in the study of nonstoichiometric phases.

The use of electron spectroscopy for the determination of the valence state of elements is mentioned in Section 9.2.1.

9.2.3. Analysis for minor constituents and of traces

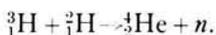
For trace analysis the sensitivity of the method is generally more important than the accuracy. Because of their high sensitivity most of the techniques mentioned in the Sections 9.2.1 and 9.2.2 can also be applied to the analysis of minor constituents (compare Table 9.2). Minor constituents can be dopants added deliberately or may originate from impure starting materials, from the solvent or from the crucible, and impurities can enter the growth system and the crystal via the furnace atmosphere. Frequently a wide range of impurities is found in the grown crystals, often in an unexpectedly high concentration. Therefore careful selection of chemicals as starting materials (with accompanied batch analysis) and careful experiments in sealed systems are necessary if crystals of high purity are to be grown. Impure solvents are particularly troublesome because of their relatively high concentration in a typical solution growth experiment. Fortunately the growing crystal rejects many impurities according to their low effective distribution coefficients, especially when the crystal can grow slowly enough as is discussed in connection with the Burton-Prim-Slichter equation (Section 9.2.4). Trace analysis has been treated, for example, in the books of Meinke and Scribner (1967), Alimarin and Petrikova (1962), Sandell (1959), Tölg (1970) and Koch and Koch-Dedic (1964). Qualitative determination of trace elements is the subject of the books of Feigl (1970) and Vogel (1966).

The most important techniques for trace analysis (determination of impurity concentrations of less than 100 p.p.m.) are *optical emission spectroscopy*, *atomic absorption*, *mass spectrometry*, *neutron activation analysis*, and the relatively simple *titrimetry* and *colorimetry*.

Optical emission spectrography is very convenient since it is particularly rapid, requires only a small sample, and can be used for most elements. Errors may arise through interference, particularly for elements having very complex spectra. The limit of sensitivity for arc and spark emission spectrography for the chemical elements has been tabulated by Addink (1957) and by Morrison and Skogerboe (1965).

Neutron activation analysis (Guinn and Lukers, 1965; De Soete *et al.*, 1971; Lyon, 1964; Kruger, 1971; De Voe, 1969; Siegbahn, 1965; Taylor, 1964; Bowen and Gibbons, 1963) is based on the principle that, if a material is bombarded with neutrons, the induced radioactivity will depend in nature, energy and intensity on the composition of the material. The effect of the bombardment on a stable isotope will normally be to produce a radio-isotope, which will decay with the emission of its characteristic radiation. As the bombardment is continued, a steady condition will eventually be reached where the rate of decay of the radioactive species is equal to the rate of production from the stable isotope. The decay rate is then proportional to the number of nuclei of that isotope. If shorter irradiation times are used, the activity can be calculated in terms of the steady value and the half life of the radio-isotope.

“Thermal” neutrons are normally used as the bombarding particles since most elements have a high capture cross-section for neutrons at relatively low energies, and high neutron fluxes are readily available from nuclear reactors. Alternatively high-energy neutron sources may be used, in instruments which are smaller and easier to erect in an analytical laboratory. These sources normally contain a target of a cooled metal tritide (^3H) which is bombarded by deuterons (^2H) accelerated to an energy of 100–200 keV. The reaction which generates neutrons is



Analysis is normally performed by measuring the γ -ray emission by a scintillation counter and pulse height analyser, with data evaluation by computer. The sensitivity is about 10^{-8} g or 0.01 p.p.m. for a 1 g sample. The precision of the determination is typically 1–3% if suitable care is taken. The majority of elements have more than one stable isotope and so a correction is required for the fraction in the element of the isotope used for the analysis. Cloete *et al.* (1969) performed neutron activation analysis of MgAl_2O_4 crystals grown from PbF_2 solution at 1200–1250°C in 100 cm^3 platinum crucibles and found 13 p.p.m. iridium (present in platinum in

small amounts), but no platinum. A remarkable result was that the authors found by absorption spectroscopy less than 10 p.p.m. lead in the spinel crystals.

Even higher sensitivity than with neutron activation is sometimes possible with *tracer methods* in which a known concentration of a radioisotope is added to the solution prior to crystallization and the activity of the crystal measured after growth. This determination is based on the assumption that the fraction of the radioisotope in the crystal is the same as that in the melt. Although the apparatus required for such a determination is relatively simple, the use of radioactive tracer methods in high temperature solution growth has been reported in the literature only recently when their application to a variety of problems was described by Janssen *et al.* (1973).

Comparable sensitivity is sometimes possible with *mass spectrometry*, the limit being around 10^{-3} ppm, with 10^{-1} – 10^{-3} ppm typical for most elements in any matrix. Wolfe *et al.* (1970) used mass spectrometry to measure impurity concentrations at the level of 10^{13} cm $^{-3}$ in gallium arsenide. The range of sensitivity between different elements with mass spectrometry is less than with most methods, being normally within a factor 3. The other chief advantage is that different areas of the sample may be studied using selective volatilization but the spectrometer is expensive and the accuracy relatively low. In addition, both mass spectrometry and neutron activation analysis are time consuming compared with optical emission spectrometry. Trace analysis much below the p.p.m. level is achieved by correlation of impurity concentration with sensitive physical properties, for example with the resistivity of metals and semiconductors. Luminescent properties are also extremely sensitive to the smallest impurity levels (see for example Meinke and Scribner, 1967). Care is necessary in these cases since they are often not specific or are easily interfered with by other impurities. Other physical techniques based on photon spectroscopy (such as *nuclear magnetic resonance*, *electron spin resonance*, and *Mössbauer spectrometry*) or on electron spectroscopical methods (see Section 9.2.2) are useful in certain cases of composition or trace determination, but their main potential lies in the study of structure and of defects, and they will be discussed further in connection with these latter aspects.

Linares *et al.* (1965) have shown that a variety of rare-earth ions could be detected in concentrations as low as 0.02 to 1 p.p.m. by *optical fluorescence* which was excited by X-rays (probably not directly but by photoelectrons which then preferentially transfer their energy to impurity atoms by inelastic scattering).

Impurities such as oxygen, nitrogen and hydrogen in the p.p.m. range in metals and semiconductors have an appreciable effect on the material

properties. The detection of such volatile traces is possible with modern apparatus by vacuum fusion as developed by Thompson *et al.* (1937), with determination of the gases by infrared absorption (CO) and other physical properties (Kraus, 1972; Paesold *et al.*, 1967) or by mass spectrometry.

Frequently preconcentration techniques such as zone melting, chromatography, electrophoresis, extraction, and precipitation are used to increase the sensitivity of the determination, and also coprecipitation and mixing techniques can be helpful in this respect.

Other methods for trace analysis are based on *chromatography*, *ion exchange chromatography* and *electrophoresis*. In these techniques a mixture of ions or molecules is separated during its travel with a solvent phase (a) along a second (immiscible) liquid layer absorbed on thin films or columns of cellulose, silica gel, alumina, organic polymers etc. (= chromatography), or (b) along ion-exchange resins which are reversibly replacing an equivalent amount of other ions, or (c) in an electric field (= electrophoresis). The determination is performed directly on the dried and fixed systems by specific colouring agents (paper chromatography, thin-film chromatography, or electrophoresis), or the separated chemical constituents are extracted and determined by other techniques. Advantages of these techniques are the possibility of separation of a variety of ions and the high sensitivity which can be lower than 1 ppm, also the apparatus is simple. Disadvantages are the inaccuracy (5–20%), the necessity of preparing solutions, and the high level of experience necessary. Monographs on the above methods have been written by Lederer and Lederer (1960) and by Lederer (1971).

9.2.4. Inhomogeneities and their detection

Inhomogeneities of the crystal composition, either of the major or minor constituents, occur on all scales. Inclusions are discussed in Section 9.4.6, inhomogeneities on an atomic scale in connection with defects in Section 9.4.1, and structural inhomogeneities in Section 9.3. Methods of producing homogeneously doped crystals and of homogeneous solid solutions have been described in Section 7.1.3.

Origin of inhomogeneities. According to the Burton-Prim-Slichter equation (1953) the effective distribution coefficient is

$$k_{\text{eff}} = \frac{k_o}{k_o + (1 - k_o) \exp(-v\delta/D)},$$

where k_o is the equilibrium distribution coefficient, v the growth rate, δ the boundary layer thickness and D the diffusion coefficient. Thus inhomogeneities are produced when any of the parameters k_o , v , δ or D

change during the course of a crystallization experiment. k_o is a function of the temperature according to the ideal solution concept (Thurmond, 1959). Also temperature-dependent equilibria in the solution and the enrichment (or depletion) of impurities in the solution during growth will affect k_o . The growth rate v is strongly dependent on the supersaturation and hence on temperature changes. In the many cases where the rate of crystallization depends on adsorption on specific faces or on the crystallographic direction, an orientation-dependent impurity incorporation is to be expected, and an example of such zonal growth is shown in Fig. 9.2. The change with temperature in the diffusion coefficient D is expected to be relatively minor, whereas the boundary layer thickness δ is more likely to cause inhomogeneities since it is sensitive to any changes in the hydrodynamics in the solution. However the most important causes of inhomogeneities in flux grown crystals are temperature variations and oscillations, the latter leading to banded growth (*striations*), and extended variations of composition are due to changes in k_o .

It is possible that the majority of striations are due to temperature

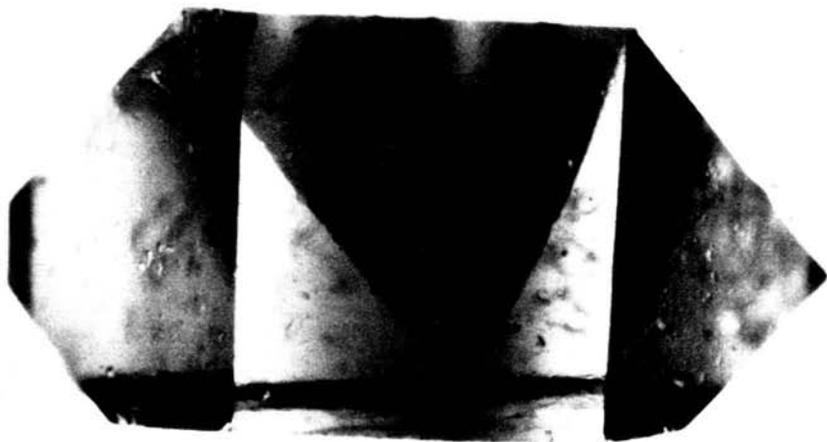


FIG. 9.2. Orientation-dependent impurity incorporation in zircon (Scheel, unpublished).

fluctuations which arise in the solution because of unstable convection. Temperature oscillations due to convective motion in fluids are well known but their importance in crystal growth was not appreciated until comparatively recently. Wilcox and Fulmer (1965) demonstrated that fluctuations in the dopant concentration in calcium fluoride crystals grown from the melt could be correlated with temperature oscillations within the melt, and many examples of the relation between such oscillations and striations in melt-grown crystals have now been reported (Hurle, 1966, 1967; Cockayne and Gates, 1967; Witt and Gatos, 1968). Striations due to variations in the Ta/Nb ratio in crystals of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ grown by top-seeded solution growth were attributed by Whiffin (1973) to temperature oscillations which were measured as $\pm 1^\circ\text{C}$ in amplitude.

The incidence of temperature oscillations is discussed in Section 6.6.2 where reference is made to "overstability" which is a probable cause of such oscillations in high temperature solutions. Figure 9.3 shows temperature oscillations at different depths in a solution of nickel ferrite in

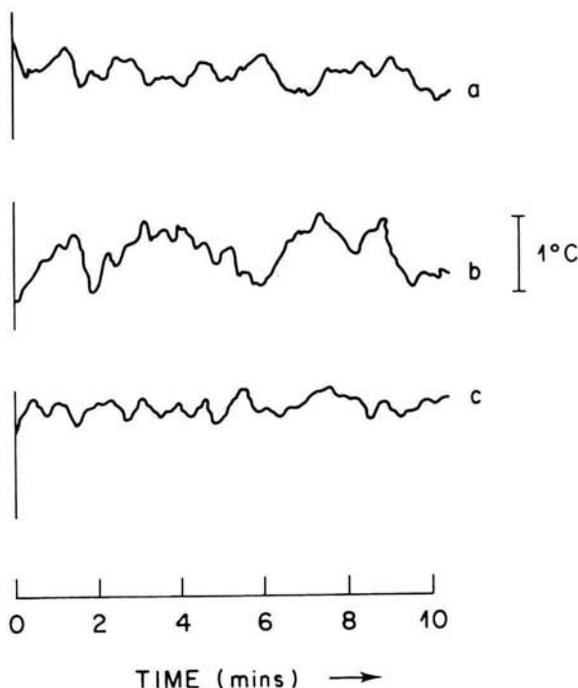


FIG. 9.3. Temperature oscillations in a solution of NiFe_2O_4 in $\text{BaO}\cdot 0.62\text{B}_2\text{O}_3$ (Smith and Elwell, 1968). (a) Thermocouple junction just below melt surface. (b) Junction 4 mm below surface. (c) as (b), but crucible rotated at 10 r.p.m.

BaO·0.62B₂O₃ at 1200°C. The melt depth in this case was only 3 cm but oscillations of amplitude 0.5°C were measured at a point 4 mm below the surface in a temperature gradient of about 10°C/cm. The amplitude could be reduced somewhat by rotating the crucible, as shown in Fig. 9.3(c).

Interesting observations in Czochralski growth of tellurium doped InSb were made by Kim, Witt and Gatos (1972). They found by "time markers" that only under thermal (convective) stability were the macroscopic and microscopic growth rates identical. Thermal stability was achieved by a stabilizing temperature gradient and by making the depth of liquid small. Otherwise oscillatory thermal instability or turbulent convection occurred leading to back melting and to microscopic growth rates more than 20 times greater than the average macroscopic growth rate. The striations produced by the temperature and the corresponding growth rate fluctuations could be made visible by selective etching and optical techniques. Time markers would be useful also in similar experiments on the origin of inhomogeneities in flux-grown crystals, and in effect such experiments are in progress according to Damen and Robertson (1972) and White (1971). The use of time markers in vapour growth was reported by Kroko (1966).

The incidence of oscillatory behaviour in high-temperature solutions can be reduced by the use of shallow melts or small temperature gradients as mentioned above. Since the depth of solution appears in Eqns (9.2) and (9.3) (which are valid for the critical range only, see Section 6.6.2) as l^3 , its effect is particularly marked. Brice *et al.* (1971) have shown that the incidence of oscillations may be reduced by the use of baffles which lower the effective depth of the melt and it is possible that similar arrangements will be necessary in HTS-growth for the growth of crystals which are particularly prone to striations. The tendency to form striations may also be reduced by using a growth rate which is well below the maximum stable value.

Other sources of growth-rate oscillations are also possible. If solute transport occurs only by diffusion, then a solution of the diffusion equations for $n(x, t)$ can give oscillatory behaviour in terms of the distance x from the interface but not in terms of the time. An oscillatory interface kinetic process has not been proposed although some periodically varying behaviour might be envisaged in the bunching of layers which leads to the formation of macrosteps. The possibility of striations due to an oscillating growth rate in an unstable supersaturation gradient was proposed by Landau (1958) and Petrov (1956).

Self-excited oscillatory motion *along* the interface near the breakdown of stability was predicted by Mullins and Sekerka (1964), and this theory was extended to growth from stirred melts by Delves (1968, 1971). A detailed discussion of these problems is given in Chapter 6.

Wilcox and Chase (1967) considered the effect of strain produced by incorporated impurities on the distribution coefficient. The authors developed an expression for the effective distribution coefficients for the case where no plastic deformation occurs. Although no experimental proof has yet been given, it seems plausible that a certain fraction of inhomogeneous impurity incorporation can be attributed to this effect.

Techniques for determination of inhomogeneities. Inhomogeneities in a bulk crystal cannot be measured quantitatively at present, but qualitative observations can frequently be made. Crystals often show effects due to variation in the refractive index, light absorption, etc., and crystals may show strain due to different lattice parameters and differing thermal expansion coefficients of the inhomogeneous regions. Since interferometry is extremely sensitive to fluctuations in optical density it is frequently used to prove qualitatively the high quality of crystals. Qualitative indication of inhomogeneous impurity incorporation is readily obtained when radioactive impurities are used (Landau, 1958) and occasionally selective etching can be used to display striations (Witt, 1967). Frequently inhomogeneities are the cause of line-broadening of X-ray diffraction patterns (see Section 9.4.2).

Quantitative determinations of inhomogeneities are performed by various techniques which allow local analysis of the surfaces of bulk crystals, of crystal sections, or of layers grown by liquid phase epitaxy. Examples of physical parameters (Curie temperature, magnetization, conductivity, optical absorption, etc.) which have been used to characterize inhomogeneities in flux-grown crystals are given later in this section.

Techniques for the analysis of inhomogeneities in crystals are based on narrow beams of electrons, photons or particles which strike the surface and excite electrons, X-rays or photons of characteristic energies or which cause local evaporation of the material. The possible techniques are summarized in Table 9.3. Many of the methods listed are applicable only to special problems, while several techniques are in the early stages of development.

Electron probe microanalysis is the most powerful and most widely used technique for the analysis of inhomogeneities and is discussed in Section 9.2.1. Here it should be added that the region which is excited and which emits X-rays has a larger diameter than the electron beam and a certain depth since the locally produced X-rays of short wavelengths excite other elements (secondary emission). Future developments in electron probe microanalysis are proceeding in the direction of narrowing the electron beam and of building sensitive X-ray detectors which allow a fast quantitative analysis of the whole X-ray spectrum.

