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GROWTH HISTORY OF NATURAL CRYSTALS BY MEANS OF X-RAY DIFFRACTION TOPOGRAPHY

RIASSUNTO. — La topografia R. X (metodo di Lang) è una tecnica di diffrazione R. X che registra la maniera e l'entità con cui un monocristallo si discosta dal modello ideale di struttura tridimensionale periodica. È una tecnica non distruttiva che consente di esaminare cristalli di molti cm² di superficie e il cui spessore può essere anche di diversi mm; ciò significa che, quando non sia possibile esaminare un campione nella sua interezza, lo studio di una lamina cristallina fornisce spesso informazioni tali da poterlo considerare realmente rappresentativo del campione nel suo complesso. Queste caratteristiche possono essere proficuamente impiegate per lo studio delle condizioni di crescita di cristalli naturali ed artificiali. È spesso possibile infatti ricostruire l'evoluzione spazio-temporale della morfologia di un minerale, distinguere cristalli non deformati da cristalli che abbiano subìto processi di deformazione e, in alcuni casi, definire le condizioni di temperatura e pressione che hanno prodotto deformazioni plastiche.

ABSTRACT. — X-Ray topography (Lang's Camera) is a technique wich record the manner and extent to wich the single-crystal departs from the ideal model of a perfect three-dimensional periodic structure. It is a non-destructive technique wich crystal of some cm² in area and up to several mm in thickness may examine: this means that, if the whole crystal do not can be examined, the examined crystalline plate is often as thick as to be truly representative of the bulk material. These capabilities can be utilized in the study of growth conditions of natural and artificial crystals. If is often possible the past morphology to reconstruct, undeformed crystal and deformed crystal are distinguished and in some cases it is possible to define the temperatures and pressures of plastic deformation.

Introduction

X-ray topography is the latest in a long line of tools for the study of crystals wich use X-ray diffraction. The use of X-ray topography is at present increasing rapidly, particularly as an aid to crystal growth studies and quality control of monolithic crystal devices. The technique is complementary to transmission electron microscopy in that X-ray topography enables a thick, nearly perfect single-crystal to be examined with a relatively poor resolution over a large area whereas electron microscopy necessarily uses thin specimens of quite high dislocation density and examines a very small area with excellent resolution. Against this handicap suffered by X-ray techniques one must set their capabilities for the non-destructive exami-

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nation of crystals. There are two aspect to non-destructive character of X-ray topography. Firstly, the X-ray will penetrate up to several millimetres in thickness of crystals containing only light elements. Thus, crystals of, say, diamond or beryl, some millimetres in diameter, may be examined whole; and in pratically all studies it is safe assume that X-ray topographic specimen is sufficiently thick so as to be truly representative of the bulk material. Secondly, the X-ray dosage received by a crystal in the course of its topographic examination is generally several orders of magnitude less than that required to produce detectable radiation damage in sensitive crystals.

Improvements in crystal growth techniques in the last five years have provided many new materials suitable for X-ray topographic study and in turn, X-ray topography has provided the crystal grower with valuable data on the quality of his products. The feed-back between topographer and crystal grower has proved so succesful that today X-ray topographic analysis is performed as a standard routine by many crystal growing groups.

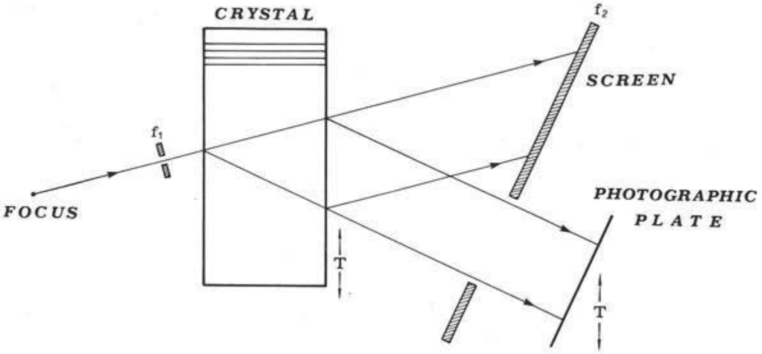

Fig. 1. — The Lang scanning method.

