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Fisica matematica. — *Twinning in minerals and metals: remarks on the comparison of a thermoelastic theory with some experimental results. Mechanical twinning and growth twinning.* Nota II di GIOVANNI ZANZOTTO (*) presentata (**) dal Corrisp. A. BRESSAN.

ABSTRACT. — In this Note II we continue the analysis of the phenomenon of mechanical twinning that we began in a preceding Note I (¹). Furthermore, we point out some fundamental properties useful in the study of growth twins, for which a fully comprehensive thermoelastic theory is not yet available.

KEY WORDS: Crystals; Thermoelasticity; Twinning.

RIASSUNTO. — *La geminazione nei minerali e nei metalli. Osservazioni sul confronto di una teoria termoelastica con alcuni risultati sperimentali. Geminazione meccanica e geminazione di crescita.* In questa Nota II si continua l'analisi del fenomeno della geminazione meccanica che si era intrapresa in una precedente Nota I (¹). Si mettono inoltre in luce alcune proprietà fondamentali utili nello studio dei geminati di crescita, per i quali ancora manca una teoria termoelastica comprensiva.

FURTHER REMARKS AND OBSERVATIONS ON MECHANICAL TWINNING

Before analyzing growth twinning, various interesting remarks can be made about the results of Note I.

REMARK II. A major consequence of what is discussed in Note I is that we are left with basically no definite connection at all between the continuum and molecolar descriptions of crystalline configurations.

In fact, were it possible to consider the sub-lattice vectors V_a in (I 3.5) fixed once and for all, they could play the role of the actual lattice vectors appearing in (I 1.10). On the contrary, the sets of vectors V_a depend on the deformation being undergone by the body, since, as shown in sect. 3 of Note I, different twinning modes are active in the same material with different sets of V's, *i.e.* with different matrices m in (I 3.6)$_2$.

This means that in (I 3.5) different tensors F are associated with different vectors V_a, and this is the reason why the possibility of establishing a definite connection between the molecular and the macroscopic descriptions is lost.

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(¹) The present Note II strongly relies on what is presented in the preceding Note I: G. ZANZOTTO: «Twinning in minerals and metals: remarks on the comparison of a thermoelastic theory with some experimental results. Generalities and mechanical twinning», in *Atti Acc. Lincei Rend. fis.*, s. viii, vol. 82, 1988, pp. 725-741.

The Introduction to the latter Note serves for this Note II as well. The references for Note II are given in Note I. For brevity we here refer to formulas in Note I by writing «I» in front of the number of the formula. For instance. (I 3.5) means formula (3.5) of Note I.

This is a point whose importance can not be overemphasized: indeed, as already mentioned in the Introduction, it suggests that it is *not* possible to apply thermoelasticity theory to model correctly the mechanics of bodies whose crystalline structure is a $(N+1)$-lattice, in terminology of Pitteri 1985*b* (see Remark IV below).

Let us notice here that, besides the Born rule, other alternative hypotheses have been put forward to model the movement of atoms and/or lattice points in a crystal undergoing twinning deformations; but these attempts to link, in special circumstances, atomic movements to gross deformation do not seem to suggest any simple rule for the general case (see Dubertret and Le Lann 1979, 1980).

Remark III. Another major consequence of the facts mentioned in Note I is that we can no longer assume, as is done for instance in many works by Ericksen, Pitteri, Kinderlehrer and others, that the material symmetry group G for elastic crystalline materials is the group $\overline{G}$ conjugate to $GL(3, \mathbf{Z})$ which has been introduced in sect. 1 of Note I. What we can say is that, if thermoelasticity theory applies, the elements of G are indeed all conjugate to elements of $GL(3, \mathbf{Z})$, with the difference that the conjugacy can be performed with possibly different matrices (with various values of the determinant) for each element, and not with the same for all. This follows from the fact that the different twinning modes solving equations (I 1.2) and equation $(\mathrm{I}\, 3.6)_1$, involve tensors $\boldsymbol{H}$ that necessarily belong to the material symmetry group G of the crystal (as mentioned below equation (I 2.1)), and for which the relation $\boldsymbol{H}\boldsymbol{E}_b = k_a^{\ b}\boldsymbol{E}_b = (m^{-1})_a^{\ s} h_s^{\ r} m_r^{\ b}\boldsymbol{E}_b$ holds (see $(\mathrm{I}\, 3.6)_2$), with $h \in \mathrm{GL}(3, \mathbf{Z})$, and with matrices m which depend on $\boldsymbol{H}$.

Remark IV. It is remarkable that in the crystals possessing a single lattice structure the Born rule has never been observed to fail. Thus, it seems well established that, for bodies whose atomic arrangement is a simple Bravais lattice, thermoelasticity theory can be used to model the macroscopic behaviour of concern to us.