TABLE 9.3. Techniques for Analysis of Local Inhomogeneities

Exciting beam	Emitted radiation or particles	Measuring technique	Local resolution	Sensitivity	Precision	References
X-rays (focussed or collimated)	X-ray diffraction	identification, cell parameters (see Sec. 9.4.2)	$\sim 50 \mu\text{m}\dagger$ $\sim 50 \mu\text{m}\dagger$	$\sim 5\%$ —	— $\sim 0.1-1\%$	See Section 9.2.4.
	X-rays (emitted) photons (luminescence) electrons	X-ray fluorescence analysis luminescence spectroscopy electron spectroscopy	$\sim 100 \mu\text{m}\dagger$ $\sim 100 \mu\text{m}\dagger$ $\sim 100 \mu\text{m}\dagger$	$\sim 0.1\%$ $\sim 0.1-1$ p.p.m.	$\sim 2\%$ $\sim 10\%$	See Section 9.2.1. Linares <i>et al.</i> , 1965 Chang, 1971; Preisinger <i>et al.</i> , 1971
UV	photons (luminescence) electrons	luminescence spectroscopy electron spectroscopy (ESCA)	$\sim 10 \mu\text{m}\dagger$ $\sim 10 \mu\text{m}\dagger$	—	$\sim 10\%$	Chang, 1971; Preisinger <i>et al.</i> , 1971; Siegbahn <i>et al.</i> , 1967
Laser	material vapour	optical emission spectroscopy	$\sim 50 \mu\text{m}\dagger$	$\sim 1-10^3$ p.p.m.	$\sim 1-10\%$	Snetsinger and Keil, 1967; Blackburn <i>et al.</i> , 1968
		atomic absorption (?) mass spectrometry	$\sim 50 \mu\text{m}\dagger$ $\sim 50 \mu\text{m}\dagger$	< 1 p.p.m.	$> 5\%$	Fenner and Daly, 1968
Electrons	X-rays photons (luminescence) electrons	electron probe microanalysis	$\sim 1 \mu\text{m}$ $\sim 1 \mu\text{m}$	$\sim 0.1-1\%$	$0.5-5\%$	See Section 9.2.1
		electron spectroscopy (Auger electr. spectr.)	$\sim 1 \mu\text{m}$	$0.1-1\%$	—	Chang, 1971
	electrons (diffraction)	identification, cell parameters	$< 0.1 \mu\text{m}$ $< 0.1 \mu\text{m}$	—	$\sim 5\%$	See Section 9.4.3 See Section 9.4.3
Neutrons, Protons and Alpha particles	neutrons and other backscattered particles	energy distribution	200Å in depth for B in silicon, < 1 mm	3 p.p.m.	—	Ziegler <i>et al.</i> , 1972; Ziegler and Baglin, 1971; Mitchell <i>et al.</i> , 1971; Davies <i>et al.</i> , 1967
Ions (sputtering)	electrons	electron spectroscopy	50Å in depth	—	—	Coburn and Kay, 1972; Gupta and Tsui, 1970 Socha, 1971
	positive ions material particles	ion microprobe mass spectrometry	—	—	$> 5\%$	Coburn and Kay, 1971
	reflected ions	ion scattering spectroscopy	—	—	—	Smith, 1971

† Focussing to $< 10 \mu\text{m}$ should be feasible.‡ Focussing to $< 5 \mu\text{m}$ should be feasible.

The analysis of impurities as a function of depth has been reviewed by Coburn and Kay (1972) who distinguish three categories of techniques: (a) non-destructive, (b) microsectioning with observation of the remaining material, and (c) microsectioning with observation of the material removed. For (b) and (c) chemical etching or preferably etching by sputtering under clean conditions has been used. The measuring techniques are included in Table 9.3.

Inhomogeneities observed in flux-grown crystals. It seems to be widely accepted that striations in crystals grown from high-temperature solutions arise from temperature fluctuations which are caused by insufficient temperature control or by convective instability. Striations have been observed in numerous cases, therefore in the following only a few examples will be given.

Striations corresponding to variations in the chromium concentration were found in the ruby crystals grown by White and Brightwell (1965). These were believed to arise because of preferred adsorption on different faces, giving rise to a series of sharp boundaries in some crystals cut parallel to the c -axis.

Chase (1968) found a variety of striations in indium oxide crystals. The bands in the innermost zone were very clear and decreased in width with distance from the growth centre. In the intermediate zone very fine striations were observed with wider bands, about 1 mm across, superimposed. The fine striations were absent in the outermost zone but less well-defined variations in colour were observed. The various types of striation could be readily correlated with the mode of growth. The most marked striations, in the inner zone, were produced at the time of most rapid growth following nucleation. In the intermediate zone, growth occurred by nucleation of layers at corners and edges of the crystals and the fine bands are presumably related to the period between the passage of successive layers. The bands of relatively minor intensity were associated with a more stable mode of growth at screw dislocations giving rise to growth hillocks. The striations could all be correlated with fluctuations in the furnace temperature resulting from an imperfect controller.

The very regular, fine bands of striations in a dysprosium orthoferrite crystal as shown in Fig. 9.4 have been attributed by Wanklyn (1975) to an on-off temperature controller. Banding may be a periodic array of inclusions caused by periodic unstable growth as demonstrated in Fig. 9.5. A careful distinction should be made if possible between striations (banding due to varying composition or impurity incorporation) and banding of inclusions. Both phenomena may be of similar origin, namely the fluctuations in growth rate caused by changes in the temperature or hydro-

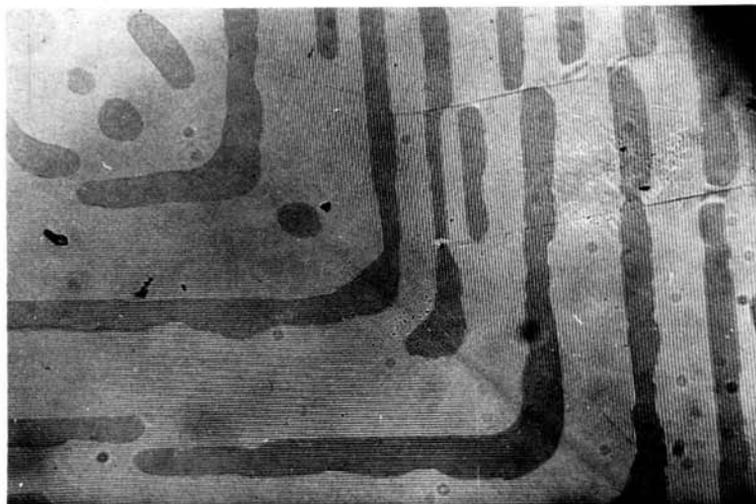


FIG. 9.4. Striations (the fine lines) in a DyFeO_3 crystal caused by an on-off temperature controller (courtesy B. M. Wanklyn).



FIG. 9.5. Bands of inclusions in GdAlO_3 parallel to as-grown faces (Scheel and Elwell, 1972).

dynamics. In several cases “striations” have been reported which could have been periodic layers of tiny inclusions due to unstable growth as discussed above. This effect is to be expected when the growth rate is near the maximum stable value. Then growth rate variations due to temperature oscillations will cause alternatively stable and unstable growth, or the

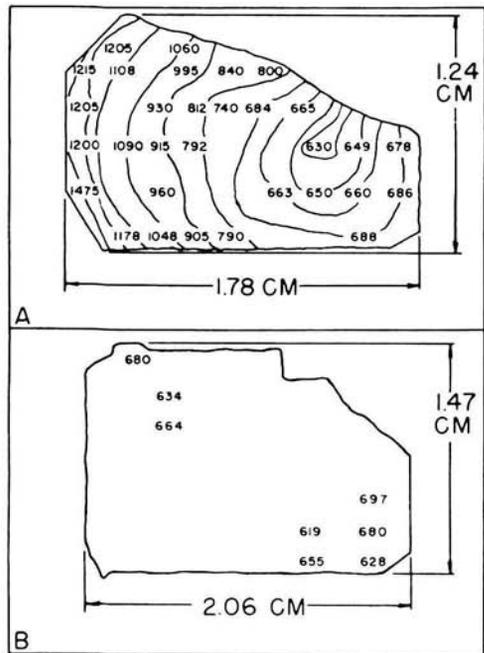
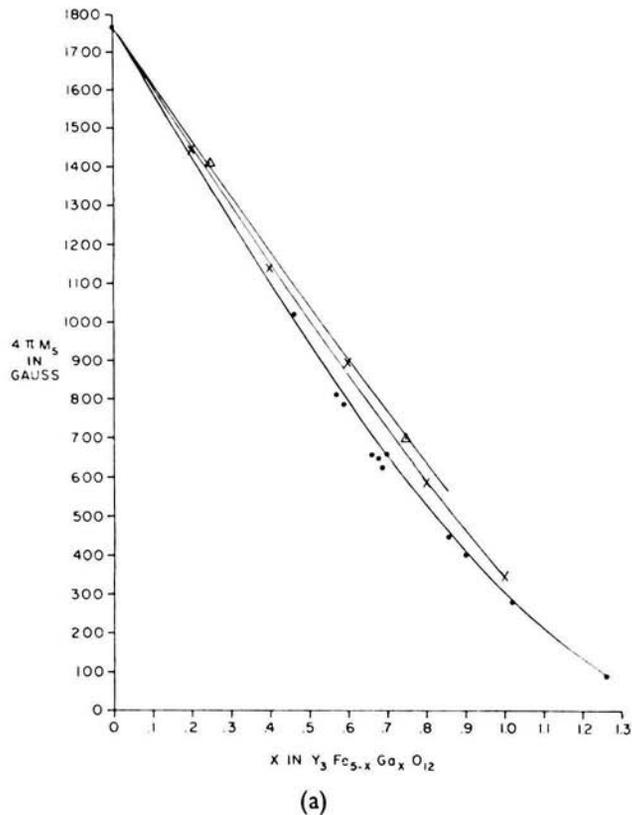


FIG. 9.6. (a) $4\pi M_s$ versus composition in $Y_3Fe_{5-x}Ga_xO_{12}$. (b) $4\pi M_s$ variations in crystal slabs of $Y_3Fe_{5-x}Ga_xO_{12}$ solid solutions (Nielsen *et al.* 1967).

growth rate variations may be self-exciting as described by Landau (1958).

Lefever *et al.* (1961) found a banded appearance of finely divided inclusions of $100\ \mu\text{m}$ diameter in yttrium iron garnet. These bands appeared to be associated with the presence of divalent iron in the crystals since their incidence could be reduced by growing the crystals in an oxygen atmosphere or by reducing the silicon concentration in the melt. Silicon enters the garnet lattice readily as Si^{4+} and so produces Fe^{2+} ions by charge compensation.

Giess *et al.* (1970) observed striations with a periodicity of about 2 to $60\ \mu\text{m}$ in rare-earth orthoferrite crystals but their origin has not been found. The lead concentration was found to vary from 1.10% in the darker bands to 0.72% in the lighter regions. These bands must therefore be formed during growth. It appears likely that the lead would be present in finely divided inclusions but the authors were unable to distinguish whether or not the impurity had entered the crystal lattice.

Few examples have been published where physical measurements were made to demonstrate the presence of inhomogeneities in crystals. In the interesting paper of Nielsen *et al.* (1967) local saturation magnetization ($4\pi M_s$) measurements on flux-grown solid solutions of $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$

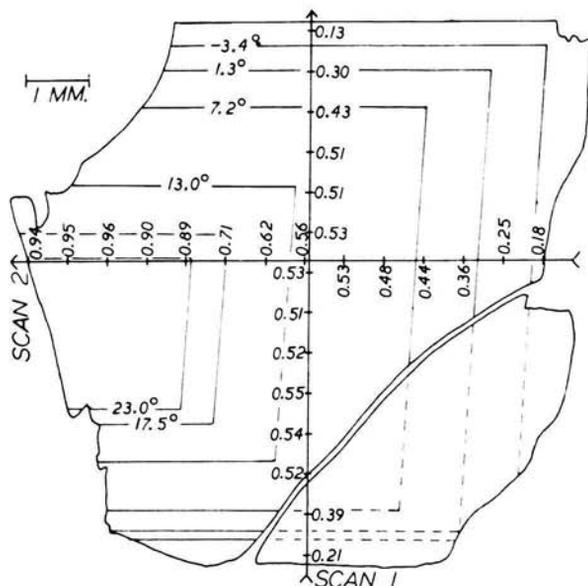


FIG. 9.7. Outline of the boundary of the surface of Rh-doped Fe_2O_3 crystal. The uncorrected Rh_2O_3 dopings are shown on the scan paths. The straight lines indicate the antiferromagnetic-weakly ferromagnetic boundaries for several temperatures (Morrish and Eaton, 1971).

could be correlated with compositional inhomogeneity using the data of Fig. 9.6(a). The authors were able to correlate the $4\pi M_s$ variation and therefore the compositional inhomogeneity with the weight loss of the solution during the experiment: a 20% weight loss (mainly by PbF_2 evaporation) resulted in a $4\pi M_s$ variation of 845 gauss along the crystal section, whereas in another experiment a 4.2% weight loss resulted in a $4\pi M_s$ variation of only 260 gauss. Typical examples of measured saturation magnetization values for various crystal sections are shown in Fig. 9.6(b), where *A* is an example of a crystal from a run with high weight loss and *B* is typical of a crystal grown in a tightly closed crucible.

The magnetic (Morin) transition temperature T_M of pure haematite at about 263°K is very sensitive to doping; Al^{3+} , Ga^{3+} , Ti^{4+} and Sn^{4+} all lower T_M whereas Rh doping raises T_M . Morrish and Eaton (1971) studied rhodium-doped haematite crystals and found a correlation between the doping level and the magnetic transition temperatures. Their results as measured by electron microprobe are shown along scan 1 and scan 2 in Fig. 9.7 for a doping level of about 0.5 mole% Rh. The isotherms of the magnetic transition were parallel to the growth front, from left to right. In the first stage much rhodium was incorporated and T_M is about 20°C, whereas the outer portion of the crystal contains little Rh and therefore shows T_M values below 0°C.

9.3. Structural Aspects and their Determination

Most physical phenomena are sensitive to the structural aspects of crystals, to the three-dimensional periodic arrangement of atoms, ions, and molecules and to the array of bonds between these species. However, only those techniques which use diffraction of a radiation with a wavelength similar to the spacings within the crystals can give a picture of the structure as will be discussed in connection with the diffraction of X-rays, electrons, or neutrons. Most physical phenomena only indicate the anisotropy (or isotropy of cubic crystals) and the symmetry of the crystals. From optical phenomena and optical measurements symmetry, orientation of the crystal, and occasionally other structural details can be very conveniently deduced as discussed below. The characterization of thin films by optical and other methods has been described by Heavens (1965).

9.3.1. Optical techniques

Microscopy. Routine examination of crystals is most frequently performed by optical microscopy, particularly if the crystals are transparent. It is considered necessary in most crystal growth laboratories to have permanent access to a polarizing microscope, preferably with a universal stage and a camera attachment.

Microscopic techniques have been reviewed by a number of authors, for example Chamot and Mason (1958), Burri (1959), Winterbottom and McLean (1960) and Schaeffer (1966). The principal applications of microscopy in the study of crystals grown from high temperature solution may be classified as follows:

- (a) Identification and examination of optical properties,
- (b) studies of surface features,
- (c) investigations of defects.

The use of optical methods in crystallography has been described by Winchell (1937), Bloss (1961), Wood (1963), Gay (1967), Rath (1969) and Hartshorne and Stuart (1969). A complete optical examination of a transparent crystal would include the following stages:

(i) Examination in unpolarized light and observations of colour, habit, edge angles, cleavage, refractive index and optical dispersion (variation of refractive index with the wavelength of light). Precautions necessary for precision measurements of refractive index are discussed by Hafner and Rood (1967), and Lawless and DeVries (1964) described the refinement of refractive index measurements of thin samples.

(ii) Use of crossed polarizers to distinguish between isotropic and anisotropic crystals and to look for twinning and strain. Measurement of the extinction angle and determination of birefringence (difference in refractive index for ordinary and extraordinary ray).

(iii) Determination of the principal refractive indices of anisotropic crystals and a study of pleochroism (variation of absorption of light with direction of vibration of polarized light).

(iv) Observation in convergent polarizing light between crossed polars, using the microscope as a *conoscope*. The advantage of convergent rather than parallel light is that the resulting image or *interference figure* depends upon the optical character in many crystallographic directions rather than in a single direction. The converging beam is produced by the condenser lens and a real image is formed by the objective. Each point in the image corresponds to a definite direction of light through the crystal and the image may be examined through the analyzer directly or by use of an auxiliary lens, the Bertrand lens, to bring the image into the focal plane of the eyepiece. The image may be used to classify anisotropic crystals as uniaxial or biaxial and to determine the positive or negative character and the angle between the two optic axes of biaxial crystals. For various optical measurements and for determining the orientation of twins, of lamellae due to unmixing, and of inclusions, the universal stage of Fedoroff and the spindle stage are useful or necessary (Reinhart, 1931; Fairbairn and Podolsky, 1951; Wilcox, 1959; Emmons, 1943).

Suitable modifications to the optical microscope permit several additional investigations. *Ultramicroscopy* is a technique in which a narrow beam of light, usually from a laser, is incident on the crystal in a direction at right angles to the axis of the microscope so that light scattered from inclusions and other defects is observed. This technique was used by Newkirk and Smith (1967) to study inclusions in BeO, and particles less than 1000 Å in diameter were detected.

Phase contrast microscopy (Zernicke, 1938; Sunagawa, 1967) and *interference microscopy* (Tolansky, 1943, 1970; Nomarski and Weill, 1954) are modifications of optical microscopy in which the image is extremely sensitive to the surface topography, and these techniques are particularly useful for the study of surface features such as growth spirals and layers. A height resolution of about 4 Å may be achieved under favourable conditions. The great advantage of Tolansky's multiple beam interference method is that the interference fringes are narrowed and sharpened relative to those in the classical Newton's rings experiment and so the height resolution is perhaps 100 times that possible in the latter experiment.