The ability to sample a large crystal volume and present on a single topographic record the variation in degree and type of imperfection over a distance in the crystal corresponding to a substantial fraction, if not all, of it period of growth is a new important tool for mineralogical and geological research.

In fact, the knowledge of the type of defects may possibly throw some light on the conditions under wich a mineral was formed and on the subsequent deformation the crystals might have undergone. In particular, the study of the growth bands is an important key to chart the past morphology of low-deformed minerals and also the study of dislocations is of remarkable interest in deformed crystals because from their geometry, particularly the direction of the Burgers vector, glide sistems can be determined.

The feasibility of making repeated X-ray topographic examinations of a given specimen renders it possible to interleave examinations between other types of experiments on the specimen, for example between mechanical deformations and/or heat treatments. This capability suggest the possibility to study a low-deformed mineral and after thermo-mechanical treatments, to compare the induced defective structure with defective structure of other naturally deformed specimens of the same mineral.

Experimental techniques

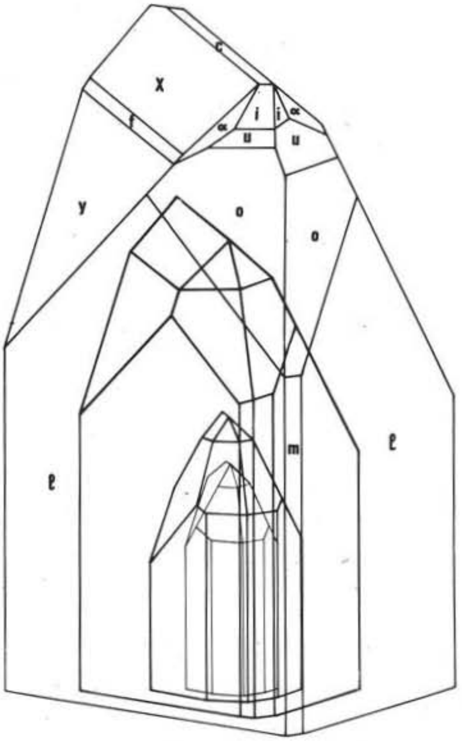

Fig. 2. — *Nigeria Topaz*. Crystal growth simplified representation. Major faces have been long the {110} faces; they are successively vanished (except the (110) face) in profit to {120} faces. The {111} and {112} faces early appear while the {113} and {d} faces only appear in the definitive habit. (After Giacovazzo et al., 1975).

In recent years, a number of experimental X-ray diffraction techniques have been developed by wich a topographical display of the microscopical defects in a crystal can be obtained. The image contrast of the defects is concerned with point- to point variation in the directions or intensities of X-ray that have been diffracted by crystals. From these variations defect structure of the crystal may be examined. Methode that mainly measure local variations in the direction of the diffracted beam are useful for the detection of gross misorientations such as sub-grains or grains (Guinier and Tennevin, 1949; Schultz, 1954; Weissmann, 1956). Intensity mapping methods are chiefly concerned with individual defects such as dislocations, stacking-faulth, inclusions, growth bands, etc. (Honeycombe, 1951; Bonse and Kappler, 1958; Lang, 1958 and 1959).

Among these last techniques, very usefull for mineralogical investigations was the Lang's Camera and here some its recent applications are presented. In this methode, a ribbon X-ray beam is collimated to an angular divergence sufficiently small that only one characteristic wavelength is diffracted by the crystal (fig. 1). A stationary opaque screen allows only the diffracted beam to reach the photographic plate. A large area of crystal can be surveyed by scanning both the crystal and photographic plate in synchronism past the incident beam.

In order to understand the contrast, general treatments of the dynamical theory of diffraction in ideal crystal are to be found in review articles (Batterman and Cole, 1964; Authier, 1970 a), and more general treatments in books (James, 1948; Von-Laue, 1970; Azaroff et al., 1974). Besides important articles for the induced effects by defects in crystals have been published: dislocations (Authier, 1967 and 1970 b); precipitates (Jun-Ichi-Chikawa, 1967), stacking-faults (Kato et al., 1967; Authier and Simon, 1968), twins (Authier et al., 1968), growth bands (Sauvage and Authier, 1965).