Indeed the experimental evidence (see Crocker *et al.* 1966, p. 1204-5, Guyoncourt and Crocker 1968, pp. 523-4, 530) is that twinning modes in simple Bravais structures would violate the common assumption that they have the minimum possible amount of shear, rather than allow for shuffling. This assumption is nevertheless stated as a general rule in many sources, as mentioned in the Introduction.

The weaker and less precise requirement that the amout of shear be «small» is also common in the literature on twinning, but seems nevertheless false. This can be seen from many examples of twins with large shear (see Tertsch 1949, p. 56), such as for instance those in iron and calcite (see Cahn 1954, p. 408). Indeed, as remarked by Cahn 1954, p. 410, the experimental evidence is that large shears are easily observed in mechanical twinning formed at high environmental pressure.

Remark V. The failure of the Born hypothesis in many twinning deformations might well be a partial explanation for the assumption that the two different definitions of Type 1 and Type 2 twins reported at the beginning of this section are equivalent. In fact, it is not difficult to prove that, if the elements of a twinning shear satisfy the conventional rationality conditions mentioned in sect. 3 of Note I, then this shear always restores at least a sub-lattice in one of the orientations (I 3.1) (2). Hence, when Born's assumption does not hold, so that a part of the lattice points is allowed to undergo some «structural» shuffling, the conventional twin laws (I 3.1) seem to be the most apt candidates for giving the final reorientation of the whole twinned lattice-because a sub-lattice is already reorientated that way (see also Remark VII and below).

REMARK VI. Let us also notice here that the conjecture about «irrational» twins put forward by Pitteri 1986, p. 103-4, seems badly posed in view of Remark I in sect. 2 of Note I. He gives an example of a twinning mode solving equation (I 2.2) with a rotation $\mathbf{Q}$ of period 2 and the matrix $h \in \mathrm{GL}(3, \mathbf{Z})$ not of finite period. He conjectures that these twins, as opposed to those in which the matrix h has period 2, which he analyzes before, «correspond to what crystallographers and metallurgists call 'irrational twins'». Now, it can be proved that:

1) the mechanical twinning modes with $h^2 = 1$ are rational of Type 1 or Type 2 (see footnote (2));

2) in a mechanical twin, $h^2 = 1$ if and only if the orientations are the conventional ones, indicated by (I 3.1), see Pitteri 1985*a*, 1986.

It is easy to check that the example Pitteri produces, with h of infinite order, has indeed a shear which is not of the conventional rational types, in that only K_1 among its elements is rational. This might suggest that the converse of 1) above holds.

Nevertheless, on one hand we give in Note I an example of a rational compound shear with matrix h of order 4. This indicates that there is the possibility of rational twins also with h of period other than 2. Omitting the details, we notice that the matrix h in the example we give is «essentially» of period 4, meaning that, even accounting for the possibilities left by Remark I in sect. 2 of Note I, it is not possible that h can be found which is of order 2 or 3 and describes the same structure.

On the other hand, it can be proved that the twinning mode indicated by Pitteri is not «essentially» of infinite order: the structure is indeed that of a Type 2 twin. In fact, taking once more into account Remark I of Note I, we now show that the twin can be described by means of the conventional orientation given by $(\mathrm{I}\ 3.1)_2$, with h that reduces to a period 2 matrix and with twinning shear of rational Type 2. Indeed, maintaining the notations of Pitteri 1986, it suffices to consider the lattice invariant shear $\widetilde{\boldsymbol{S}} = \mathbf{1} + \boldsymbol{e}_1 \otimes \boldsymbol{n}$ and to replace the given twinning shear $\boldsymbol{S}$ with the following $\widetilde{\boldsymbol{S}}$:

$$\widetilde{\boldsymbol{S}} = \widetilde{\boldsymbol{S}}\boldsymbol{S} = \mathbf{1} + (\boldsymbol{a} + \boldsymbol{e}_1) \otimes \boldsymbol{n} = \mathbf{1} + \widetilde{\boldsymbol{a}} \otimes \boldsymbol{n}, \qquad h_s^r = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{1.1}$$

It is not difficult to verify that the twinning equation can be solved with the above shear $\widetilde{\boldsymbol{S}}$ and matrix h, and with the *same* rotation $\mathbf{Q}$, so that the structure of the twin

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(2) The proof of these facts will be published elsewhere. We also mention that it can be proved that Type 1 and Type 2 twins are of rational Type 1 and rational Type 2 respectively, but the converse does not hold, as the example (I 3.4) shows. See also Remark VI.

certainly does not change. Since h has period 2, the mode is either of Type 1 or of Type 2: it is indeed of Type 2 because $\widetilde{\boldsymbol{a}}$ (and hence the direction η_1) is rational while $\boldsymbol{n}$ (and hence K_1) is irrational. This can be checked directly on equations (17)-(19) in Pitteri 1986.