Infrared microscopy (Sherman and Black, 1970; Sunshine and Goldsmith, 1972) is useful for materials which absorb in the visible but are partially transparent in the infrared, such as many chalcogenides and ferrites. Valuable information on the magnetic domain structure (which is sensitive to defects) of the magnetic bubble domain materials and devices may be obtained using polarized infrared light, and defects in several semiconductors may be studied easily, especially in thin films.

Infrared absorption analysis may sometimes be usefully applied to the identification of inorganic materials or impurities (Lawson, 1961; Moenke, 1962; Nakanoto, 1963; Kendall, 1966; Harrick, 1967).

Crystal handling. In the case of materials of low transparency, interior features of the crystal may be examined if it is cut into thin sections. Thin crystal slices with as little damage as possible are also a necessity for X-ray topography as will be discussed in Section 9.4.3. The method used for sectioning will depend on the material and will normally involve *cleaving*, *sawing*, *chemical or electro-chemical machining* or *spark-cutting*. The latter can be used only for electrically conducting materials and it produces surface damage as does mechanical sawing. The most suitable saw blades are normally thin metallic discs impregnated with diamond grit which are rotated at high speeds. The main disadvantage of such saws is that the amount of damage will increase with ageing of the blade as the number of irregularities increases. In general the damage is less for an annular blade impregnated along its inner edge and supported along its perimeter than for a blade supported at its centre and with a peripheral cutting edge,

and even less damage is reported for the use of a diamond-impregnated wire saw. Successful cleaving depends upon the existence of a cleavage plane within the crystal, and relatively few flux-grown crystals of practical interest will cleave easily. Chemical machining, as with an acid saw, produces the least damage but the cutting rate is often prohibitively slow.

It is normally assumed that cutting will result in some damage to the crystal and that the damaged layer must be removed if it is required to examine the "as grown" crystal characteristics. The slice is first *mechanically polished* on some abrasive paper to give a flat surface. It is sometimes desirable to mount the crystal in a cylinder of transparent plastic to facilitate handling and to prevent rounding of the edges during polishing. Progressively finer grades of abrasive paper are used to give a good polish and the final stage is normally performed with fine powder such as alumina, magnesia, chromic oxide or jeweller's rouge. The powders are dispersed on napless cloth of cotton or silk, with velvet of fairly deep pile used for the final polish. Alternatively the whole polishing process may be effected using diamond pastes, containing diamond grit of various diameters down to about $0.1 \mu\text{m}$. A jig for holding specimens for automatic polishing using diamond paste and soft metal lapping plates has been described by Bennett and Wilson (1966). The crystal in this case is held in position by wax and polishing is effected by rotating the lapping plate at 10–60 r.p.m. while the jig traverses this plate on a reciprocating arm.

A process which is currently very popular for a final polish involves the use of "Syton".† This is a silica abrasive in an alkaline colloidal suspension, which gives a good surface finish on, for example, refractory oxides.

Metal slices may be thinned by electrolysis, and this *electrolytic polishing* has the advantage that there is no mechanical disturbance. The principal disadvantage is that it frequently does not result in a smooth surface, since selective attack tends to occur in the region of any tiny cracks, pores or inclusions.

An alternative technique is to combine mechanical polishing with chemical attack, for example by impregnating a polishing cloth with a chemical reagent.

Since any mechanical polishing will normally result in some surface damage and the generation of dislocations, the final stage in the preparation of thin samples is normally *chemical polishing* in which a uniform layer of crystal is removed by the action of a solvent. Fused salts have been used quite commonly for this purpose but suffer from the disadvantage that the specimen cannot be observed during the polishing process. Shick (1971) has proposed the use of phosphoric acid at 380–425°C as a chemical polish for orthoferrites. The polishing rate in his experiments was about

† Trade mark, Monsanto Company.

10 $\mu\text{m}/\text{min}$ compared with 3–6 $\mu\text{m}/\text{hr}$ for Syton, and an improved surface finish was obtained. Shick found rotation at about 40 r.p.m. to give a surface of optimum smoothness and describes a jig for this purpose. In his experiments layers of orthoferrite initially 0.1 mm in thickness were reduced to half this value and the resulting improvement in the sharpness of the domain pattern is evidence for the complete removal of the strained outer layers. Phosphoric acid was also used by Basterfield (1969) as a chemical polish for yttrium iron garnet, while Reisman *et al.* (1971) preferred mixtures of phosphoric acid and sulphuric acid for spinel and sapphire.

Certain solvents have the property of causing preferential attack at strained regions rather than removing a layer uniformly. The preferential attack results since atoms in these regions are less tightly bound because of the strain energy. Solvents which possess this property are unsuitable for use in chemical polishing but may be used as etchants for measurement of the concentration of those defects which give rise to the strain. The most likely cause of *etch-pits* are dislocations and counting of etch-pits is the most convenient method of studying the concentration and distribution of dislocations in crystals. Etch-pit counts may, however, underestimate the dislocation density if selective etching of edge or screw dislocations occurs. Reviews of etching for the study of dislocations have been given by Regel *et al.* (1960) and Amelinckx (1964); some typical etchants are also listed by Laudise (1970). Examples of dislocation densities determined by etching are listed in Table 9.4.

Examples of optical appraisal studies. A large number of appraisal studies of crystals grown from high-temperature solution have appeared in literature, and we shall consider only a few typical examples.

Lefever *et al.* (1961) examined polished sections of yttrium iron garnet crystals by transmitted light and were able to observe the dendritic core, layers of inclusions and striations. Janowski *et al.* (1965) studied the types of inclusion in ruby crystals by transmission microscopy and attempted to relate their distribution to that of dislocations revealed by etching the same crystals. They were thus able to show that dislocations were sometimes produced by solvent inclusions. In addition, twin planes were observed and were found to be associated with groups of etch pits only infrequently, the more common result of etching being to produce a shallow groove along the twin boundary.

Nelson and Remeika (1964) used a Twyman-Green interferometer to investigate the optical homogeneity and departure from face flatness of ruby crystals used for laser generation. The variation in optical path across the crystal was about $\lambda/10$ for red light. A conoscope was used to look for strain but this was barely detectable.

TABLE 9.4. Dislocation Density of HTS-Grown Crystals

Material	Solvent/flux	Count	Face	Method	Reference
Al ₂ O ₃	Various	0 (over 1–2 cm ²)	—	etch	Linares, 1965b
Al ₂ O ₃	PbO/PbF ₂	10 ²	{001}	etch	Stephens and Alford, 1964
TiO ₂	Alkali borates	4 × 10 ¹	—	etch?	Berkes <i>et al.</i> , 1965
BaTiO ₃	KF?	10 ² –10 ⁴	{001}	etch	Waku, 1962
Y ₃ Al ₅ O ₁₂ ; Y ₃ Ga ₅ O ₁₂		10 ² –10 ⁴	{110}; {211}	X-ray topography/etch	Belt, 1969
ThO ₂	Li ₂ W ₂ O ₇	10 ^{9±2}	{111}	X-ray rocking curve	Finch and Clark, 1965
Al ₂ O ₃	PbF ₂	10 ² –10 ⁴	{001}	etch	White and Brightwell, 1965
Y ₃ Al ₅ O ₁₂	PbF ₂ /PbO/B ₂ O ₃	6 × 10 ³	{110}	etch	Timofeeva <i>et al.</i> , 1969a
Al ₂ O ₃	Bi ₂ O ₃ /PbF ₂ ; Bi ₂ O ₃ /BiF ₃	1–10	{001}	etch	Janowski <i>et al.</i> , 1965
Al ₂ O ₃	PbO/B ₂ O ₃	1 × 10 ⁴	—	etch	Sahagian and Schieber, 1969
Al ₂ O ₃	PbF ₂	10 ² –10 ⁴	—	etch	Champion and Clemence, 1967
MgAl ₂ O ₄	PbF ₂	50–200	{111}	X-ray topography	Wang and McFarlane, 1968
MgAl ₂ O ₄	PbF ₂	0–200	{111}	X-ray topography	Wang and Zanzucchi, 1971
Graphite	Fe, Ni	10 ⁷	{001}	etch	Austerman <i>et al.</i> , 1967
		10 ^{3–5}	other planes	etch	
BaTiO ₃	TiO ₂	10	{100}	etch	Belruss <i>et al.</i> , 1971

Detailed optical tests on rubies grown by various methods were performed by Bradford *et al.* (1964). A conoscopic investigation was used to look for variations in the optic axis, based on the disturbance of the normal "isogyre" figure which occurs when the crystal is not perfectly uniaxial. (An isogyre is characterized by dark arms extending in the directions of polarization of the polarizers, with a set of dark circles filling the otherwise bright areas.) On the flux-grown ruby the disturbance of the figure was found to be very slight, and was attributed to strain near the edges of the crystal.

The tests also included *shadowgraphs* produced simply by passing light from a zirconium arc through a filter and the crystal onto a distant film. The resulting photographs show up defects in the crystal as variations in the intensity of the image. The shadowgraphs included some taken with crossed polarizers, which may be expected to reveal contrast due to photoelastic effects and possibly also due to variations in the optic axis. *Small angle scattering* of a laser beam was also used as an indication of general optical quality; the degree of scattering depends upon the number and nature of scattering centres in the crystal. The quality of the flux grown crystals was generally good, but all crystals suffered from variations in the distribution of the chromium dopant.

Newkirk and Smith (1965) and Austerman *et al.* (1965) examined the surface features and inclusions in crystals of BeO. Oblique illumination was used to reveal the central projection associated with the inversion twin (see Section 5.5.3) and the height of this projection was measured by an interference method.

A fairly detailed microscopic study of defects in yttrium aluminium garnet was reported by Timofeeva *et al.* (1969). Observations were made by transmitted, reflected and by scattered light, and polarized light was used to show the stress distribution. Refractive index variations were also monitored using a Michelson interferometer. These observations permitted a distinction to be made between inclusions arising during growth and those which occurred during the subsequent cooling, since the latter were not accompanied by high stress. Many inclusions were in the form of small particles of size less than $1\ \mu\text{m}$, which were best revealed by ultramicroscopy. Crystalline inclusions of Al_2O_3 , Nd_2O_3 and Y_2O_3 were also observed and found to give rise to large stress fields.

Photoelastic stress patterns associated with dislocations were observed by Bond and Andrus (1956) and in yttrium gallium garnet by Prescott and Basterfield (1967). The dislocations in this material were found to be introduced and propagated during the growth process. An example of the use of this technique is given in Fig. 9.8, which shows the pattern in the region of the growth centre on a (110) face of $\text{Y}_3\text{Ga}_5\text{O}_{12}$. The difference in

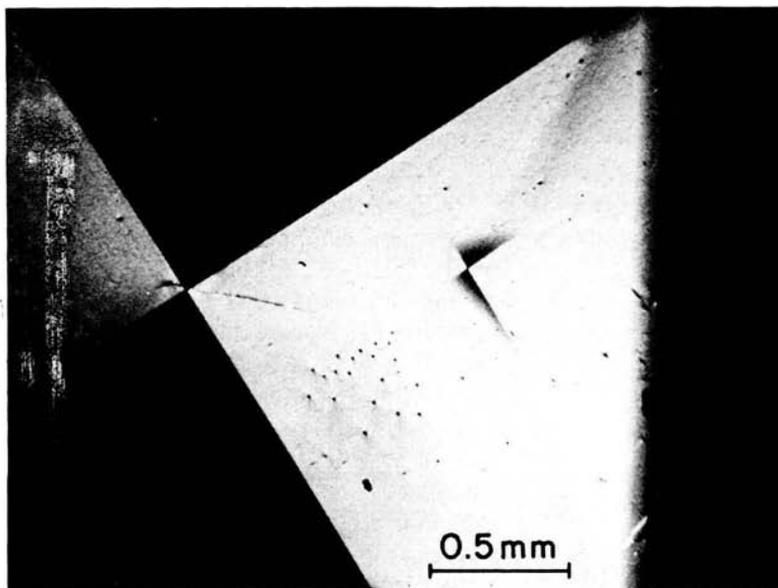


FIG. 9.8. Stress birefringent pattern on (110) growth face of $Y_3Ga_5O_{12}$ (Prescott and Basterfield, 1969).

strain direction in adjacent quadrants is clearly indicated, as is the presence of a secondary growth centre in the right-hand quadrant.

Spectroscopy. The increasing use of crystals in lasers has encouraged the use of *optical spectroscopy* as a means of characterization. A good example is the study of optical emission spectra of Cr^{3+} in ruby by Linares (1965b). The room temperature fluorescence linewidth was found to be the same in crystals grown by the Verneuil flame fusion method as in crystals grown by various fluxes. At 77 K, however, rubies grown from fluxes free from fluorine exhibited a linewidth of less than 0.5 cm^{-1} , comparable with the best flame fusion ruby, while crystals grown from PbF_2 or BaF_2/AlF_3 fluxes exhibited linewidths greater than 1.5 cm^{-1} . The emission studies also revealed fluorescence due to contamination from the crucible material, whether platinum, iridium or rhodium was used. The same author (Linares, 1967) also reported spectroscopic studies of CeO_2 and ThO_2 .

Wang and Zanzucchi (1971) made emission, absorption, reflection and transmission measurements on $MgAl_2O_4$ crystals grown from a PbF_2 flux and also on crystals grown by the Czochralski and flame fusion methods. All crystals were found to be transparent between $0.3\ \mu\text{m}$ and $7.2\ \mu\text{m}$, but the flux-grown crystals exhibited a much sharper absorption edge below

0.28 μm which was attributed to Fe impurity. Reflection measurements were made in the range 10–40 μm in which bands occur due to lattice vibrations associated with the octahedral and tetrahedral sites in the spinel lattice. The reflectivity of the flux-grown crystals was rather lower than that of the Czochralski or flame fusion crystals, again probably because of chemical impurities or inclusions. The emission linewidth of all the synthetic crystals was much broader than that of natural MgAl_2O_4 , an observation which rules out the possible application of the synthetic spinel as a laser host material.

Infrared absorption spectroscopy was used by Wickersheim *et al.* (1960) to determine the concentration of silicon in yttrium iron garnets.

9.3.2. X-ray methods

X-ray diffraction is by far the most popular method for the identification of substances and for the investigation of crystal structure and degree of crystal perfection. Many diffraction techniques have been developed, for a wide range of problems. A simple approach to X-ray diffraction is provided by the Bragg (1913) condition

$$n\lambda = 2d_{hkl} \sin \theta_{hkl},$$

where n is the order of the diffracted beam, θ_{hkl} the angle between the incident X-ray beam and the atomic planes hkl which give rise to the diffraction peak considered, d_{hkl} the spacing between such planes and λ the X-ray wavelength. Alternatively it may be convenient to consider the reciprocal lattice P_{hkl} which may be envisaged by rewriting the Bragg condition in the form (for $n=1$)

$$\sin \theta_{hkl} = \frac{1/d_{hkl}}{2/\lambda} = \frac{P_{hkl}}{2/\lambda}.$$

Diffraction occurs when a reciprocal lattice point passes through the surface of the sphere of reflection from the hkl planes. The relation between the various diffraction techniques and the reciprocal lattice concept have been treated by Azaroff (1968). Azaroff also gives a clear overview of the application of X-ray diffraction techniques to crystal structure analysis, which is discussed in detail by Buerger (1960, 1962), Lipson and Cochran (1966), Guinier (1962), Barrett and Massalski (1966), and by Stout and Jensen (1968).

Identification of inorganic substances by X-ray diffraction patterns. The observation of a characteristic diffraction pattern provides a convenient means of identification of a crystal, to demonstrate the incidence of twinning or polycrystallinity, or to determine imperfections such as stacking

fault densities (Warren, 1969). Single crystals are normally necessary for the identification of new compounds since indexing of powder patterns is difficult unless the symmetry is high. If only small single crystals of less than 1 mm are available (minimum size 0.05 mm, optimum size 0.1–0.2 mm) information on the crystal symmetry (point group and space group) and on the unit-cell geometry may be obtained from X-ray diffraction data with the single-crystal diffractometer (Arndt and Willis, 1966), the Buerger precession camera (Buerger, 1964), or the Weissenberg camera. Of the two latter, the precession camera is preferable since it gives photographs of the undistorted reciprocal lattice of the crystal, although the Weissenberg camera presents the complete (but distorted) reciprocal lattice. With this information and some knowledge of the elements present in the compound, of the density etc. it should be possible to identify any known compound using "Crystal Data" of Donnay *et al.* (1963, 1972) or "Crystal Structures" of Wyckoff (1963–1968).

One of the easiest and yet most reliable techniques to identify crystalline phases is by X-ray diffraction of powders. Generally about 10 mg powder of the unknown material is available so that the more convenient powder diffraction patterns obtained, for example by the Guinier-DeWolff camera, can be used for identification. The d -values of the lines can be directly measured by means of a ruler, or the distances (angles) of the diffraction lines from the primary X-ray beam are measured and converted into the d -values. With these d -values of the 3 to 8 strongest lines a reliable identification is normally possible by use of the Powder Diffraction File (1973), especially with some additional chemical or physical knowledge of the material. In not too complex cases even the constituents of mixtures can be identified and their approximate concentrations estimated.

Since the identification of crystals of known compounds from their powder diagrams is generally much easier than from single crystal data, Gandolfi (1967) has developed a camera which allows a powder pattern to be obtained from a small single crystal. This technique is very useful when crystals cannot be powdered due to their value or rarity.

Precision measurement of lattice parameters. The exact lattice constants may be used as a measure of the composition of the crystal, since changes in lattice dimensions are caused by substitution of ions which differ in size from those of the host crystal. For accurate determination of lattice constants, powder samples (optimum crystallite size of the order of 5 μm) are normally preferred. X-ray powder techniques have been reviewed by Klug and Alexander (1954), by Peiser *et al.* (1955) and by Azaroff and Buerger (1958), and the precise determination of lattice constants by Bond's method and the refinement of the lattice constants by a least

squares computer programme has been described by Barns (1967) and by Segmüller (1970).