Natural occuring crystals

Although it is four decades since it was proposed (Orowan, 1934; Polanyi, 1934; Taylor, 1934) that dislocations in crystals play a mayor role in the plastic deformations of crystalline solids, although it is little less than three decades since it was proposed (Frank, 1949; Burton and Cabrera, 1949 a and 1949 b; Burton et al., 1951) that dislocations terminating in the surface with a screw component play a preminent role in the growth of real crystals, there are relatively few people that attempt to apply this ideas to geo-mineralogical research.

The aim of this review is to illustrate some important result that can be obtained about the growth, and in some cases about the past morphology of the minerals (fig. 2) (Giacovazzo et al., 1975; Scandale et al., 1978 a, 1978 b) by means of the observable defects: threedimensional, twodimensional, linear defects.

Threedimensional defects

Impurity precipitated after growth and foreing particles accidentally included during growth both produce intense local strain fields wich give rise to characteristic diffraction contrast effect. The relationship between the dislocation configuration and these localized strain centers can show wheather the latter arise from precipitates or inclusions.

Precipitates will generally be found along the grown-in dislocations, decorating them (fig. 3), or will be formed close to the crystal surfaces by annealing; in this last case precipitate appear as circular image wich consist of two semicircles separated by a contrast-free plane parallel to the reflecting plane (fig. 4). From this contrast, the sign of strain around the precipitates can be determined: determination of the sign is important in identification of inclusions (Jun-Ichi-Chikava, 1967).

On the other hand, primary inclusions will generate dislocations by lattice closure errors (fig. 5), secondary inclusions (micro-inclusions) will not generate dislocations.

In the majority of the cases, inclusions are either distributed throughout the crystal or localized along growth horizons. In the last case it is possible that a flux grouth mechanism was responsible for deposition (Scandale et al., 1978 b). The number of three-dimensional defects is very sensitive to the purity of the mother solution and also depends on the stability of the supersaturation during growth (Izrael et al., 1972).

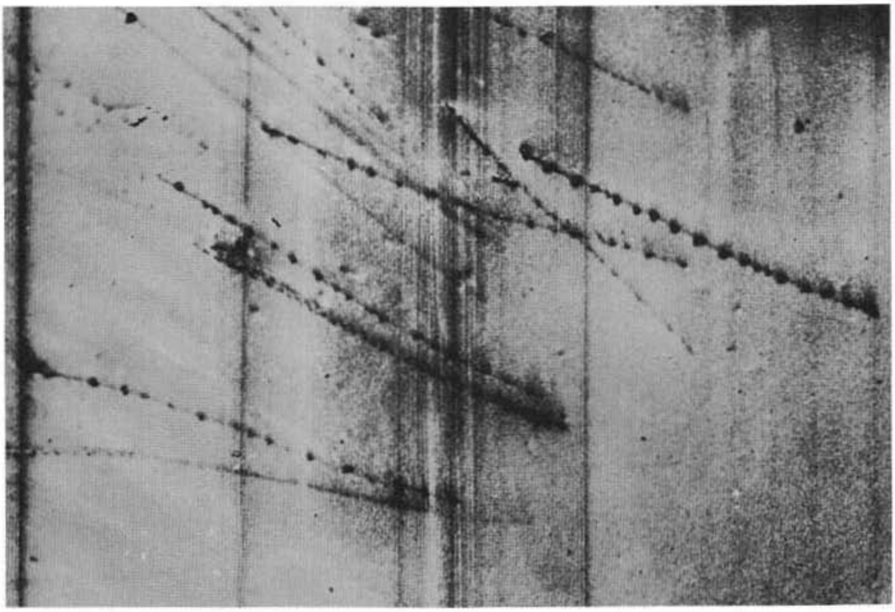

Fig. 3. — *Tunisia Dolomite*. Decorated dislocations. (After ZARKA, 1969).