Thus, the description of the twinning mode by Pitteri is obscured by the adjunction of the lattice invariant shear $\widetilde{S}^{-1}$ to $\widetilde{S}$; the latter is the «essential» twinning shear in this case.

Besides, this also shows that the rationality properties of twinning shears are not conserved under composition with lattice invariant shears. Hence, any conjecture like Pitteri's on rationality should be worded to take this fact into account. These and other questions of kinematical nature about Type 1, Type 2 and rational twins are matter of current investigation.

Let us now go back to the general case of equation (I 2.1) or (I 2.2). As far as the twinning operation $\mathbf{Q}$ is concerned, the theoretical predictions delivered by equation (I 2.1) leave open a wide range of possibilities, other than the Type 1 and Type 2 twins discussed above and in Note I (see Ericksen 1985, 1986, Pitteri 1985*a*, 1986, 1987), and a number of special solutions are known, that do not involve rotations of the type (I 3.1). Twin laws with periods other than 2 are possible in theory, typically, but not only, with crystallographic periods 3, 4, 6; actually, these are often postulated in the literature to be the only allowable periods, both in mechanical ad growth twins. Indeed, there is a common opinion reported, but not shared, by Buerger 1960, according to which the individuals in a twin pair can be related by period 3, 4, or 6 operations; only the two-fold conventional orientations (I 3.1) would be allowed. The others are denied or considered as giving rise to mere «intergrowths», rather than twins. In many mineralogy and metallurgy textbooks only Type 1 and Type 2 twins are considered, but this seems to be a matter of nomenclature, rather than a real questioning about the polycristalline configurations actually observed. We shall continue to follow the definition of mechanical twinning agreed with in sect. 2 of Note I.

In sect. 2 we discuss the possibility of rotations with crystallographic periods to be active laws of twinning when a rather common assumption on the rationality of the interface is met. This, as we will see, is another important feature of most twins.

Let us now restrict for a moment our attention to *metals*; then, two important facts seem to emerge from the experimental reports:

REMARK VII. 1) There is no conclusive evidence of twins with non-conventional orientations in metals (see Bevis and Crocker 1969, p. 527); 2) not only have non-conventional laws never been observed, but, indeed, also Type 2 twins (*not* of the compound type) are very rare, only a few well documented observations being available. Cahn 1953, studying the twinning deformations in orthorhombic Uranium, presented the first example of a mode of Type 2 ever observed in metals. Only a few other instances of modes of Type 2 could be found reported in the literature: again in Uranium, by Daniel *et al.* 1971, in crystalline Mercury, by Crocker *et al.* 1966, Guyoncourt and Crocker 1968, and in Cu-Al-Ni shape-memory-alloys, by Ichinose *et al.* 1985.

Furthermore, no twinning shears except rational of Type 1 or Type 2 have ever been observed without doubt in metals (see Bevis and Crocker 1969, p. 527) (³), and indeed all the observed (rational) twinning shear involve one of the orientations (I 3.1), as already mentioned in 1) above. This agrees with, and perhaps is a basis for, the common assumption spoken about in Remark V above.

Owing to these facts, rationality of the shear elements plays an important role in all the presentations of twinning in mineralogical and metallurgical literature. Such rationality assumptions appear to have been dropped for the first time in the research program carried out in the 1960's and 1970's by a number of British metallurgists. They formulated a purely kinematical theory of twinning with the explicit aim of studying possible non-conventional mechanical modes in metals (see for instance Crocker 1962, Bilby and Crocker 1965, Bevis and Crocker 1967, Bevis 1968, Bevis and Crocker 1969, Acton *et al.* 1970, Crocker 1982 and other listed references by the same authors). However, as mentioned above, they were unable to observe without doubt any of the predicted non-conventional and irrational twinning modes (see Bevis and Crocker 1969, p. 527).

It is interesting that what is stated in Remark VII seems also to be true for mechanical twinning in *minerals*, although in this case the situation is a little more confused than with metals (for a detailed discussion of the mechanical twinning modes in various minerals, see for instance Friedel 1926, pp. 490-3, Cahn 1954, pp. 381-3, pp. 409-11, Kelly and Groves 1970, pp. 296-304).

The prejudice mentioned above, that «true» twins involve only period two operations hence seems to have possible roots in the fact that only these configurations seem to be actually observed, at least for *mechanical* twinning. The reasons why this happens are not really clear yet; they seem to be related to what is mentioned in Remark V, and this also is a matter of current investigation. Two theorems on twinning appear to offer at least a partial explanation for the above Remark VII, but this issue will be more clearly discussed in sect. 2, below equation (2.12).