For the Debye-Scherrer method a powder camera of large diameter, 14.5 cm or more, is necessary to give good resolution. In order to achieve the highest accuracy, corrections are necessary for the film position and shrinkage, eccentricity of the specimen, absorption by the specimen and divergence of the X-ray beam. Temperature stabilization is also necessary for very high accuracy. The best accuracy which can be achieved is normally not better than a few parts in 10^5 , so that the uncertainty in the determination is in the fourth decimal place if sufficient care is taken.

Counter diffractometers have considerable advantages over film cameras and can give somewhat higher precision. The counter used to detect the X-rays is normally located at a greater distance from the sample and improved resolution is possible by the use of *Soller slits* which limit the horizontal and vertical spread of the beam. In addition, use is made of the tendency of a divergent beam of X-rays to come to a "focus" after diffraction by the specimen in the normal *Bragg-Brentano* arrangement. If the counting arrangement is automated, the profile of a diffraction peak can be plotted very accurately. In this way Baker *et al.* (1966) were able to measure *changes* in lattice parameter of 1 part in 10^7 , using on-line computer control.

The geometrical arrangement of Seeman (1919) and Bohlin (1920) in which the diffracted X-rays converge to a point can also be used to give improved resolution in film cameras. Particularly high resolution can be obtained if this *parafocussing* geometry is used together with a curved-crystal monochromator as in the *Guinier* (1937) camera. Such cameras, for instance the Guinier-De Wolff and the Jagodzinski camera, have an accuracy approaching 1 part in 10^5 and, under ideal conditions, even one order of magnitude better, especially when good reference samples with well-defined lattice constants (Si, NaCl, Al, etc.) are used. Another advantage of the two focussing camera types mentioned is that three or four samples can be analyzed simultaneously.

As an example of the changes in lattice parameter which may be expected, Wang and McFarlane (1968) found that the lattice parameter of 7 batches of MgAl_2O_4 crystals varied from 8.0797 to 8.0848 Å, with impurities in the range 10–100 p.p.m. The crystal of highest purity had a lattice parameter of 8.0830 Å.

It is clearly preferable if measurements are performed on single crystals since local variations in lattice parameter can be studied and the possibility is avoided of changes brought about by strain in the process of powdering. Isherwood (1968) has applied the *double diffraction* technique (Isherwood and Wallace, 1966) to the precise determination of the lattice parameter

of yttrium iron garnet. The precision of any one measurement was $\pm 0.0004 \text{ \AA}$, and the lattice parameter of crystals of various impurity levels and grown from a $\text{PbO/PbF}_2/\text{B}_2\text{O}_3$ flux was found to vary between 12.3752 and 12.3800 \AA . This variation appeared to result from a change in the lead content of the crystals rather than the level of rare-earth impurities. An interesting result of this investigation was the observation of a departure from cubic symmetry caused by a deformation in the growth direction, for both $\langle 110 \rangle$ and $\langle 211 \rangle$. A reversion to cubic symmetry occurred on light abrasion of the crystal surfaces. This anisotropy is of interest in the application of garnets in bubble domain devices, and is discussed in Chapter 8.

Willoughby *et al.* (1971) correlated non-stoichiometry of gallium arsenide with precisely measured lattice parameters.

Orientation of crystals. In order to orient crystals for cutting or for physical measurements, optical techniques are useful when the crystal is transparent (Bunn, 1961; Wood, 1963). Greater convenience and precision are obtained when the crystal is oriented by X-ray diffraction. Although other single-crystal diffraction techniques are frequently used for this purpose the Laue back-reflection geometry is the most convenient and popular technique for crystal orientation (Barrett and Massalski, 1966; Wood, 1963). From Laue photographs, the symmetry may be easily obtained as well, whereas indexing of the Laue spots in order to obtain some structural information has become unnecessary in view of the development of the elegant single crystal techniques and especially of the powerful computer-automated single crystal diffractometers (Ahmed, 1969).

9.3.3. Electron and neutron diffraction

X-rays interact with the electron shell whereas an electron beam interacts more strongly (by a factor of about 10^4) with the nucleus of the atom so that the absorption by the sample is much stronger and only very small crystals ($< 1 \mu\text{m}$) or very thin layers ($< 1000 \text{ \AA}$) can be examined by transmitted electron diffraction. Strongly absorbing samples can only be examined by electron back reflection. Generally electron diffraction is performed in electron microscopes with the necessary accessories. Normally the lattice constants may be determined to no better than 1%. Electron diffraction is especially powerful for the detection of impurities and of unmixing, with a sensitivity of about 0.1% depending on the distribution. Also for the identification of the constituents of complex mixtures and for indexing X-ray powder diagrams electron diffraction might be of help since it produces an undistorted pattern of the reciprocal lattice which in X-ray diffraction is only achieved by, for example, the precession method

for the study of single crystals. Another application of electron diffraction is in the observation of magnetic and ferroelectric domain boundaries, although the application of electron diffraction to structure determination is limited. The wavelength of the electron beam can be adjusted by the applied voltage, and in the case of long wavelength (of the order of 1 Å) electrons one speaks of Low Energy Electron Diffraction (LEED) which is used for surface studies (see Section 9.4). Electron diffraction is the topic of the reviews of Pinsker (1953) and of Vainshtain (1960, 1964), and is treated also in the books on electron microscopy.

In *neutron diffraction* (Bacon, 1962) the neutrons interact with the nucleus and no Coulomb interactions occur. Because of the complexity of the instrumentation and of the limited applicability of neutron diffraction it is only used for structure determination when other techniques such as X-ray and electron diffraction are not applicable. For example, monochromatized thermal (slow) neutrons are used for the determination of hydrogen positions in H-containing compounds, and for the cation distribution of elements with similar atomic weights but with different scattering amplitudes for neutrons (e.g. Fe, Co).

Since neutrons possess magnetic dipole moments they interact with electronic magnetic moments or electronic magnetic fields. Thus the magnetic scattering amplitude depends on the electronic structure of the atoms, and the magnetic structures of many ferromagnetic, ferrimagnetic and antiferromagnetic materials have been analyzed (Bertaut, 1963; De Gennes, 1963; Forsyth, 1970).

9.3.4. Various physical techniques

In addition to the classical methods for the study of crystal structures or structural aspects, several physical techniques have been used with increased emphasis in order to obtain "indirectly" information on the structure and on the relative positions of atoms in crystals. For example, the point group can be determined by optical dielectric constants, acoustic measurements, magnetostriction and electrostriction. The local symmetry around specific atoms or ions and the local point group can be derived by electron spin resonance (ESR, EPR), nuclear magnetic resonance (NMR), optical absorption spectroscopy and by Mössbauer spectroscopy, whereas magnetic symmetry properties of crystals are studied by neutron diffraction, magnetic measurements (of susceptibility, saturation magnetization, magnetic anisotropy and magnetostriction), NMR, Mössbauer spectroscopy, and the Kerr and Faraday effects. By several of the above-mentioned techniques it is possible to analyze the cation distribution in, for instance, spinels or garnets and so to study order-disorder phenomena.

In several cases critical temperatures and pressures at which crystallo-

graphic, magnetic or electronic *phase transitions* occur can help in the characterization. Such critical data are obtained with the polarizing microscope, by X-ray, neutron or electron diffraction, by calorimetry (differential thermal analysis DTA or measurement of specific heat), by measurement of the magnetic or dielectric susceptibility, by determination of the resistivity or the thermoelectric power, of dilation and elastic constants, or by EPR, NMR and Mössbauer spectroscopy under the appropriate conditions. Only the most important or popular phenomena which are sensitive to phase transitions have been mentioned and many other physical properties and phenomena are sensitive to phase changes. Several of the physical techniques are discussed briefly in connection with defects (Section 9.4.5).

9.3.5. Determination of material constants

A complete description of a material contains its physical properties, thermodynamic data, and chemical properties. These properties are related to the structure, but most of them are too unspecific or cannot be measured with the necessary accuracy in order to obtain information on the structure. The exceptions have been mentioned in previous sections. Many properties are, of course, very sensitive to specific deviations from the ideal structure or composition. For example, by precise determination of the density a deviation from stoichiometry or the presence of vacancies can be detected, and mechanical properties such as hardness, ductility, tensile strength or elasticity are sensitive to dislocations and other imperfections. The melting point, vapour pressure and other thermodynamic data are useful and often necessary if an optimum choice of a crystal growth technique and crystal growth parameters has to be made. Also chemical corrosion behaviour, the thermal expansion coefficient and many other properties not mentioned above might be of value to potential crystal users and to other crystal growers and should be published when they are measured. Most of such measurements, however, are only meaningful when the material is sufficiently characterized by its chemical composition, by its structure and by inhomogeneities and defects.

9.4. Defects in Crystals and their Determination

9.4.1. The nature of defects in crystals

In Table 9.5 are listed the more important defects which may be found in crystals grown from high-temperature solution (and in crystals generally). The list is not exhaustive and the classification not perfectly rigorous, but no system of classification is ideal. The defects could alternatively be grouped into chemical defects, such as foreign atoms and nonstoichiometry,

TABLE 9.5. Defects in Crystals

Point Defects
Schottky defect (vacancy)
Frenkel defect (interstitial and compensating vacancy)
Interstitial atom
Foreign (substitutional) atom
Colour centre
Line Defects
Dislocations
Planar Defects
Low angle boundaries
Stacking faults
Twin boundaries
Bulk Defects
Mosaic structure
Compositional inhomogeneity, striations
Inclusions (solid, liquid or gas)

and physical defects such as dislocations and twin boundaries. Defects in general have been treated by Van Bueren (1960) and Bollmann (1970).

Point defects. *Vacancies* are unoccupied sites in the crystal lattice. The majority of vacancies in alkali halides are *Schottky defects* which are in thermodynamic equilibrium with the lattice and arise because of thermal fluctuations. The concentration of Schottky defects increases exponentially with temperature according to $n_v/N \approx \exp(-\Delta G_v/kT)$ with n_v/N the ratio of vacancies to atoms and with ΔG_v the heat of formation of a vacancy. The vacancy concentration becomes particularly significant as the melting point is approached. Cation vacancies are compensated by anion vacancies in charge-compensated systems. Another type of vacancy is compensated by an interstitial atom in the neighbourhood of the vacancy, and this is the *Frenkel defect*. The number of Frenkel defects is given by

$$n = (NN')^{1/2} \cdot \exp(-\Delta G_F/2kT)$$

with N' the number of possible interstitial sites and ΔG_F the heat of formation of a Frenkel defect. *Nonstoichiometry* can be produced by a high concentration of vacancies. The crystal then contains an excess of cations or anions rather than exhibiting a simple cation-anion ratio. Compounds of the transition metals are particularly prone to departures from stoichiometry according to their stability range and, for example, the Fe:O ratio in "FeO" can show large departures from unity depending on the partial pressure of oxygen in the growth atmosphere and to the growth temperature.

Frenkel defects are formed during growth or during heat treatment by the migration of atoms from their normal lattice sites to interstitial positions. The concentration of such defects, as of Schottky defects, is clearly lower in crystals grown from HTS than in crystals grown from the melt.

Foreign atoms will be present in any crystal to a greater or lesser extent according to the effective distribution coefficients, to the purity of the chemicals used and to the solvent from which the crystal was grown. The impurity atoms will usually be present substitutionally in a site normally occupied by the atoms in the host lattice, but they may be in interstitial sites. The dependence of the impurity concentration on the choice of solvent has been discussed in Chapter 3.

Colour centres are light-absorbing point defects (*F*-, *V*-centres etc.), which may be present in (nonstoichiometric) compounds. For example, if sodium chloride contains an excess of sodium compared with the chlorine, the excess sodium will be present as an atom rather than as a Na^+ ion. The valence electron of the sodium atom, located in a Cl^- vacancy, will have a characteristic absorption in the visible range and so will produce coloration of the crystal. Colour centres may also be introduced by the presence of certain impurities, or by bombardment of the crystal by ionizing radiations. Complex centres may be formed by groups of simple colour centres or by the trapping of electrons by pairs of ions. An *exciton* is a neutral, mobile excited state of a crystal, usually a bound electron-hole pair. The term is sometimes used more generally for any local excited state.

Monographs on point defects have been written, for example by Van Bueren (1960), Kröger (1964), Schulmann and Compton (1962), Markham (1966), Fowler (1968) and by Crawford and Slifkin (1972).

Dislocations. Strain in the crystal will cause displacements of atoms from their equilibrium positions. The magnitude of such displacements will depend on the severity of the strain, which may result in dislocations and other defects. A large number of books and reviews on the theory, the effects and the detection of dislocations have been published. As examples the books of Van Bueren (1960), Cottrell (1953), Friedel (1964), Hirth and Lothe (1968), Nabarro (1967), Read (1953), Rosenfield *et al.* (1968) and Simmons *et al.* (1970) (see also Discussions Faraday Society (1964) on the theory or general aspects of dislocations) are cited, whereas monographs on dislocation detection techniques will be mentioned under electron microscopy, etching, X-ray topography etc.

Dislocations occur at regions in the crystal where adjacent planes of atoms fail to meet perfectly. They may be classified as *edge* or *screw* dislocations according to whether the lattice displacement is perpendicular or parallel to the slip direction. The importance of screw dislocations for

the nucleation of layers on the surface of the crystal is discussed in Chapter 4.

Measurement of the dislocation density (the number of dislocations per unit area of crystal) gives a valuable indication of the perfection of the crystal. In Table 9.5 are listed a number of determinations of the dislocation density in HTS-grown crystals. The normal value is between 10 and 10^4 cm^{-2} which is lower than the average for melt-grown crystals. Examples are quoted where crystals have been grown dislocation-free or containing large regions without measurable dislocations. Evidence from a large number of investigators indicates that dislocations are normally generated either on nucleation or seeding, or by solvent inclusions. Figure 9.9 shows etch pits which correspond to dislocations generated by a solvent inclusion in a tantalum carbide crystal (Rowcliffe and Warren, 1970). The relation between inclusions and dislocations will be discussed in more detail in section 9.4.6. In addition, Wagner (1967) has noted that silicon whiskers produced by the VLS method are dislocation-free. The dislocation density of epitaxial films of III-V semiconducting materials depends primarily on that of the substrate crystal but a reduction by typically a factor 3–10 is normally observed in the regrown layer.

Decorated dislocations occur when the dislocations act as nucleation centres for the precipitation of some solid phase. The decoration may

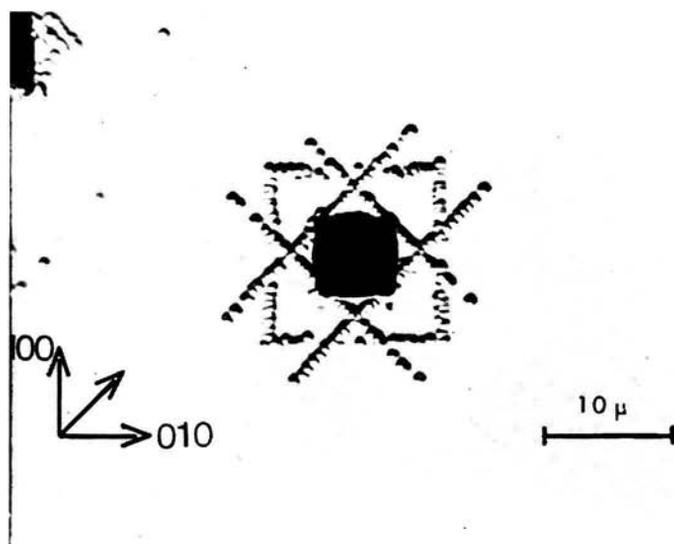


FIG. 9.9. Etch pits around a solvent inclusion in TaC (Rowcliffe and Warren, 1970).

occur during growth of the crystal or may be deliberately produced subsequently as a means of revealing the presence and distribution of the dislocations.

Misorientation. Strain may also result in the separation of the crystal into many crystallites each of which is misoriented with respect to neighbouring regions by a small angle, typically a few minutes of arc. The crystal is then said to exhibit a *mosaic structure* with the relatively perfect mosaic blocks, about 500–5000 units cells in diameter, separated by the small misorientation boundaries. If the crystallites and misorientations are larger, the terminology is changed and the crystallites are referred to as *grains*. The *low-angle grain-boundaries* between such grains may be formed from a number of dislocations, as illustrated in Fig. 9.10. The dislocations arise since some planes of atoms must terminate at the boundary and an edge dislocation will run through the crystal normal to such terminations, as shown in the diagram.

The rather simple situation shown in Fig. 9.10 rarely occurs in practice

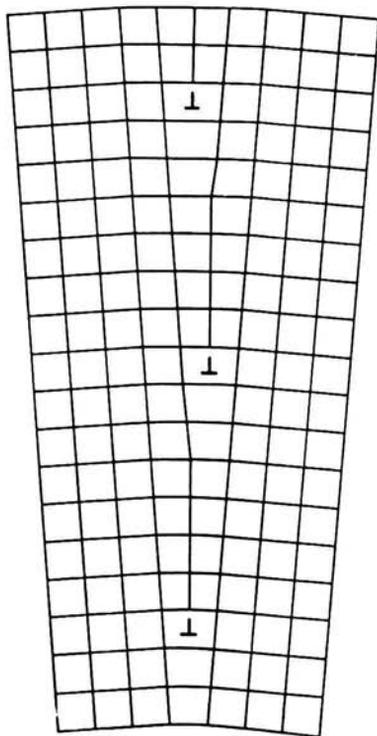


FIG. 9.10. Simple tilt boundary with edge dislocations denoted by the symbol \perp .

since the misorientation between neighbouring grains may have a component normal to the plane of the diagram. The misorientation may be resolved into a *tilt* component in the plane of the grain surface (as in Fig. 9.10) and a *twist* component normal to this surface. Twist boundaries will generate screw dislocations, whereas tilt boundaries generate only edge dislocations. A detailed discussion of grain boundaries has been given by Read (1953), Nabarro (1969) and by Chaudhari and Matthews (1972). Table 9.6 shows data by a number of investigators on the misorientation

TABLE 9.6. Lattice Misorientation in HTS-Grown Crystals

Material	Solvent	Mis-orientation	Method	Reference
Al ₂ O ₃	PbO, B ₂ O ₃ ; PbO, PbF ₂	22"	X-ray double crystal	Berkes <i>et al.</i> , 1965
ThO ₂	Li ₂ W ₂ O ₇	3'	X-ray linewidth	Finch and Clark, 1965
Al ₂ O ₃	PbF ₂	<2'	X-ray topography	White and Brightwell, 1965
Al ₂ O ₃	PbF ₂	20"	X-ray topography	Champion, 1969
KNbO ₃	K ₂ CO ₃	10'	Neutron diffraction	Hurst and Linz, 1971
LaAlO ₃	PbO/PbF ₂ /V ₂ O ₅	6"	Neutron diffraction	Kjems <i>et al.</i> , 1973

measured in some HTS grown crystals. The best value which has been realized in practice is seen to be about 10 seconds of arc, although an improvement by perhaps a factor 3 might be expected for crystals grown under very stable conditions.