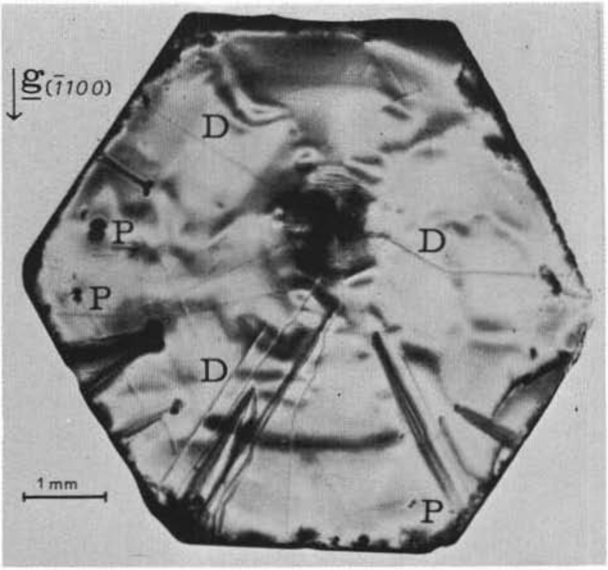

Fig. 4. — *Brazil Beryl*, basal plate. ($\bar{1}$100) Reflection. D: dislocations radiate from a center. P: precipitates. (After SCANDALE et al., 1978 b).

X-ray topographs have shown (IZRAEL et al., 1972) that while the number of precipitates decorated dislocations does increase with the growth rate, the number of precipitates outside dislocations does not seem to increase significantly.

Generally primary inclusions are involved in the growth mechanism of a face only if the generated dislocations have a screw component normal to the deposition face.

Secondary inclusions, along growth horizons localized, growth rates seem to lessen. For this reason often, the crystal habit « fast » faces can exhibit.

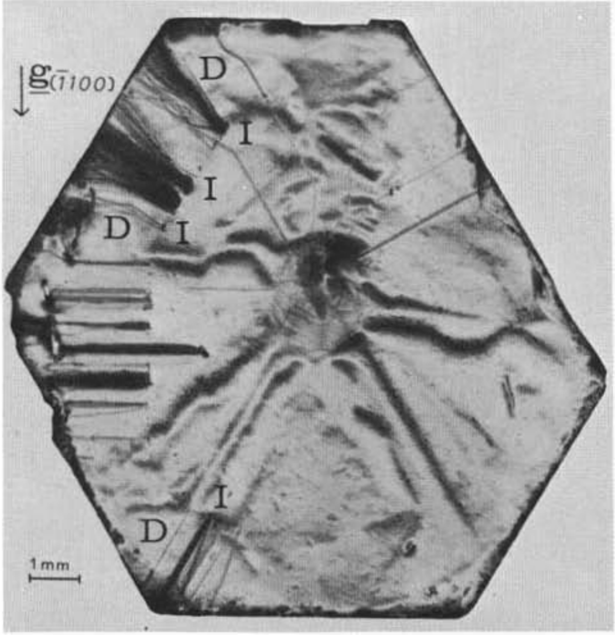

Fig. 5. — *Brazil Beryl,* basal plate. ($\bar{1}100$) Reflection. I: inclusions. D: generated dislocation. (After SCANDALE et al., 1978 b).

Twodimensional defects

When planar defects of stacking-fault type, which exhibit on X-ray topographs a fringe pattern, occur in natural crystal, their analysis by diffraction contrast the fault vectors determine. The fault surfaces involved in the present discussion do not disturb the parallelism of the lattice on one side of the fault with respect to that on the other. The conditions characterizing the fault are thus that lattice-parallelism is mantained but lattice-coincidence is not. The fault surfaces so characterized include mainly growth layers and boundaries between growth sectors.

The former (fig. 6) arise due to fluctuations in lattice parameter during crystal growth: the lattice is distorted normal to the growth front by inclusion of impurities and, for example, a rapid fluctuation in temperature will cause a large fluctuation in impurity content and hence lattice parameter. When the change is large enough to cause interbranch scattering, fringes are observed (Zarka, 1969). As the distortion is normal to the growth front, the « fault » disappears when the diffraction vector lies in the plane of the growth front. In addition to fringe contrast, very strong contrast occurs at the intersection of the growth band with the surface of the specimen (Sauvage and Authier, 1965). This fault is well know, it is often visible by naked eye, and it is very important for the reconstruction of the past morphology.