With regard to the question of mechanical twins not of order two, let us notice

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(³) About the existence of non-rational mechanical twins, we mention here the only scattered example that could be found in the literature, which are of very uncertain interpretation. The first regards some irrational twin bands in Magnesium, reported by Reed-Hill and Robertson 1957, and studied for instance by Crocker 1962. In this work, Crocker proposes an interpretation of the phenomenon in terms of a double twinning mechanism, which would lead to an equivalent irrational single shear mode. Nevertheless, this interprets the observations only partially (Crocker 1962, p. 1923), and indeed it is «inconsistent with the experimental results» according to Dubertret and Le Lann 1979, p. 498, and others quoted therein. The latter authors attempt an explanation of these bands by means of a model, already mentioned in the text, according to which there is no shear movement at all in the microscopic scale, not even of a fraction of the lattice points. Also Bevis 1968, p. 237, attempts with no success to interpret the phenomenon, in terms of some particular twinning modes in hexagonal close-packed materials. These bands seem as yet unexplained. The second case of possibly non-rational mechanical twinning modes regards some twins with apparently irrational interfaces observed in studies on the plastic deformation of Fe-Ni-C martensites and of an Fe 5-wt pct Be alloy (a solid solution of Beryllium in Iron) performed by Richman 1963 and Richman and Conard 1963. Nevertheless, the discussion on these cases by Crocker *et al.* 1963 and by Bevis *et al.* 1968, shows that the experimental observations do not allow for a clear interpretation of the phenomenon, and that no evidence is produced that these modes are indeed irrational twins.

that Friedel 1926, pag. 490, admits the possibility of their existence, stating: «l'étude des macles mécaniques d'ordre 3, 4, 6, reste à faire ... mais il est très probable que de telle macles ... existent». Nevertheless, the analysis of a transformation twinning mode in leucite which he describes as four-fold, does not seem a proper example, since, in view of Remark I of Note I, it cas also be described with a two-fold twin law (see the Appendix).

We list here for convenience a number of sources in which are tabulated the crystallographic data for twinning modes in a great number of minerals and metals: Barrett and Massalski 1966, pp. 415-6, Cahn 1954, p. 411, Hall 1954, pp. 56-7, Kelly and Groves 1970, pp. 303-4, Klassen-Nekliudova 1964, pp. 166-76, Mathewson 1928, p. 563, pp. 565-6, Reed-Hill *et al.* 1963, p. 979, Tertsch 1949, p. 56, Zoltai and Stout 1984, p. 65.

GROWTH TWINS, STABILITY PROPERTIES UNDER CHANGES OF THE EXTERNAL PRESSURE AND TEMPERATURE, RATIONAL INTERFACES AND CRYSTALLOGRAPHIC PERIODS

As is clear from the discussion in sect. 3 of Note I and in sect. 1, the twinning operations Q of a mechanical twin cannot be arbitrary, but need to satisfy some definite conditions, *i.e.* equations (I 2.1) and (I 2.2) or (I 3.6), respectively. This only allows for particular orientations to be considered true laws of *mechanical* twinning; in a similar way, we are interested in finding the conditions restricting the possible orientations in the case of *growth* twins.

In spite of some early attempts to rationalize the phenomenon from various points of view (see for instance Buerger 1945, Cahn 1964, Curien and Kern 1957, Kern 1961, Hartman 1956, Holser 1958, 1960, and others), as already mentioned, there is not yet a clear understanding, according to the theory of thermoelasticity, of the mechanisms ruling the growth of crystals in twinned shapes.

However, one general assumption seems reasonable in most cases, *i.e.* that growth twins could be modelled as polycrystals which can exist in stable stree-free equilibrium states («natural states») while in contact with an environment described by the two control parameters p and θ ranging within a two-dimensional domain of the plane.

The scalar quantity p expresses the intensity of the external hydrostatic load on the body while «growing» in contact with a heat bath at temperature θ. Most growth sites are reasonably well described, and growth conditions accounted for, when the two variables p and θ are used; we assume they have their domains restricted enough so as to keep the body away from phase transitions, this being a phenomenon which we do not consider here (see for instance Ericksen 1980*a*, Parry 1981, 1982).

Motivations for the above assumption are diverse: they are explained in detail by Zanzotto 1990. On one hand, a common point of view assumes that the most favourable conditions for crystal growth are those allowing for rather stable or metastable states of the (poly)-crystalline edifice. On the other hand, growth twinning usually (but not always: see the Remark VIII below) originates at the beginning of crystallization, and persists throughout the whole growth process which can in turn be influenced by the external temperature-pressure conditions. The assumption we make accounts for this, in that the structure of a polycristal meeting the conditions stated above is capable of «adjusting» to the environmental changes possibly taking place all along with crystallization. Thus the crystal maintains itself in those natural states best suited to a continuous growth process, consistent with environmental changes. Furthermore, large stresses are not created at the joints and interfacial energies are likely to be maintained low (in the scheme described they are indeed vanishing) so that fracture or damage has less chance to occur.