Twinning. *Twin boundaries* occur between the components of a composite crystal when these components are related in a simple crystallographic manner. Of particular interest to the crystal grower are *growth twins* which are formed during growth rather than during subsequent deformation of the crystal. Examples of the influence of twinning on the growth mechanism have been discussed in Chapter 5 and particularly in Section 4.14.

Stacking faults. Stacking faults are irregularities in the sequence of atomic layers which cause departures from the arrangement in a perfect lattice. For example, if in a perfect lattice the repeat units are stacked in a regular sequence $\nabla\Delta\nabla\Delta\nabla\Delta\dots$ and so on, the insertion of an extra plane would result in a sequence such as $\nabla\Delta\Delta\nabla\Delta\nabla\Delta\dots$. The relative ease of formation of such faults depends strongly on the type of structure. Stacking faults may be determined by X-ray diffraction (see Section 9.3.2) and other techniques, and have been reported in a number of HTS-grown crystals, for example by Belt (1967), Cook and Nye (1967) and Wang and McFarlane (1968).

Inclusions are regions within the crystal occupied by some phase other than that of the host crystal. There are a great variety of types of inclusion which may form either during growth or during subsequent cooling to room temperature. Inclusions which are formed on cooling due to a decreasing solubility in the crystal of some solid are referred to as *precipitates*. *Foreign particles* of various kinds may be trapped by the growing crystal if they are present in the solution. Inclusions of platinum metal are quite common in crystals grown from fluxed melts, particularly if the flux has a fairly high solubility for platinum. *Gas* and *liquid* inclusions are comparatively rare in solution-grown crystals but are observed frequently in naturally occurring minerals.

The most serious defects in HTS-grown crystals are often *solvent inclusions*, which tend to form whenever growth becomes unstable (see Chapter 6). Solvent inclusions may be classified as follows (Wilcox, 1968; Elwell, 1975):

- (a) *Filled-in dendrites*. The initial growth following spontaneous nucleation is frequently "dendritic" with arms extending along the fast growth directions and a very high concentration of inclusions may be trapped as facets form and join up the ends of the dendrite arms. Such inclusions have been very widely observed, for example by Doughty and White (1960) and Giess (1962) (see Fig. 4.28a).
- (b) *Veils*. These are thin sheets of small inclusions which may have a variety of origins. The mechanism of formation of *starvation* veils was described by Carlson (1959). These are due to a low supersaturation at the centre of a crystal face such that layers spread from corners and edges of the face and overgrow the central region, trapping inclusions there. Veils may also arise due to cracks which develop during growth and which enclose a film of solvent as the crack heals by subsequent growth. The film then tends to break up into a number of tiny droplets. The formation of such veils has been filmed by Powers (1970) during observations of sucrose growth from aqueous solution.
- (c) *Ghosts*. These are oriented veils, parallel to a natural face of the crystal. They form at various stages during growth and so trace out the development of the crystal, hence the name. Ghosts, or less regular veils, may form when growth occurs erratically in a periodic sequence of relatively rapid and unstable growth followed by an interval of stable growth at lower supersaturation.
- (d) *Clouds*. Inclusions are sometimes observed not in bands but in localized "clouds" or aggregates of very fine particles, of say, less than 1 μm diameter. Such clouds have been observed, for example, by Timofeeva *et al.* (1969b).

- (e) *Fjords* are narrow channels of inclusions which are trapped between fine projections, a good example being shown in Fig. 6.13. The projections of the crystal may be in a direction perpendicular to the growth direction, if growth is erratic as described in the previous section, or normal to the crystal surface. The tendency of an interface to develop an instability which exhibits a regular periodicity was described in Section 6.3.

The nature and concentration of solvent inclusions depend on the conditions of growth, and these inclusions can be eliminated completely if growth occurs under stable conditions. These conditions have been discussed extensively in Chapters 6 and 7.

9.4.2. Optical methods

Optical techniques as described in Section 9.3.1 may be applied to the detection of many of the defects mentioned above. The handling of crystals for optical studies has been described in Section 9.3.1 so that in the following only a brief summary of the potential of optical methods for the detection of defects will be given.

Optical absorption spectroscopy allows the detection of a variety of point defects. Optically active vibrational modes near atomic point defects show IR isotope effects, whereas optically inactive vibrational modes show the Raman effect for the case where a sufficient concentration of point defects (10^{19} cm^{-3}) is present. Luminescence (fluorescence, phosphorescence, thermoluminescence) and photoconduction are relatively sensitive ($\sim 10^{10} \text{ cm}^{-3}$) to specific point defects. Optical microscopy is useful for the detection of decorated dislocations or of etch pits and allows in favourable cases the detection of 1 line defect per square micron (spatial resolution $1 \mu\text{m}$). Twinning and low-angle grain-boundaries may be seen in the polarization microscope or by optical reflection on the as-grown or on the etched faces. Optical techniques for the detection of inclusions are presented in Section 9.4.6.

9.4.3. X-ray topography

A simple means of assessment of the perfection of a crystal is provided by the size of the spots in a normal X-ray single crystal diffraction pattern or *Laue photograph*. If mosaic structure causes a spread in the lattice parameter over a range of values Δd , the spots will have an angular width given by differentiation of the Bragg condition as

$$\Delta\theta = -\tan\theta \frac{\Delta d}{d}.$$

The width $\Delta\theta$ is greatest for high values of $\tan\theta$, and so the degree of

imperfection is best determined from back reflection photographs. The directional variation of the imperfection may be assessed by rotating the crystal, so that back reflection photographs are obtained for a number of orientations. An extensive discussion of the use of conventional X-ray crystallography for appraisal studies has been given by Guinier (1962).

Laue photographs may also be used to demonstrate the existence of twinning and the presence of precipitates or inclusions, but only when these are present in concentrations of about 2–5%. The sensitivity to defects is, however, inferior to that obtained by X-ray diffraction topography which has been particularly developed for crystal quality appraisal studies.

X-ray topography is the examination by X-ray diffraction of the surface or bulk of a crystal, either of a particular region or of the whole crystal. The term embraces a variety of techniques which are distinguished from studies using, for example, the size of the Laue spots in that the region of the crystal which produces each part of the image can be identified. An X-ray topograph is thus a representation of the crystal which is sensitive to imperfections of the crystal lattice.

The techniques of X-ray topography have been reviewed by Barrett (1967), Bonse, Hart and Newkirk (1966) and Lang (1970) and the arrangements of source, crystal and film which have been most widely used are shown in Fig. 9.11.

The simplest arrangement is probably that due to Schulz (1954), shown in Fig. 9.11(a). A beam of white X-rays diverging from a point source is diffracted by a crystal inclined at about 25° to the beam. The image is a series of Laue spots and is about the same size and shape as the crystal, and faults in the crystal cause gaps or overlap regions in the image. White radiation is used so that there is no major variation in intensity due to the different angle of incidence of the beam on various regions of the crystal. The exposure time with this technique can be very short, of the order of minutes, but the sensitivity and resolution are poor. A similar technique using transmitted radiation was proposed by Guinier and Tennevin (1949).

Figure 9.11(b) shows the arrangement for the Berg-Barrett technique (Barrett, 1945) which uses monochromatic radiation from a collimated line source. The photographic plate in this case is mounted very close to the crystal, in order to minimize doubling of the image due to K_{α_1} and K_{α_2} radiation and to obtain maximum resolution. Typically, the source to specimen distance is 30–50 cm and the specimen to film distance is about 1 mm. Newkirk (1959) was able to achieve a resolution of about $1 \mu\text{m}$ and so resolve single dislocations. The area of specimen irradiated is about 1 mm^2 and the size of the image about $5\text{--}10 \text{ mm}^2$, depending on the angle of incidence of the beam. Relatively soft radiation may be used and this

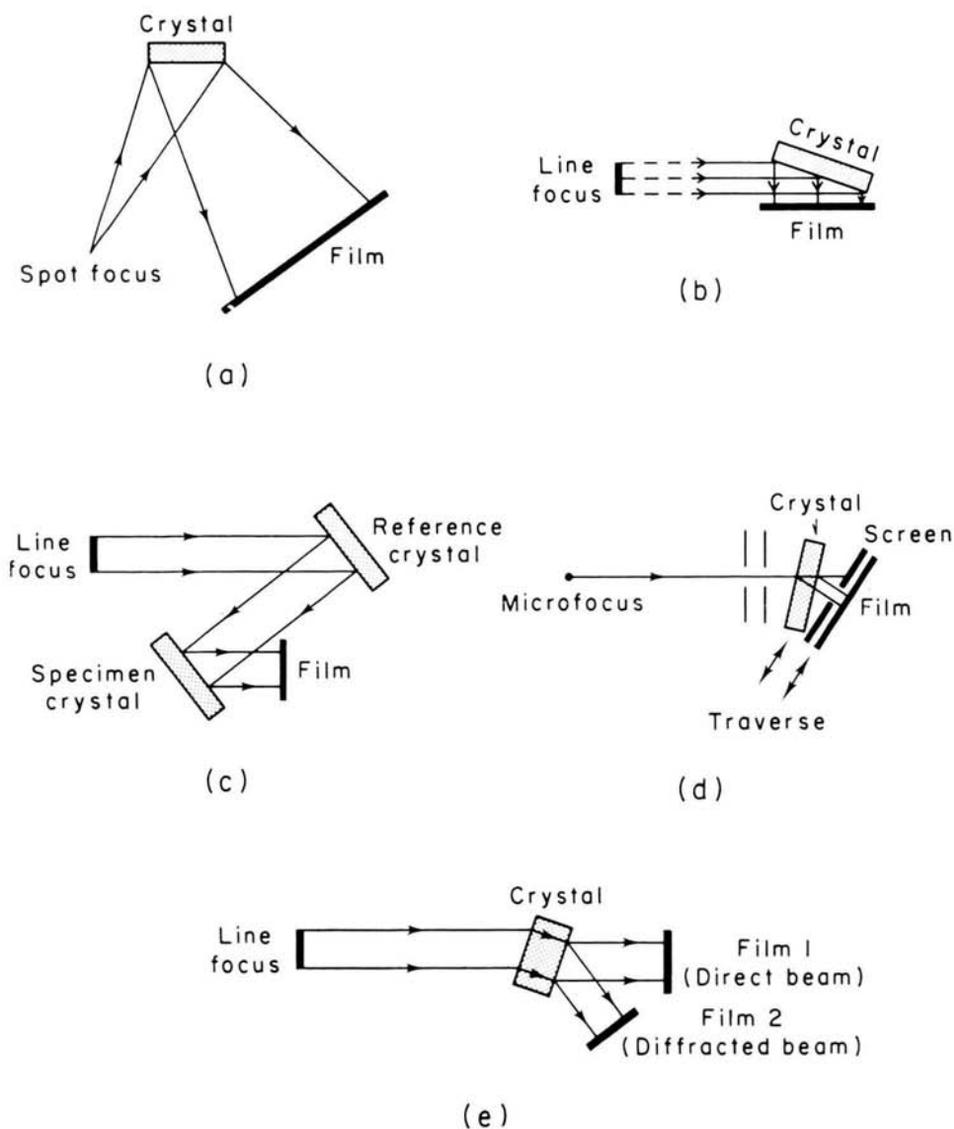


FIG. 9.11. X-ray topographic techniques: (a) Schulz (1954). (b) Berg-Barrett (Barrett, 1945). (c) Double-crystal spectrometer. (d) Lang (1957). (e) Transmission (Borrmann *et al.*, 1958).

has the additional advantage that the photographic emulsion may be thin, so that it is not essential for the beam to strike the film normally. Other topographic methods require nuclear emulsions, and dense emulsions may be necessary to achieve convenient exposure times.

The Berg-Barrett technique is the most widely used reflection method and is particularly suitable for the rapid examination of crystals in order to distinguish good quality crystals from those containing a high concentration of defects. A similar method may be used for transmitted diffracted radiation (Barth and Hosemann, 1958).

The double-crystal spectrometer (Bond and Andrus, 1952; Bonse and Kappler, 1958) shown in Fig. 9.11(c) uses Bragg reflection at a relatively perfect crystal C_1 and then from the specimen C_2 before the radiation reaches the film F . Similar materials are used for C_1 and C_2 so that the result is substantially independent of the spread $\Delta\lambda$ of the radiation used. The intensity pattern of F is very sensitive to local misorientations in the crystal C_2 , and changes in interplanar spacing of about 1 part in 10^4 can be detected.

The most popular method of X-ray topography is probably that due to Lang (1957), shown in Fig. 9.11(d). A narrow beam of characteristic radiation is diffracted by the crystal and a screen S is set so that only the diffracted beam reaches the photographic plate F . The orientation of the crystal slice is such that the diffracting planes are approximately normal to the faces of the slice. A topograph of the whole slice may be obtained by traversing the sample and film simultaneously across the stationary slit.

The maximum resolution of the Lang technique approaches the theoretical limit, typically a few μm , which is related to the effect on the diffracted image of the region around the highly strained "core" of the dislocation. The area of which X-ray topography will detect the dislocation depends on the width of the rocking curve for the perfect crystal and so on the wavelength and order of the reflection (Authier, 1967, 1970). The resolution is clearly much less than that possible with transmission electron microscopy but this disadvantage is more than compensated by the greater penetrating power of X-rays and the relative absence of damage produced by the beam itself. The attainment of optimum resolution requires a highly collimated beam, produced either by a microfocus generator or by use of a long source-to-crystal distance. The beam must be sufficiently narrow that it acts as its own collimator, with only the image due to say K_{α_1} radiation being recorded on the plate.

A phenomenon which has also been used in transmission topography is that of anomalous transmission (Borrmann *et al.*, 1958). In a perfect crystal the incident and diffracted waves form a standing wave pattern fitting onto the atomic planes. The energy transport of the wave field depends on the

position of the antinodes of this pattern and anomalously low absorption will occur if the antinodes lie between the planes. A perfect crystal will therefore transmit X-rays at a thickness which would absorb nearly all the energy in the absence of the interference between the incident and diffracted beams. Any imperfection in the lattice causes a reduction in the intensity of both the diffracted beam and the beam which is transmitted in the direction of incidence, and both these transmitted beams may be used to obtain topographs, see Fig. 9.11(e).

Contrast in the image obtained in X-ray topography is caused by a local departure from the Bragg condition and by its gradient (Authier, 1966). Even when the distortions are not so great, "dynamical contrast" due to bending of the diffracted beam and to a shift of energy between incident and diffracted beams may be observed in reflection and transmission methods, respectively. The contrast in dynamical images will differ from that in the direct images and the theory of image contrast in X-ray topographs is rather complex. A review of this topic has been given by Authier (1970).

Table 9.7, which is taken from the review of Bonse *et al.* (1966), gives a comparison between the various techniques of X-ray topography. The table summarizes the practical advantages and disadvantages of the techniques described above and includes information on the types of defect for which each is most suitable.

Many examples of X-ray topographic studies of HTS-grown crystals have appeared in the literature, and these have often provided data which have been invaluable for an understanding of the growth mechanism.

Austerman *et al.* (1965) obtained both Berg-Barrett and Lang topographs of BeO crystals grown from a lithium molybdate flux. These topographs showed the boundary of the twin core and confirmed that the twin boundary intercepts the growth face at the base of a conical feature, so forming a re-entrant angle. Parallel bands were observed crossing the crystal at rather irregular intervals along the core axis. Radial bands were also noted on the oxygen-rich side of a transverse section, but not on the Be-rich side, suggesting that these are caused by a stress field associated with the twin core. The other notable feature was a screw dislocation forming a helix of pitch 200–500 Å along the axis of the crystal.

Wallace and White (1967) studied the growth of Al_2O_3 crystals from PbF_2 flux by Lang topography, and clearly demonstrated the existence of twinning, the importance of which to the habit of alumina crystals was discussed in Chapter 5. Striations arising from imperfect temperature control were also observed. Champion (1969) used the Berg-Barrett technique to compare the perfection of Al_2O_3 crystals with those grown by the Verneuil method, and established that the misorientation in the flux-grown crystals was less than 20 seconds of arc.