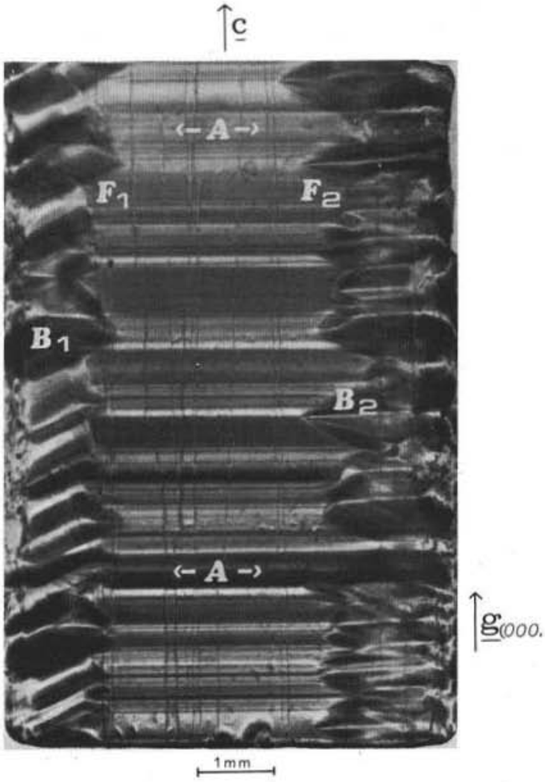

Fig. 6. — *Madagascar Beryl,* plate parallel to *c.* (0002) Reflection. A: growth layers which define the (0001) growth sector. B_1 and B_2: $(\bar{2}112)$ and $(\bar{2}11\bar{2})$ growth sectors respectively. F_1 and F_2: boundaries between (0001) growth sectors and $(\bar{2}112)$ and $(\bar{2}11\bar{2})$ growth sectors respectively. (After Scandale et al., 1978 a).

The growth sector boundaries are fault surfaces, arising to imperfect connection between growth sectors (fig. 6), that show more strongly in crystals wich also show pronunced images of growth stratifications (Lefaucheux et al., 1973). This defect supply noticeable informations about relative growth rates on various faces in the time.

Linear defects

A common dislocation configuration found in crystals is one in wich dislocations radiate from a central point within the crystal and run outward to the crystal faces (fig. 4). The interpretation of the pattern — that the dislocations were generated at the crystal nucleus and were subsequently grown into the crystal — is doubtless correct, but it leaves unsettled the question wheter the nucleation was homogeneous or heterogeneous. Rapid initial growth under the conditions of supersaturation that attend homogeneous nucleation could lead to the introduction of dislocations, especially if the initial growth were dendritic (Lang, 1974). However, if the topographs show a concentration of strain at the nucleus greater than that attributable to the dislocations, then it is likely that a foreing body is present there, and that nucleation was heterogeneous, the dislocations being generated by initial imperfect growth on this body. These dislocations are often straight and perpendicular to the growth faces: calculation of the minimum dislocation energy explains the orientations of dislocations during the solution growth of natural and synthetic crystals and also explains the sudden change of orientation of dislocations when they pass from one growth sector to another (Epelboin et al., 1973).

It is interesting to note that X-ray topographic study of dislocations into fluorite specimens (Beswick and Lang, 1972) showed bundles of dislocations in good agreement with calculations for minimum line energy, but in one crystal they found sub-grain boundaries containing tangles of dislocations much closer related to the configurations found in melt-grown crystals than solution-grown crystals. It is presumed that this crystal suffered considerable plastic deformation subsequent to growth.

An illuminant example of the use of dislocation glide systems will be found in a recent work on olivine crystals (Slind and Sorum, 1976). Two distinct types of glide systems (okl) [100] and (100) [001] were observed. The former obtained in olivine crystals deformed at temperatures higher than 1000° C with confining pressure of 5 kbar (Raleigh, 1968), the latter obtained in olivine crystals deformed at temperatures less than 900° C and 15 kbar (Green and Radcliffe, 1972): the observed glide systems (Slind and Sorum, 1976) may be explained if the crystals have been naturally deformed at different temperatures.

Conclusions

The studies described above emphasise the unity of the defect configuration occuring in the studied crystals. The presence of straight dislocations running in the direction of minimum elastic energy is a dominant feature in solution grown crystals. Growth rates on various faces have been found to be sensitive to presence of screw dislocations: the final morphology is thus determined both by surface free energy and the dislocation configuration. Further, it has been found that impurities can inhibit growth on otherwise favourable faces.

The use of growth bands to chart the past morphology of minerals and the use of the glide systems of dislocations to study the deformation conditions are certain to increase in the future.

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