These formations are therefore those whose growth and survival thereafter are the most favoured. They have hence the highest chances of being observed with regularity in a given mineral, differently from the what happens with fortuitous, randomly occurring associations. The formations so selected are the most likely to feature the main characteristics that are commonly attributed to genuine twins. As mentioned in the Introduction, among these features are in fact the frequence and «reproducibility» of a well determined reorientation (see Dana 1962, vol. 3, p. 73, p. 96, Friedel 1926, p. 421, and Cahn 1954 among others), and reduced energy at boundaries (see Cahn 1954, pp. 392-3, Buerger 1945, pp. 470-1, 475, Holser 1960 among others).

The point of view adopted here implies that the joints of the polycrystals be stress-free, in the jargon of Ericksen 1983 and James 1984; this leads to some definite conditions that the orientations needs to satisfy, in order that they be considered actual twinning operations.

The bodies exhibinting these properties fall in the first of three classes in which polycrystals are subdivided by Zanzotto 1990. In the second class are the aggregates formed according to twin laws which are seldom observed, and, the third class collects what are considered to be random events in mineralogical literature.

A detailed analysis, made according to these premises, of some particular cyclic twins in quartz, is shown by Zanzotto 1990 to deliver in general some information that allows one to assess the history of the mineral; this is of interest for the applications to the Earth Sciences. It seems that this approach might be fruitful in questions related to mechanical twinning, too.

Nevertheless, it is not completely clear which are the limits of validity of the assumption above, and whether other conditions need to be satisfied to truly account for all of the experimental observations. As already stressed, one further condition that very likely must be taken into account is that of reduced interfacial energy, a property which does not follow from the requirement of stress-free joints. This request on the morphology of a polycrystal, in fact, only guarantees that it is capable of deforming according to the environmental changes in such a way to *maintain* the stress at the joints low, whenever the *original* stress is low. For instance, there can be stress-free joints, and consequently stable formations, also in the case of boundaries on irrational planes (see below), although these are usually connected with high surface energy.

As will become clearer in the sequel, it seems likely that we need to impose both of the requirements above, *i.e.* stability of the edifice *and* reduced interfacial energy, to pick out «true» growth twins; some further discussion can be found in Remark II of the Introduction in Zanzotto 1990.

REMARK VIII. It is made clear by Shalkowsky and Shubnikow 1933 (see also Friedel 1933) that twinning sometimes takes place at the end of the crystallization process, occuring by reoriented agglutination of preexisting crystals, as in the case of the alum formations described in sect. 2 of Note I. It is obvious than this kind of growth twins might or might not fit into the scheme adopted above.

In fact, neither do they seem to exhibit the lowest possible boundary energies, nor does it happen that variations of environmental conditions play any essential «selection» role during the growth of the individual crystals. After forming at certain given values of p and θ, it is unlikely that the twin can survive many environmental changes. Perhaps this is a partial explanation of the relative rarity of such formations. Indeed, the existence of this kind of twins was shown beyond doubt as late as 1933 (see Friedel 1933 and below for more details).

Granted that one characteristic feature of growth twinning is reduced energy at boundaries, it is a common opinion that this property be related to a «good fit» of the various individuals, *i.e.* to the sharing at the interfaces of the «most possible» structural elements (see Buerger 1945, Cahn 1954, p. 392, Holser 1960). In fact, for instance Buerger 1945, pp. 470-1, states that «the location of interfaces ... is conditioned by requirements of minimum interfacial energy, and low energy is made possible by the existence of a plane of atoms in common between the two phases». He then continues «... the most probable orientations are such as to provide the greatest number of structural elements in common», and «... rational intergrowths have naturally higher probabilities than non rational intergrowths». Similar opinion is held for instance by Holser 1960, p. 20, and others. «Rational» means here that the twinning operation «transforms a net into itself» (Buerger 1945, p. 471), and this net is meant as giving the contact plane. Moreover, a very common request in the literature is that these rational contact planes have «small» (integral) indices.

We stress that many observations suggest that this is not always the case, neither in mechanical nor in growth twinning. It is well known that in Type 2 twins (*not* compound, as the mechanical twins in metals we mentioned in sect. 3 of Note I and in sect. 1) the interface is *irrational*; it is a plane known in literature as the «rhombic section» (Friedel 1926, p. 487, Cahn 1954, pp. 388-9, pp. 408-9) which is an irrational contact plane reported also in various growth twins (see for instance Cahn 1954, pp. 408-9, Curien and Kern 1957, pp. 129-32, Zoltai and Stout 1984, p. 66). We remark that, even though this seems to be the most common kind of irrational interface reported in the literature, it is not the only one. Curien and Kern 1957, p. 130, Hartman 1956, p. 231, mention how an indefinite assemblage of rational and irrational planes is often observed in «penetration» twins. Such is the usual denomination for twinned crystals intergrown in such that they have more than one composition plane or surface, as opposed to «contact» twins in which the interface is a single, well individualized plane.