TABLE 9.7. Comparison of X-ray Topographic Techniques

Technique	Schulz; Guinier and Tennevin	Berg-Barrett	Double crystal	Wide beam transmission (Barth and Hosemann)		Scanning transmission (Lang)	
apparatus	simple	simple	complicated	$\mu_0 t > 10$ simple	$\mu_0 t < 10^\dagger$ simple	$\mu_0 t \sim 3$ complicated	$\mu_0 t < 1^\dagger$ complicated
exposure time	10–25 hr	~1 hr	~1 hr	~10 hr	~1 hr	10–30 hr	2–10 hr
defect for which technique is most suitable	grain mis- orientation, subgrains	subgrains, dislocations	subgrains, dislocations, stacking faults	dislocations	subgrains, dislocations, stacking faults	dislocations	subgrains, dislocations, stacking faults
best resolution	50 μm	1 μm	1 μm	1 μm	1 μm	1 μm	1 μm
sensitivity to deformations	low	low	high	high	low	high	low
sensitive to sense of deformations	tilts: yes inhomogeneous deform: no	subgrains: yes dislocations: no	yes	yes	no	yes	no
thickness t of specimen contributing to topograph	$S \leq 5 \mu\text{m}$ $G \ \& \ T \ 50\text{--}100 \mu\text{m}$	$\leq 5 \mu\text{m}$	$\leq 5 \mu\text{m}$ (ref.) $\leq 300 \mu\text{m}$ (transm.)	1–5 mm	0–2 mm	0.1 → 5 mm	0–2 mm
dislocation image width	—	1–5 μm	up to 150 μm	$\geq 50 \mu\text{m}$	~5 μm	up to 150 μm	1 → 10 μm
upper limit of dislocation density	—	5×10^6	10^5	5×10^3	5×10^6	5×10^3	5×10^6

$\dagger \mu_0$ is the absorption coefficient of the material.

Belt (1967) examined lithium ferrite crystals grown from a $\text{PbO/B}_2\text{O}_3$ flux by means of Lang topography. Highly perfect regions were found, together with defective areas mainly associated with flux inclusions on the $\{111\}$ habit planes. Additional contrast observed in the crystals was attributed to strain or impurities in $\{110\}$ planes and to stacking faults on $\{111\}$. The same author (Belt, 1969) made a careful study of defects in $\text{Y}_3\text{Fe}_5\text{O}_{12}$ and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ crystals by etching and topography and showed that etch pits are not necessarily associated with dislocations. The crystals exhibited microscopic parallel bands, located principally on the fast growing $\{100\}$ and $\{111\}$ planes. Defects clearly identifiable as dislocations were also present and possible Burgers vectors determined. The origin of the bands was difficult to ascertain, but impurities and strain arising from thermal fluctuations were thought to be responsible for these defects.

Basterfield and Prescott (1967) used Lang topography to investigate the domain structure in $\text{Tb}_3\text{Fe}_5\text{O}_{12}$, but did not comment in any detail on the perfection of the crystals studied. Stacy and Tolksdorf (1972) compared X-ray topographs of magnetic garnet crystals with the domain structure detected optically by means of Faraday rotation. The domain pattern was found to be correlated with strain which was responsible for a non-cubic magnetic anisotropy.

MgAl_2O_4 was studied by Wang and McFarlane (1968) using the Lang method. The topographs showed dislocations, in low concentration, and striations leading to strain along the $\langle 111 \rangle$ directions, normal to the growth facets. Precipitates surrounded by an isotropic strain field were also observed, together with stacking faults.

The Borrmann technique of anomalous transmission topography has been comparatively little used in appraisal studies but a good example of its use was described by Wolff and Das (1966). They employed this technique to confirm the improvement in perfection of the GaSb layer grown by the travelling solvent method compared with that of the seed crystal. The regrown material had a dislocation density of $3 \times 10^3 \text{ cm}^{-2}$ and the topographs showed that the elimination of 70% or more of the dislocations present in the seed was due to the formation of closed loops or half loops, or a transformation to propagation in a direction perpendicular to the growth direction. This elimination occurred in the first 100 μm of regrown material. Examples of X-ray topographs of crystals grown from solution are given in Section 9.5.

9.4.4. Electron microscopy, LEED

Continuous advances in *transmission electron microscopy* have led to its increasing use, particularly for studies requiring high magnification.

Lattice planes with spacings of about 3 Å have been resolved, and techniques for the resolution of heavy atoms in a rigid matrix are being developed. The main limitation of electron microscopy arises from sample preparation. Because of the low penetrating power of electrons, samples for 100 kV electron microscopy have to be thinner than 500 to 5000 Å depending on the material. In the recently developed high-voltage electron microscopes with accelerating voltages up to several MV, thicker samples up to a few microns can be used but resolution decreases with sample thickness. However, high-voltage electron microscopy is useful for the study of precipitates, although its application in the study of mixed phases is limited by the difficulty of preparation of thin samples.

Sample preparation techniques are described in Section 9.3.1, and special thinning techniques (chemically by a jet of etching solution or physically by ion bombardment at low angles) have been developed. Literature on electron microscopy is extensive and includes the books of Heidenreich (1964), Thomas (1962), Amelinckx (1964), Nicolson *et al.* (1965), Hawkes (1972), Thomas *et al.* (1972) and the review of Phillips and Lifshin (1971). Murr (1970) has described the applications of electron optics in materials science. In the following, examples of applications of electron microscopy in the characterization of HTS-grown crystals are given.

Lefever *et al.* (1961) used transmission electron microscopy to investigate the nature of striations in yttrium iron garnet. They were able to demonstrate that the bands contained a relatively opaque material in the form of fine particles, about 0.1 μm in diameter. Electron micrographs of *small particles* of BaTiO₃ were used by Nielsen *et al.* (1962) in an investigation of the nucleation on such particles of the "butterfly twin" crystals.

An alternative to the use of thinned samples is to make a thin-film replica of the crystal surface either in the as-grown or etched condition. Replication imposes a limit on the resolution of features and introduces uncertainties in interpretation. Resolution with the etch pit method for the determination of dislocation densities is, however, much higher than is possible with the optical microscope (Boswell, 1957). Replication was used by Lefever *et al.* (1961) in their study of banding in YIG and they were able to use the resulting high magnification to show the form of the precipitate in the impurity bands. Newkirk *et al.* (1967) studied surface features at twin boundaries of BeO crystals by a replica technique.

Cook and Nye (1967) examined replicas of the surface features on crystals of hexagonal ferrites as well as of cleaved and etched surfaces. They were able to observe stacking faults and also the nature of the inclusions. A systematic study of the stacking faults and the layered structure of hexagonal ferrites by combined X-ray diffraction and electron microscopy

has been reported by Kohn *et al.* (1967), and Savage and Tauber (1967) describe the growth of complex hexaferrites and X-ray identification of the layer types.

The electron microscope with appropriate accessories may also be used in the investigation of crystal perfection by electron diffraction, particularly in the identification of dislocations and stacking faults. The diffraction pattern for a crystal at known orientation is compared either with a computed micrograph (Humble, 1970) or an optical transform (Taylor and Lipson, 1964). Differences between ideal and observed patterns may be analyzed to identify the types of defect.

Scanning electron microscope. The scanning electron microscope (SEM) differs strongly in concept from the transmission electron microscope, and has a resolution intermediate between that of the latter and that of an optical microscope, namely of about 100 Å at present. In the normal mode of operation, electrons accelerated by a potential of 5–50 kV are directed onto the sample, and scanning coils cause the beam to move across the specimen surface in a square raster. The secondary electrons which are emitted from the specimen strike a collector electrode and the resulting current is amplified and used to modulate the brightness of a corresponding spot which is displayed on a cathode-ray tube. The time associated with emission and collection of the secondary electrons is negligible compared with the time of the scan, and so the number of secondary electrons collected from any point on the specimen is determined only by the “brightness” of that point. Image contrast can, in fact, arise from a number of factors, particularly surface topography, atomic number, electrical conductivity, specimen orientation and electric or magnetic fields. The scanning electron microscope has no imaging lens and magnification depends only on the ratio of the sizes of the raster on the cathode-ray tube and that on the specimen. The minimum spot size, and hence the maximum magnification, is determined by aberration in the electron lenses. Practical limitations in resolution are set by the number of lines in the raster, the time of recording and noise in the instrument, and magnifications greater than 20,000 times are rarely used.

The great advantage of the scanning electron microscope is its very large depth of focus, which permits convenient observation of relatively large features on a crystal surface. (The instrument is therefore complementary to the interference microscope which has high sensitivity to surface topography.) The other advantage is that the SEM can be used in a large number of modes, and alternative images obtained, for example from reflected electrons or from monitoring the current through the specimen. Reviews of the principles, modes of operation and applications of SEM

have been given by Kammlott (1971), Booker (1970), Reimer and Pfefferkorn (1973), Thornton (1968) and by Oatley *et al.* (1965), while Minkoff (1967) reviewed the applications of SEM in materials science.

Since the image formed using secondary electrons is obtained from the first 10–100 atomic layers, the SEM is used mainly in the study of surface features rather than of defects inside the crystal (see, for example, Elwell and Neate, 1971).

Accessories to electron microscopes allow analysis of the characteristic X-rays produced by the electron beam so that electron micrographs and elemental analysis by *electron probe microanalysis* can be made from the same spot on the sample. Such a combination of techniques is very valuable since under high magnifications the localization of special features on the sample is extremely difficult.

Another way of obtaining information on composition and the type of bonding is to analyze the energy distribution of secondary electrons using special accessories to the electron microscopes, as described in Section 9.2.2.

Photo-emission electron microscopy (PhEEM). As described in Section 9.2.2, the energy distribution of the emitted electrons excited by photons can be used for chemical analysis. By a geometrical arrangement of electron lenses corresponding to that of an electron microscope the emitted electrons give an enlarged picture of the sample surface. The principle is shown in Fig. 9.12. Contrast in the image is given by the specific electron emission of various (chemical) materials, but the electron emission is also dependent on the crystallographic orientation and on defects. Topographic contrast locally distorts the electrical field, and therefore carefully polished samples should be used. In order to prevent contamination, surface cleaning, for example by a short ion bombardment, a high vacuum, and heating the sample to temperatures over 250°C, are necessary or advantageous. The photo-emission electron microscope has only been developed recently (Wegmann, 1969, 1970), but its successful application to various characterization problems in conducting samples and in insulators has been demonstrated (Weber, 1972; Wegmann, 1972).

A composition of PhEEM with SEM has been given by Bode *et al.* (1971), and its use for quantitative measurements is discussed by Wegmann and Dannöhl (1971). Lateral resolution in PhEEM is of the order of 150 Å, and the electrons originate from a maximum depth of about 100 Å. Examples of photo-electron emission micrographs are shown in Fig. 9.13. In (a) a corner is shown of a polished natural crystal of SnO₂, and the intensity changes are due to a variation in the Fe content. The contrast in (b) which shows the surface of a graphite crystal, is mainly topographic

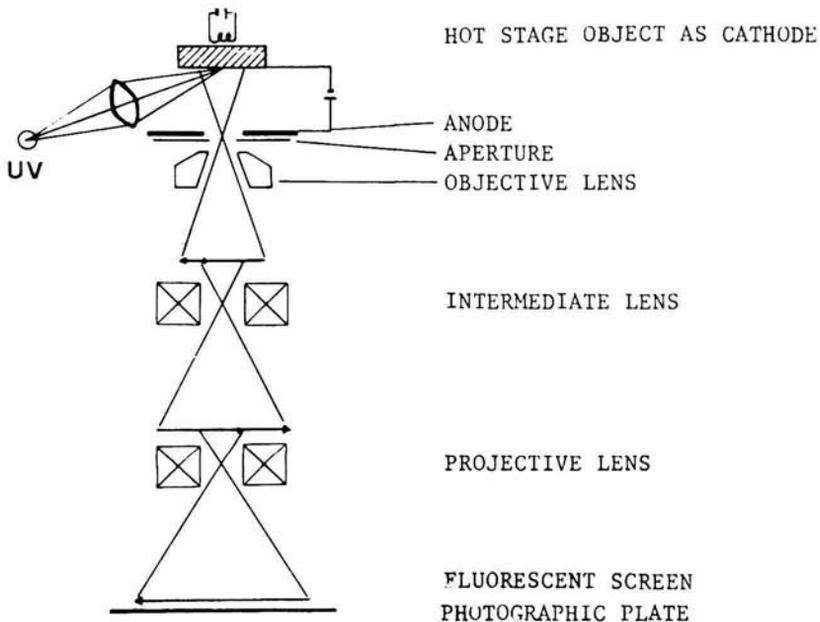
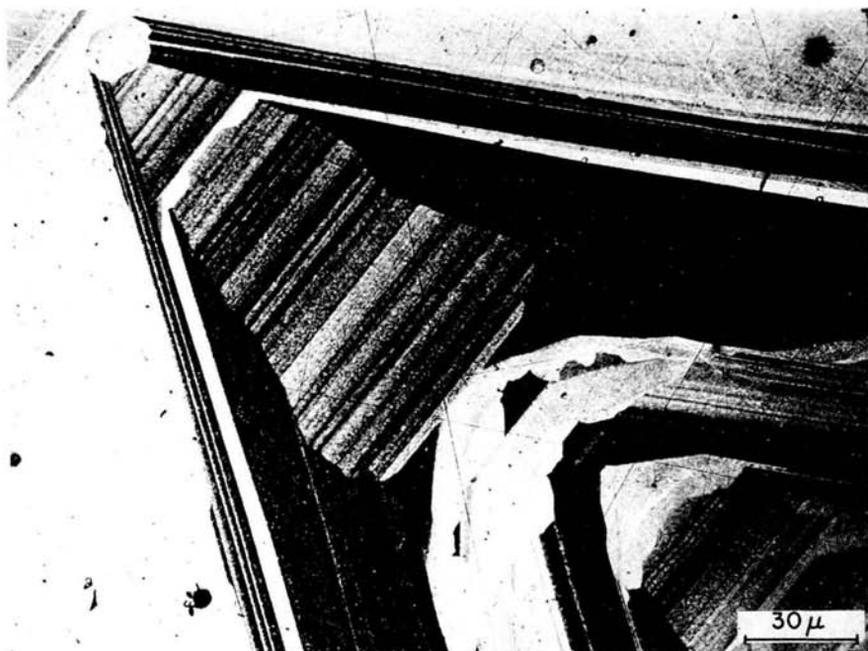


FIG. 9.12. Photo-emission electron microscope (diagrammatic).

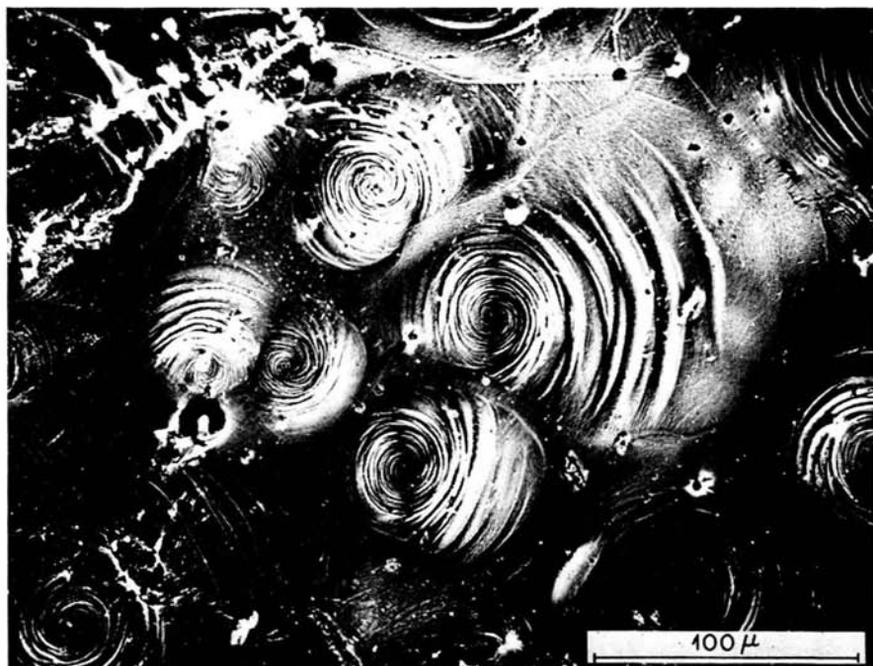
and this photograph demonstrates the potential of PhEEM for studies of surface features.

Field-emission microscopy and *field-ion-emission microscopy* developed by Müller allow resolution of single heavy atoms and are used for the study of defects but their application is limited to refractory metals and alloys. The latter technique has been reviewed by Bowkett and Smith (1970) and by Müller and Tien Tzou Tsong (1969).

Low-energy electron diffraction (LEED). LEED provides structural information on the first two or three atomic levels. This implies that very special preparation techniques and ultra-high vacuum have to be used. Frequently the interpretation of LEED patterns is difficult because of surface damage introduced during sample handling or by electron impact. So LEED and the recently developed reflection-mode high-energy electron diffraction (RHEED) are mainly used for the study of adsorption layers, surface reactions and crystallite reorientation in surface layers (Somorjai, 1969; Marcus, 1969; Jona, 1970; Estrup and McRae, 1971). Very little application of electron-diffraction techniques for characterization of flux-grown crystals and layers has been reported.



(a)



(b)

FIG. 9.13. Photo-electron emission micrographs. (a) Cassiterite SnO_2 , showing variation in Fe content. (b) Graphite, showing growth hillocks (Wegmann, 1972).

9.4.5. Miscellaneous physical techniques

The assessment of crystal perfection is often made by a wide variety of physical measurements other than the optical and more general techniques described above. These measurements are often specific for the type of material considered and the information obtained is supplementary to that obtained by such methods as X-ray topography, and should not be considered as a substitute for a general study of crystal perfection. Table 9.8 lists the property measurement techniques as classified by Laudise *et al.* (1971).