Another interesting example from this point of view is the alum twin described in sect. 2 of Note I, which exhibits an interface where two non-congruent lattice planes meet, with a relative orientation such that the closest packed row of atoms is in common. Other twins are known with this feature (see for instance some of the quartz twins reported by Zyndel 1914 and Dana 1962, vol. 3, p. 96-8).

Since interfacial energies are likely to be comparably high where non equivalent or irrational crystallographic planes meet, such energies must probably be taken into account for a closer analysis of this kind of phenomena.

In order to understand clearly which are the lowest-energy interfaces in polycristals we would need a general constitutive theory of thermoelasticity capable of accounting for interfacial energies at crystalline boundaries. We have not thoroughly examined the literature concerning this topic, but this seems not yet available.

In any case, formations whose individuals meet at an interface S with crystallographically equivalent planes on the two sides, and sharing the lattice points on it, are by far the most commonly and frequently observed in both mechanical and growth twins (Type 1 and compound twins share for instance this property). This kind of naive but nevertheless important and common rationality assumption seems hence worth a closer investigation: following an initial idea of Ericksen, we illustrate here some of its main consequences.

Let S_0 be the planar interface for a twin composed by the two homogeneous individuals R and $\bar{R}$, and let $\boldsymbol{N}_0$ be the normal to S_0; we have, for suitable integers N_a:

$$\boldsymbol{N}_0 = N_a \boldsymbol{e}^a, \tag{2.1}$$

where $\boldsymbol{e}_a[\boldsymbol{e}^a]$ are [reciprocal] lattice vectors in R.

Let us suppose that the lattice-planes lying on the two sides of S_0 are crystallographically equivalent; they have thus the same indices with respect to suitable *isometric* bases of the two lattices (see footnote (2) of Note I). This means that there are lattice vectors $\bar{\boldsymbol{e}}_a$ for $\bar{R}$ satisfying

$$\boldsymbol{N}_0 = N_a \boldsymbol{e}^a = \lambda N_a \bar{\boldsymbol{e}}^a, \tag{2.2}$$

for some scalar λ, $\bar{\boldsymbol{e}}^a$ being reciprocal lattice vectors in $\bar{R}$.

Let us call $\boldsymbol{R}_0$ the rotation such that

$$\bar{\boldsymbol{e}}_a = \boldsymbol{R}_0 \boldsymbol{e}_a, \qquad \text{whence} \qquad \bar{\boldsymbol{e}}^a = \boldsymbol{R}_0 \boldsymbol{e}^a; \tag{2.3}$$

such a rotation exists because $\boldsymbol{e}_a$ and $\bar{\boldsymbol{e}}_a$ are isometric, and for $R \cup \bar{R}$ to be a true twin, $\boldsymbol{R}_0$ must not belong to the point group of R.

We then immediately have

$$\boldsymbol{N}_0 = N_a \boldsymbol{e}^a = \lambda N_a \bar{\boldsymbol{e}}^a = \lambda N_a \boldsymbol{R}_0 \boldsymbol{e}^a = \lambda \boldsymbol{R}_0 (N_a \boldsymbol{e}^a) = \lambda \boldsymbol{R}_0 \boldsymbol{N}_0, \tag{2.4}$$

whence we get, since $\boldsymbol{R}_0$ is a rotation:

$$\lambda = \pm 1, \qquad \text{i.e. } \boldsymbol{N}_0 = \pm \boldsymbol{R}_0 \boldsymbol{N}_0. \tag{2.5}$$

Conversely, if $(2.5)_2$, (2.3) and (2.1) hold, then we get

$$\pm N_a \bar{\boldsymbol{e}}^a = \pm \boldsymbol{R}_0 \boldsymbol{N}_0 = \boldsymbol{N}_0 = N_a \boldsymbol{e}^a, \tag{2.6}$$

this implying that R and $\bar{R}$ meet at equivalent lattice planes.