However, one powerful technique for the detection of impurities (or ions possessing an unfilled electronic shell) and for the detection of colour centres should be particularly mentioned here, namely, *electron paramagnetic resonance* EPR (or ESR for electron spin resonance). Since ions of more than half of the elements of the periodic table have incomplete shells (e.g., the transition metal ions) EPR absorption can be used to identify a number of these ions when they are diluted in a diamagnetic

TABLE 9.8. Property Measurement Techniques

1. Electric field	2. Magnetic field
Resistivity	Magnetic susceptibility
Dielectric constant	Coercive force
	Uniaxial anisotropy
3. Gravitational field	4. Optical field
Density	Refractive index
	Birefringence
	Spectroscopic absorption (bandgap)
5. Thermal field	6. Stress field
Thermal conductivity	Elastic moduli
Heat capacity and heat of transition	Mode of permanent deformation
Thermal expansion	
7. Multiple fields	
Coefficients	
Thermoelectric, photoelectric, photoelastic, elasto-optic, piezoelectric, pyro-electric, electro-optic, acousto-optic, magneto-optic, lifetime of carriers, mobility of carriers, residual resistance ratio, electroluminescence, photoluminescence	
Transitions	
Superconducting temperature, Curie temperature, phase-matching temperature, spin reorientation temperature	
Resonance	
Nuclear magnetic, paramagnetic, Mössbauer, cyclotron, nuclear double resonance	

crystal. The g -factor (magnitude of splitting of the groundstate level by an external magnetic field), the ligand field splitting, the nuclear hyperfine splitting and the spin-lattice relaxation time are characteristic of a paramagnetic ion and its local symmetry. Due to the high sensitivity of EPR the transition metal ions can be detected in the concentration range of p.p.m. to a few percent. Limitations of the application of EPR are due to: (1) a high symmetry which is useful for interpretation of the spectra, although recently EPR spectra of paramagnetic ions in monoclinic and triclinic crystals have been interpreted; (2) strain in the crystals; (3) the presence of other paramagnetic ions in high concentrations.

EPR has been reviewed by Ayscough (1967), Abragam and Bleaney (1970), Low (1960, 1963) and Pake (1962). It is surprising that, although EPR has been widely used to investigate structural aspects around the incorporated ions, phase transitions (Müller, 1971) and qualitatively to detect the presence of certain ions, EPR has not been widely used for quantitative trace determination despite the fact that Burns proposed this in 1964.

The detection of Pb^{3+} in ThO_2 grown from $\text{PbF}_2\text{—B}_2\text{O}_3$ flux by Scheel (unpublished) is of interest: Röhrig and Schneider (1969) found in crystals containing 1% lead a large hyperfine interaction for the isotope ^{207}Pb at 77 K, and $\text{Pb}^{3+}\text{—F}^-$ centres would account for the weak satellite lines near the Pb^{3+} lines.

Wertheim *et al.* (1971) have reviewed the determination of the electronic structure of point defects by spin resonance and by Mössbauer spectroscopy.

Ultrasonic attenuation and dispersion might become interesting as a nondestructive characterization technique since ultrasonic waves are not bound to optical transmission, electrical conductivity and so forth, so that all kinds of crystals and crystalline layers can be tested. Another advantage is the high sensitivity to defects of phonon scattering. The main difficulties are, experimentally, to obtain reliable and reproducible coupling to the transducer and, theoretically, to correlate the phonon spectra with the types of defect. Ultrasonic techniques for characterization are reviewed in the books of Herzfeld and Litovitz (1959), Filipczynski *et al.* (1966), and Sharpe (1970).

The importance of ferrimagnetic oxides has been mentioned at several points in the text and a valuable measurement for such materials is the *saturation magnetization*. This property will be affected by solvent inclusions, which contribute to the mass but not to the magnetization, and by impurities, the effect of which will depend on the Bohr magneton number of the ion and on its location in the crystal lattice. Nielsen *et al.* (1967) took samples from various regions of Ga-doped yttrium iron garnet

crystals and plotted their results in the form of contours of equal magnetization on a representation of the crystal surfaces (see Fig. 9.6b). The resulting plot illustrates dramatically the variation in gallium concentration across the crystal face.

The local concentration of a non-magnetic impurity such as gallium will also affect the *Curie temperature* and the difference in Curie temperature between different parts of a crystal will be low if the crystals are relatively homogeneous. Linares (1965a) plotted histograms showing the spread in Curie temperature among doped garnet crystals in batches grown respectively by slow cooling and thermal gradient transport (see Fig. 9.14). The spread was found to be much less in the crystals grown by gradient transport, as may be expected since the growth is isothermal; the relatively large variation in crystals grown by slow cooling arises from the high effective distribution coefficient of gallium.

A parameter which is of considerable importance in studies of magnetic oxides of iron is the concentration of Fe^{2+} or Fe^{4+} ions. This concentration

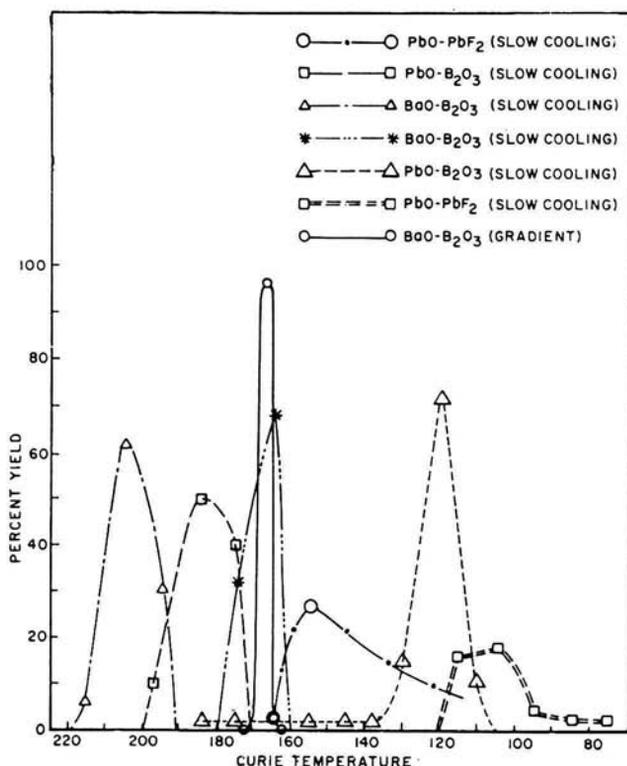


FIG. 9.14. Yield of yttrium iron garnet vs. Curie temperature (Linares, 1965a).

is often small compared with that of Fe^{3+} and is difficult to determine to high precision. The problem of determining the Fe^{2+} concentration in yttrium iron garnet was discussed by Robertson and Elwell (1969) who considered several measurements in addition to wet chemical analysis: electrical conductivity, thermoelectric power, infra-red absorption, saturation magnetization, ferrimagnetic resonance linewidth and magneto-crystalline anisotropy. The electrical conductivity is very sensitive to the Fe^{2+} concentration but also varies rapidly with temperature and with the concentration of impurities. Thermoelectric power is less sensitive to impurities and appears to be one of the most reliable methods for concentrations greater than about 2%, but calibration is required using samples of known Fe^{2+} concentration. Infra-red absorption curves have been plotted by Wood and Remeika (1966) for both Si- and Ca-doped yttrium iron garnet containing Fe^{2+} and Fe^{4+} ions, respectively. The absorption shows a sharp edge for wavelengths just above $1 \mu\text{m}$ and the absorption coefficient at a fixed wavelength will give the Fe^{2+} or Fe^{4+} concentration; a wavelength of $1.2 \mu\text{m}$ was used by Nassau (1968), who formulated a model of Fe^{2+} — Fe^{4+} equilibrium. Ferrimagnetic resonance linewidth is frequently used as a measure of the quality of magnetic oxide crystals, since the linewidth increases with the Fe^{2+} concentration and with the concentration of inclusions. It is not normally possible to separate these two main contributions to the linewidth, but a more reliable estimate of the Fe^{2+} concentration can be obtained from the increase in linewidth at low temperatures. For a quantitative measurement the anisotropy of ferrimagnetic resonance or a torque magnetometer may be used to determine the temperature dependence of the magneto-crystalline anisotropy constant K_1 . The Fe^{2+} concentration is determined from the contribution to K_1 due to the ferrous ions, and is accurate only if the energy level splitting of the lowest doublet of the Fe^{2+} ions is known.

Measurements of ferrimagnetic resonance linewidth and anisotropy have also been used extensively in other investigations, notably by Makram and co-workers (Makram and Krishnan, 1967; Makram, 1968; Makram *et al.*, 1968).

The properties of HTS-grown dielectric materials have also been investigated intensively as a means of crystal characterization. As an example, Giess *et al.* (1969) measured the spread in the ferroelectric Curie temperature of different barium sodium niobate crystals as a means of assessing homogeneity.

Reference has been made in Chapter 1 to examples of measurements which demonstrate the higher quality of semiconductor layers deposited by liquid phase epitaxy compared with that of the substrate crystals. In the original paper of Nelson (1963), diodes formed by LPE were reported

to have improved performance as tunnel diodes over those produced from the melt, and diodes used as lasers had lower thresholds. Shih and Blum (1971) reported a high efficiency of light emission from $\text{Ga}_{1-x}\text{Al}_x\text{As}$ diodes for display devices.

9.4.6. Determination and removal of inclusions

The origin of inclusion formation and the theoretical and experimental conditions to prevent unstable growth are discussed in Chapter 6, and Figs 6.6, 6.12 and 6.13 show typical examples of inclusions found in flux-grown crystals. The theory of stability of plane interfaces predicts a periodicity of inclusions of the order of 10–30 μm , and inclusions of that periodicity have been found. Depending on the growth system and the experimental parameters inclusions of submicroscopic size as well as bulk inclusions are formed.

Macroscopic inclusions are clearly detectable by the naked eye. In the following, a few techniques will be briefly mentioned which are used or which could be used for the detection and analysis of microscopic and submicroscopic inclusions. *Optical microscopy* is of course the simplest way of detecting inclusions of a size larger than 1 μm in transparent crystals, either in the as-grown crystals or in thin sections. Special microscopic techniques for examining inclusions in natural gemstones for identification purposes have been described by Gübelin (1953). Newkirk and Smith (1967) used *ultramicroscopy* where light scattered from a light source (here a helium-neon gas laser) perpendicular or at least diagonal to the microscope axis is examined and photographed. Thus inclusions of a size less than 1000 Å can be detected, but it is difficult to determine the exact size distribution and the morphology of the inclusions by examination of the scattered light. *Light scattering* is reviewed in the books of Van de Halst (1957) and of Stacey (1956). Orientation-dependent light scattering was observed from a variety of rotating cylinders of synthetic crystals by Guseva *et al.* (1971).

Several materials (e.g. ferrites, semiconductors) opaque to visible light have transmission windows in the infrared so that they can be examined by *infrared microscopy* (Sherman and Black, 1970; Sunshine and Goldsmith, 1972). Ferroelectric and magnetic domains are sensitive to inclusions, probably influenced by the strain produced by the inclusions. This strain is partially released by the formation of dislocations, so that *X-ray topographs* may indicate the presence of inclusions. *Ultrasonic dispersion*, as mentioned in Section 9.4.5, is extremely sensitive to tiny inclusions.

For the study of submicroscopic inclusions *transmission electron microscopy*, *replica electron microscopy* and *scanning electron microscopy* are

valuable techniques when the problem of preparation of appropriate samples is solved.

Some of the techniques suitable for the analysis of chemical inhomogeneities are also valuable for the detection and analysis of inclusions (e.g. *electron microprobe analysis*), see Section 9.2.4. A semiquantitative determination of the inclusion content of a crystal is possible by grinding the crystal, extracting the inclusions and determining the total content of matter included in the extract.

X-ray radiography has been used by Doughty and White (1960) to examine bulk crystals for major defects and inclusions. While this technique is very insensitive, it will reveal major flaws in opaque crystals, such as the dendritic core frequently present in crystals grown by spontaneous nucleation. Radiography is relatively simple and may be used to examine rapidly a batch of crystals in order to eliminate those containing gross defects prior to subsequent cutting and polishing of sections for the application intended.

It was pointed out by Chase and Wilcox (1966) that the migration of a solvent zone in a temperature gradient may be used to remove solvent inclusions from HTS-grown crystals. The main objective of inclusion removal is to permit more accurate determinations of such properties as density, optical absorption coefficient or the concentration of substitutional impurities. However this technique may also be used as a simple means of determining the inclusion concentration (Elwell *et al.*, 1972). The crystal is heated in a strong gradient at a temperature well above the melting point of the solvent for a time sufficiently long to allow all the solvent to migrate to the hotter surface. After cooling the crystal to room temperature, the high temperature solvent may be removed by dissolution in nitric acid or some alternative reagent, and the resulting change in weight of the crystal will be a measure of the initial concentration of solvent inclusions.

Wilcox (1968) has given a review of the topic of *inclusion removal* from crystals grown from both high temperature and aqueous solutions. The rate of migration of inclusions is given approximately by

$$v_R = \frac{D(dT/dz) \rho_{sn}}{m(1 - w_o) \rho_c},$$

where dT/dz is the temperature gradient, D the solute diffusion coefficient, m the slope of the liquidus, w_o the solute concentration (expressed as a weight fraction) and ρ_c and ρ_{sn} the density of crystal and solution, respectively. Some examples of removal rate using this equation are quoted in Table 9.9 together with experimental data where these are available.

Agreement between theory and experiment is as good as can be expected since the theory leading to the expression for v_R is highly simplified. In

TABLE 9.9. Rate of Movement v_R of Solvent Inclusions in Crystals

Crystal	Solvent	Temperature °C	dT/dz °C/cm	w_0 wt fraction	m °C/wt fraction	D cm ² s ⁻¹	ρ g cm ⁻³	ρ_{SN} g cm ⁻³	v_R mm hr ⁻¹ Theory	Expt.	Reference
Al ₂ O ₃	PbF ₂	1200	100	0.13	6700	$5 \times 10^{-5}\dagger$	4.0	7.6	0.06	—	Wilcox (1968)
BaTiO ₃	KF	1200	100	0.42	670	$5 \times 10^{-5}\dagger$	5.0	3.5	0.3	—	
CaCO ₃	Li ₂ CO ₃	690	400	0.48	1500	$1 \times 10^{-5}\dagger$	2.71	2.2†	0.015	0.2	Bélin <i>et al.</i> (1972)
GaAs	Ga	900	750	0.21	1300	1×10^{-4}	4.22	5.0†	3.1	0.46	Mlavsky and Weinstein (1963)
Ge	Al	667	31	0.74	1100	1.7×10^{-4}	3.5	3.0†	0.6	0.76–1.8	Wernick (1957)
InAs	In	800	500	0.39	530	2×10^{-4}	5.67	6.0†	1.2	0.7	Kleinknecht (1966)
NiFe ₂ O ₄	BaO/B ₂ O ₃	1200	20	0.10	1000	2×10^{-5}	5.37	4.55	0.014	0.05	Elwell <i>et al.</i> (1972)
SiC	Si	2000	100	0.012	1.4×10^4	2×10^{-4}	2.96	2.15	0.03	—	Wilcox (1968)
ThO ₂	PbF/Bi ₂ O ₃	1200	400	0.006	6000	5×10^{-5}	10.0	8.2	0.12	0.1	Wilcox (1968); Chase and Wilcox (1966)

† Denotes an estimated quantity.

practice the travel rate may depend on the size of inclusions and on the interface kinetics (Tiller, 1963). The data reported in the table on the semiconductors GaAs, Ge, InAs and SiC were taken on crystal-growth experiments by the travelling solvent method and were used to obtain values of the diffusion coefficient by an equation related to that given above for v_R .

The rather large discrepancy between experimental and theoretical values of v_R for GaAs and InAs indicates a difference of interpretation between Wilcox (1968) and the original authors. It may be that the values either of the temperature gradient or of the diffusion coefficient have been overestimated in these examples.

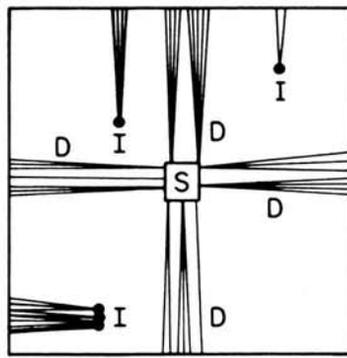
Disagreement between theory and practice in the experiments of Bélin *et al.* (1972) is to be expected since the crystal was rotated so that growth was probably not limited by diffusion in that case. For a more detailed discussion of inclusion removal, reference may be made to Wilcox (1968).

9.5. The Growth History of a Crystal as deduced from Characterization

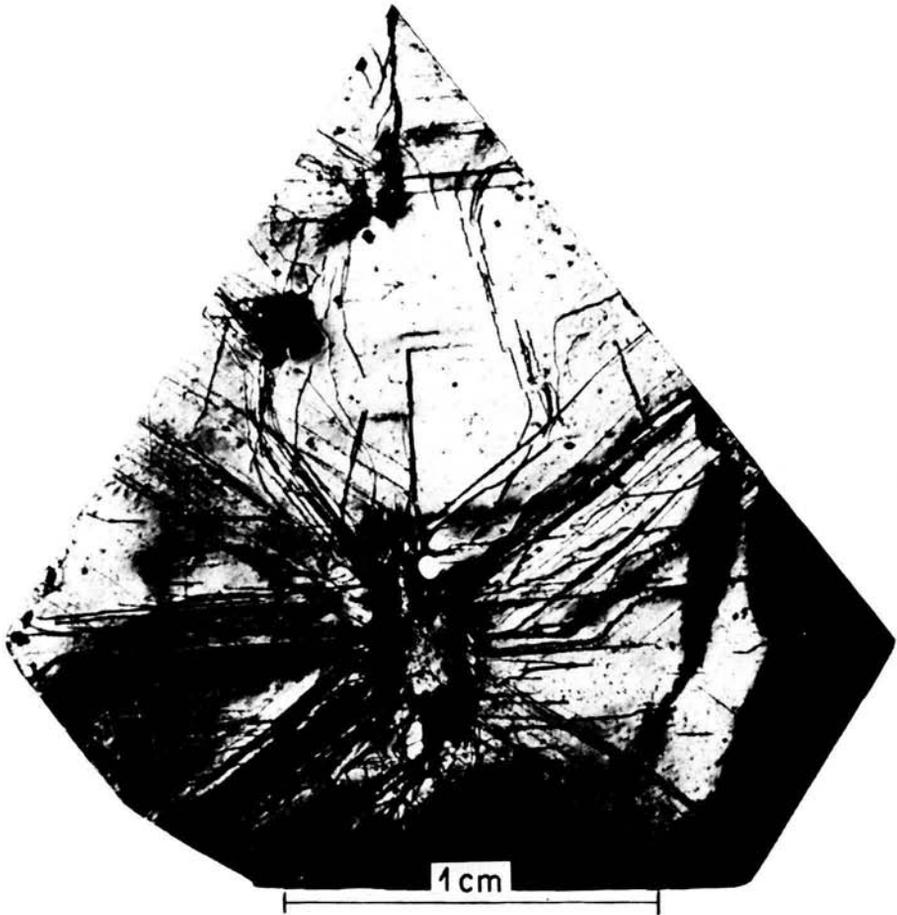
Reference has been made at various parts in the text, especially in Chapter 4, to the mode of growth of crystals following nucleation or seeding. It is instructive here to consider the information to be obtained from characterization, particularly from X-ray topography, on the growth history and on the generation and propagation of dislocations and other defects. Detailed studies have in general been made of crystals grown from aqueous solutions but the evidence available suggests that similar results will be obtained on crystals grown from high-temperature solution.