Now, introducing the axis $\boldsymbol{e}$ of $\boldsymbol{R}_0$,

$$\boldsymbol{e} = \boldsymbol{R}_0 \boldsymbol{e}, \qquad \text{with} \qquad \boldsymbol{e} \cdot \boldsymbol{e} = \boldsymbol{N}_0 \cdot \boldsymbol{N}_0, \tag{2.7}$$

we see that $(2.5)_2$ and (2.7) hold together if and only if

$$\text{either } \boldsymbol{e} = \pm \boldsymbol{N}_0 \quad \text{or} \quad \boldsymbol{e} \cdot \boldsymbol{N}_0 = 0. \tag{2.8}$$

In fact, when $(2.5)_2$ holds with the positive sign, then uniqueness of the axis of

$\boldsymbol{R}_0 \neq 1$ gives $(2.8)_1$. If $(2.5)_2$ holds with the negative sign, then $\boldsymbol{R}_0$ has eigenvalues 1 and -1, and this implies $\boldsymbol{R}_0^2 = 1$ since the third eigenvalue in also -1, because $\det \boldsymbol{R}_0 = 1$. Furthermore, $\boldsymbol{N}_0 \cdot \boldsymbol{e} = -\boldsymbol{R}_0 \boldsymbol{N}_0 \cdot \boldsymbol{R}_0 \boldsymbol{e} = -\boldsymbol{N}_0 \cdot \boldsymbol{e}$, so that $(2.8)_2$ holds.

Hence condition $(2.5)_2$ implies the following restrictions on $\boldsymbol{R}_0$:

Case 1) The twinning operation has axis perpendicular to the interface S_0.

Case 2) The twinning operation is a rotation of π about an axis lying on the interface S_0.

The existence of a net η of atoms belonging to S_0 and in common between R and $\overline{R}$ has not been considered, yet. It gives further restrictions on the twinning operation $\boldsymbol{R}_0$, because it is equivalent to the requirement that η be invariant under R_0. We have:

Case 1) The condition that $\boldsymbol{R}_0(\eta) = \eta$ is expressed by the equations

$$\boldsymbol{R}_0 \boldsymbol{v}_a = \boldsymbol{R}_{0a}{}^{b} \boldsymbol{v}_b, \qquad \text{where } \boldsymbol{R}_{0a}{}^{b} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & r & s \\ 0 & p & q \end{bmatrix}, \tag{2.9}$$

with r, s, p, q, integers such that $rq - sp = 1$. Here we have set $\boldsymbol{N}_0 = \boldsymbol{v}_1$, whence $\boldsymbol{v}_2$ and $\boldsymbol{v}_3$ are some vectors generating the crystallographic net η.

Equation (2.9) implies that $\boldsymbol{R}_0$ has period 2, 3, 4, or 6. This can be concluded by standard analysis of the integral trace of $\boldsymbol{R}_0$; as already mentioned, such a restriction is sometimes assumed *a priori* for twinning operations in crystallography textbooks. Notice that these morphological features are not exhibited by the alum twins of sect. 2 of Note I, nor by many of the twins reported in Dana 1962, vol. 3, pp. 96-98, for quartz (see below).

Case 2) For the net η to be invariant under $\boldsymbol{R}_0$, the rotations axis $\boldsymbol{e}$ must in this case be a mirror-symmetry axis of η. The resulting twins are particular instances of Type 2 twins.

For a given lattice, the actual existence of a twinning operation $\boldsymbol{R}_0$ depends now upon the vector $\boldsymbol{N}_0$ (*i.e.* upon the interface S_0 chosen) and of course on the crystal symmetry. It is interesting to note that the only twinning operation with the properties above regarding the interface, and which is possible in *any* lattice, and on *any* lattice plane S_0 is that of period 2 of case 1): $\boldsymbol{R}_0 = -\boldsymbol{1} + 2\boldsymbol{N}_0 \otimes \boldsymbol{N}_0$; it corresponds to the entries $\boldsymbol{r} = -1$, $\boldsymbol{s} = 0$, $\boldsymbol{p} = 0$, $\boldsymbol{q} = -1$ in equation (2.9). These are rotations of π about the axis $\boldsymbol{N}_0$ orthogonal to S_0; the resulting twins are of Type 1, defined in sect. 2 of Note I.

It is perhaps even more interesting that Type 1 and Type 2 twins always exhibit stress-free joints. In the case of Type 1 twins, this can be proved in the following way.