Emara *et al.* (1969) investigated the distribution of dislocations in potash alum grown by spontaneous nucleation. The majority of dislocations are generated in the early stages of growth and radiate as bundles or sometimes as single dislocations, in a direction roughly perpendicular to the crystal faces (see Fig. 6.8). Additional dislocations are generated at growth accidents occurring at a later stage, usually at an inclusion because of imperfect lattice closure. The number of dislocations remains approximately constant as growth proceeds, so that the dislocation density decreases.

Veils of solution were observed in these crystals, and those in the faster-growing sectors gave rise to a high degree of strain. "Clouds" of inclusions in the form of small bubbles were also observed. Some bubbles act as dislocation sources but in other instances the dislocations terminate on bubbles so that the lattice heals when closing around a bubble of solvent. It was frequently observed that the small crystal faces have a relatively high density of dislocations, indicating that a high density of dislocation leads to more rapid growth.



(a)



(b)

FIG. 9.15. (a) Distribution of dislocations in crystal grown from solution (diagrammatic, after Authier, 1972). S = seed, D = dislocation bundles, I = inclusions. (b) X-ray topograph (Authier, 1972) of TGS, showing dislocations generated at the seed and at inclusions.

Generally similar observations were reported by Ikeno *et al.* (1968) who investigated crystals of Mn-doped NaCl. They also noted additional dislocations which appeared to be generated at the position where the crystal was in contact with the beaker. These authors stress the observation that the crystals appeared to grow in six parts, each specified by one of the {110} growth surfaces and separated by a diagonal surface passing through the nucleus.

In a review of the applications of X-ray topography in crystal-growth studies, Authier (1972) considers seeded growth from aqueous solution. The majority of the dislocations originate at the seed and are propagated normal to the crystal faces, so that distribution of the dislocated regions is very similar to that in unseeded crystals. Figure 9.15(a) shows schematically the location of dislocations in a crystal of cubic habit. An actual topograph made by Mrs. A. Izrael is shown in Fig. 9.15(b) which shows a crystal of triglycine sulphate. In this case the dislocations propagate in six main bundles and large areas of crystal are substantially dislocation-free. Two regions can be seen where large solvent inclusions have resulted in the generation of further bands of dislocations. The mechanism of generation of dislocations at inclusions has been discussed by Matthews (1972).

Klapper (1971) made a topographic study of benzyl crystals grown from solution in xylol, and also found dislocation bundles radiating from the nucleus or from inclusions. He demonstrated that the direction of dislocations corresponds to a minimum of potential energy per unit length. Thus dislocations deviating 10° from the growth direction were found in benzyl, and Fig. 9.16(a) shows a topograph of a crystal of lithium formate hydrate of which the explanation is given in Fig. 9.16(b). The preferred orientation of dislocations can be calculated from the elastic constants of the material according to Klapper (1972, 1973).

An interesting series of topographs was obtained by Vergnoux *et al.* (1971) on strontium formate and sulphur crystals. Their observations confirm what appears to be a general tendency in solution growth for the dislocations to propagate in bundles (see Fig. 6.8). Some of the dislocations were found to originate in the seed rather than in the region of initial growth on the seed. As indicated by other observations of surface features, a tendency was noted for the number of dislocations to decrease during growth. During slow growth of sulphur crystals, the dislocation density on the (100) face was observed to fall from 200 cm^{-2} after 8 days to 40 after 32 days and to 1 after 58 days. However, any disturbance in the growth process is unfavourable and results in a production of new dislocations. As an example, an interruption in stirring led to a remarkable increase in dislocation density (see Fig. 7.38).

LPE studies have shown that the number of dislocations in the crystal

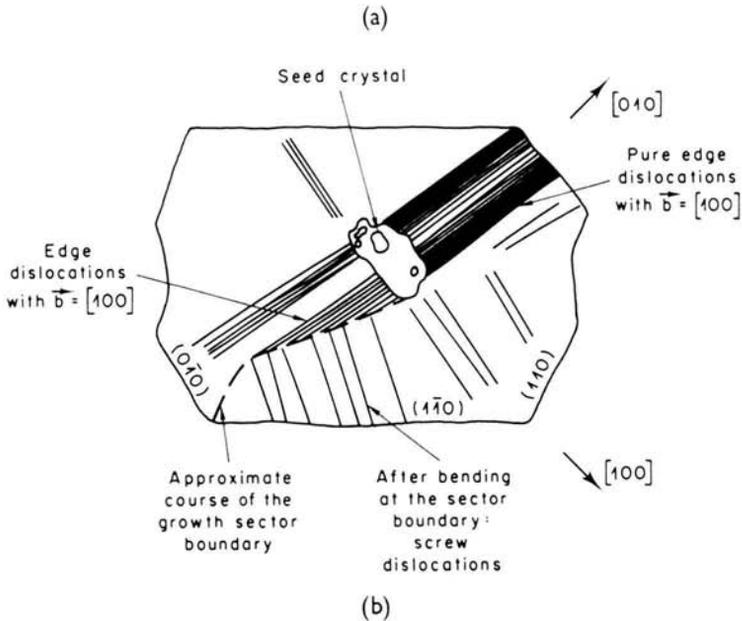
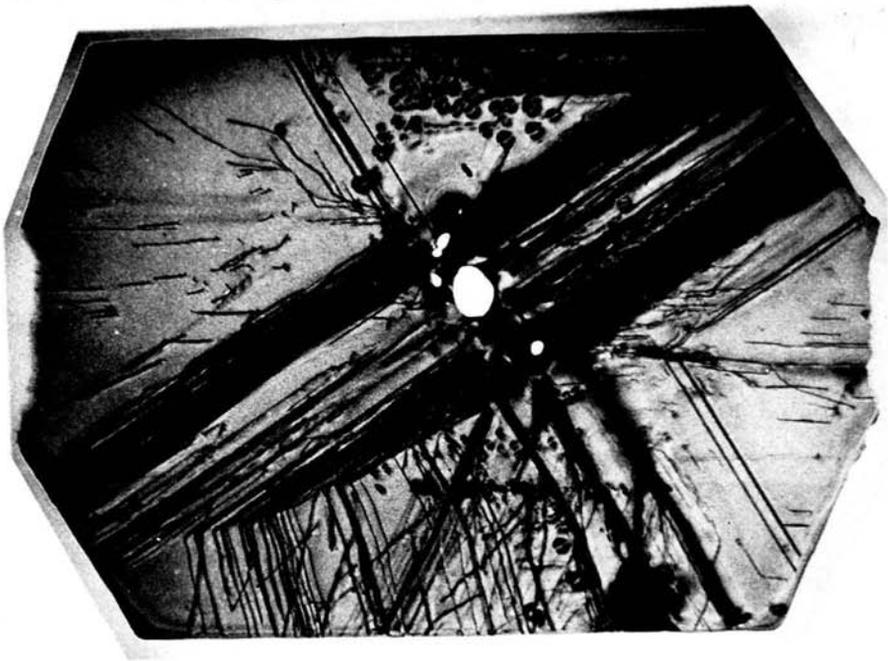
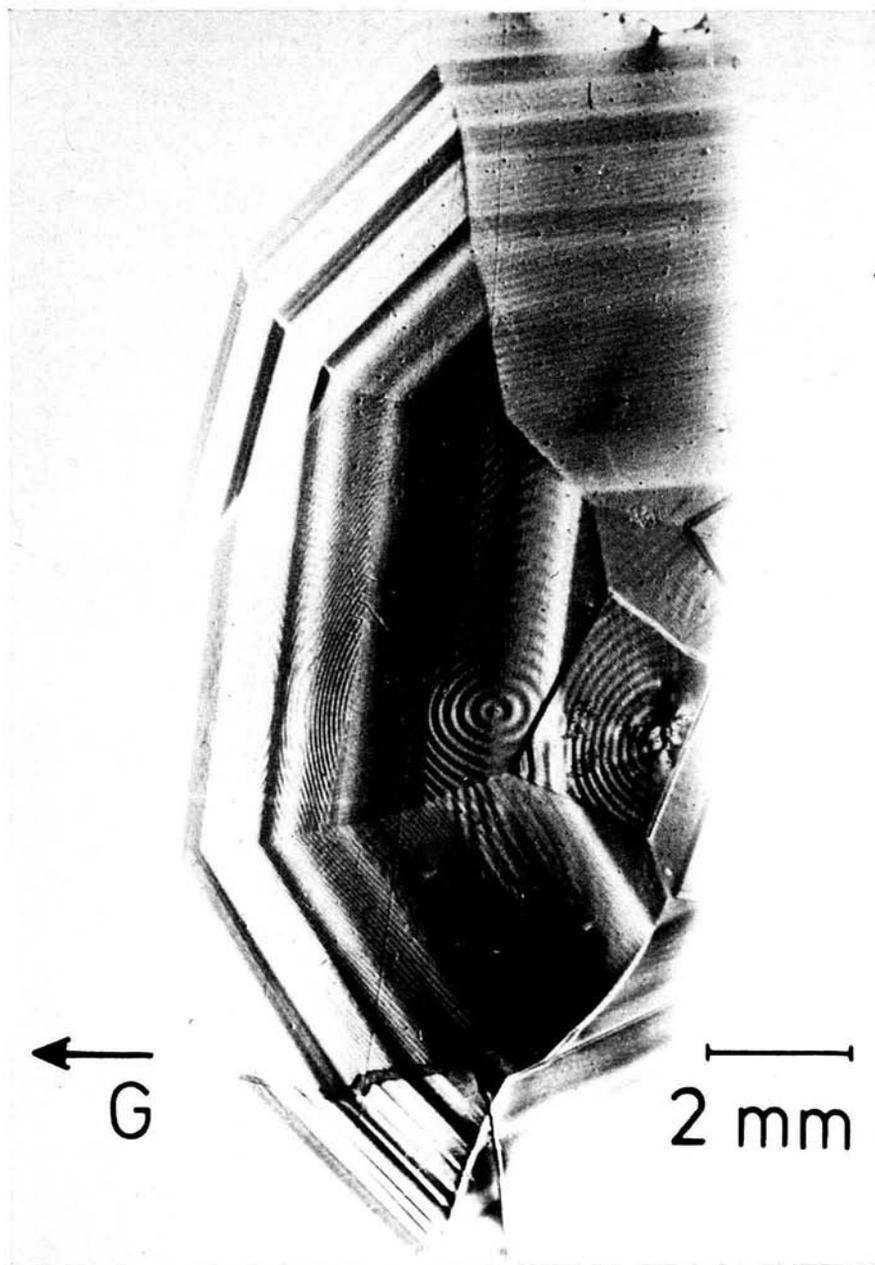


FIG. 9.16. (a) X-ray topograph of lithium formate hydrate crystal. (b) Interpretation of Fig. 9.16(a). After the formation of screw dislocations at the growth sector boundary, enhanced growth of the $(1\bar{1}0)$ face is observed (Klapper, 1973).

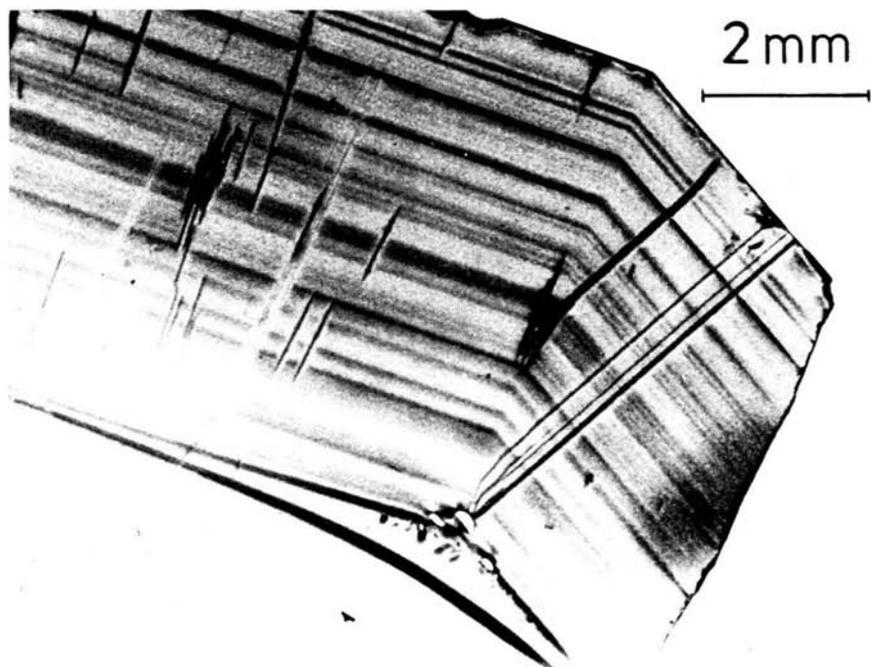


(a)

FIG. 9.17. X-ray topographs of (a) (111) slice of $Y_3Fe_{4.45}Ga_{0.55}O_{12}$, grown by Pavlik, showing "growth ripples"; (b) enlargement of dominant feature shown in (a); (c) $Y_3Fe_4GaO_{12}$, grown by W. Tolksdorf, showing striations and inclusions generated by dislocations (Courtesy Dr. W. T. Stacy, Phillips Research Laboratories).



(b)



(c)

should ideally be less than that in the seed, and so more perfect crystals than those described above could be grown by careful seeding. A change in growth direction through 90° may also be effective in reducing the number of dislocations produced by an imperfect seed, as proposed by Schroeder and Linares (1966).

Relatively few topographic investigations of flux-grown crystals have been reported in the literature, but some particularly interesting topographs by W. T. Stacy are shown in Fig. 9.17. The "growth ripple" of Fig. 9.17(a) is formed by a dislocation surrounded by concentric regions of alternating strain. The dislocation, seen more clearly in Fig. 9.17(b), runs perpendicular to these bands and is associated with a growth hillock on the (111) face. Fig. 9.17(c) shows typical striations and the generation of dislocations at inclusions incorporated during a period of rapid growth following partial dissolution.

9.6. Proposed Standard for Routine Characterization of Crystals

As outlined at the beginning of this chapter there is no doubt that much material published in the literature is of dubious validity because insufficient effort has been made to characterize the materials, both in terms of their composition and structural perfection. As far as we are aware, only one proposal has been made, by Roy (1965), to specify the minimum data desirable for the characterization of a crystal on which results are presented for publication. An analogous set of recommendations for the acceptance of new minerals (including synthetic crystals) has been proposed by Donnay and Fleischer (1970).

In Table 9.10 we have outlined a proposal for a set of data which should be presented when measurements on crystals are reported or in publications on the synthesis of a novel material in single-crystal form. The experimental techniques which may be used to obtain these data are also indicated. In addition, in papers on physical measurements on crystals either details of the growth technique or a reference to the corresponding crystal-growth publication containing the details should be given. It is proposed to present the characterization data and the crystal-growth data in the form of one or two tables in order to keep publications short. A few details on any heat treatment following growth and on sample preparation (surface damage!) should be given.

Data of flux-grown crystals approximating those of Table 9.10 are quite rare in literature. Among the best characterized crystals are ThO_2 (Finch and Clark, 1965) and BeO (Newkirk and Smith, 1965, 1967; Newkirk *et al.*, 1967; Austerman *et al.*, 1964). Compilation of such characterization data, when done with the necessary care, is of course very time-consuming and needs a large effort on apparatus. It would be very valuable if the national

TABLE 9.10. Data Required for Crystal Characterization

Parameter	Experimental methods
Nominal chemical formula	
Chemical analysis for major constituents, deviation from stoichiometry	Chemical and physical techniques for chemical analysis
Trace analysis	Emission spectroscopy, activation analysis, colorimetry, etc.
Homogeneity of major and minor constituents	Electron microprobe analysis; local variation of T_c etc.
Colour	In several cases the optical absorption spectrum might be of interest
Crystal habit, cleavage, twinning, refractive index, optical activity	Optical goniometry, microscopy
Size and weight of single crystals, size of inclusion-free regions, density	Three-dimensional data on size
X-ray identification	X-ray focussing powder cameras, X-ray diffractometer, Gandolfi camera for small crystals
For new crystals: space group (+ structure determination)	Single crystal X-ray diffraction techniques, automatic single crystal diffractometer
Precision determination of lattice constants	Focussing X-ray powder techniques, automatic single crystal diffractometer
Low-angle boundaries, degree of misorientation	Laue X-ray patterns, X-ray topography
Quantity and distribution of inclusions, cracks, twinning, strain	Microscopy, ultramicroscopy, X-ray topography, etc.
Dislocation density, distribution of dislocations	Etching, X-ray topography
For metals, alloys, semiconductors: Resistivity	4-probe
For magnetic materials: saturation magnetization	Magnetic balance, vibrating sample magnetometer

research institutions were to support or to maintain specialized laboratories for characterization. Ideally the characterization specialist should participate in the research programme along with physics and crystal-growth specialists, with the characterization service provided free of charge to collaborating establishments.

A greater emphasis on characterization would probably reduce the rate of publication but would be highly beneficial in the long run for all interested parties.

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