Let the vectors $\boldsymbol{E}_a$ generate a lattice, R_1, say, let $\boldsymbol{N}_0$ be the unit normal to a rational plane S_0 in R_1 and consider the rotation $\boldsymbol{R}_0$ above. We then consider the reference configuration R for a polycrystal obtained joining the lattices R_1 and $\boldsymbol{R}_0 R_1$ along the plane S_0. Now, let us consider a homogeneous crystal whose structure is given by the lattice

R_1 when in a heat bath of temperature θ and loaded by the hydrostatic pressure p. Then, if we admit that for such a crystal there is a locally unique surface $\overline{U}(p,\theta)$ of minimizers of the Gibbs free energy, it can be proved (see Ericksen 1983, James 1984) that the requirement of stability for the twin pair is fulfilled when the equation

$$(2.10) \qquad \boldsymbol{R}(p,\theta)\overline{\boldsymbol{U}}(p,\theta)\boldsymbol{R}_0^t = \overline{\boldsymbol{U}}(p,\theta)\widetilde{\boldsymbol{S}}(p,\theta),$$

can be solved for suitable rotation $\boldsymbol{R}(p,\theta)$ and simple shear $\widetilde{\boldsymbol{S}} = \boldsymbol{1} + \boldsymbol{A}(p,\theta) \otimes \boldsymbol{N}_0$. According to the theorem by Gurtin 1983, p. 22, this equation can always be solved when we consider, as we do, actual twins in which $\boldsymbol{R}_0$ does not belong to the point group of the structure. Indeed, in this case, for any $\boldsymbol{R}_0$ such that $\boldsymbol{R}_0^2 = 1$, a solution exists for the equation $\boldsymbol{RFR}_0^t = \boldsymbol{FS}$, no matter what $\boldsymbol{F}$ is. Hence, setting $\boldsymbol{F} = \overline{\boldsymbol{U}}(p,\theta)$, we obtain the solutions of (2.10) we were looking for. Gurtin 1983 also shows that $\boldsymbol{R}(p,\theta) = -\boldsymbol{1} + 2\boldsymbol{N}(p,\theta) \otimes \boldsymbol{N}(p,\theta)$, where $\boldsymbol{N}(p,\theta) = \text{unit}\,[\overline{\boldsymbol{U}}^{-1}(p,\theta)\boldsymbol{N}_0]$ is the normal to the interface in the deformed configuration.

A similar argument leads to the solution of an equation like (2.10) for a polycrystal whose reference configuration R is a Type 2 twin.

The fact that Type 1 and Type 2 twins are found by these considerations to be always stable formations, and that hence they place themselves among the easiest formations to grow, might be a reason for their occurrence with great frequency and preponderance, and it can also be connected to part 1) of Remark VII in the preceding section: it gives some reason for the fact that mechanical twinning seems to have never been observed in modes other than Type 1 or Type 2, and it could also be related to the opinion already mentioned in sect. 3 of Note I, according to which the conventional orientations (3.1) are the only ones possible in either mechanical or growth twinning.

We notice here that another theorem can be connected to part 2) of Remark VII above. Indeed, Ericksen 1985 proves that, if $\boldsymbol{H}$ is given in the twinning equation $\boldsymbol{QFH} = \boldsymbol{FS}$, then there are two solutions or none.

These can be shown to correspond to the so called «conjugate» twinning modes of metallurgical and mineralogical literature. We only mention here that conjugate modes have the feature that planes K_1 and K_2 exchange their indices as well as directions η_1 and η_2, and Type 1 twins have their reciprocal mode of Type 2, and vice versa. Pitteri 1986 gives a proof of this in the case of Type 1 and Type 2 twins, which is the most interesting to us, in view for Remark VII.

These remarks show that, when a given twinning law is observed, then the reciprocal law has the kinematical possibility of being active, too. Now, if the twin is *not* compound, the two conjugate laws have one important difference: the Type 1 always has a rational interface K_1 (see footnote (^{2})) and an irrational K_2, and since conjugate laws exchange indices for K_1 and K_2, the Type 2 always has an *irrational* contact plane, as we already stressed when discussing the «rhombic section». According to our previous remarks about boundary energies, irrationality seems to be an unfavorable condition at the interface, that probably causes twins of Type 2, which are not compound, to have less chances of actually bein observed. As mentioned in Remark VII, part 2), they are indeed quite rare.

As we already noticed above, the alum twin described in sect. 2 of Note I exhibits what can be considered and odd kind of interface, where non-equivalent *rational* planes meet. The structure is nevertheless a stress-free joint, because, owing to the cubic symmetry of the crystal, $\overline{U}(p,\theta) = \alpha(p,\theta)\,\mathbf{1}$ with α a scalar, and stability under changes of p and θ is in this case travially proved. This means that the energy near the interface (which could be high owing to a great local «misfit» of structure elements, although it is likely to be some kind of minimizer) is not increased by environmental changes.

Finally, there are twins whose twinning law does not meet any of the requirements made here. This means that the interfacial energy, which might be originally high because of the absence of common crystallographic elements, is likely to be furthermore increased by the change of environmental conditions. Examples are some of the rare but documented twinning laws for quartz reported by Zyndel 1914 and Dana 1962, vol. 3, pp. 97-98. These considerations can perhaps account for their rarity.

As already stressed, we still miss a precise statement about the relation existing between the «misfit» at a crystalline interface and the energy there stored. An informal exemplification of this is given by Buerger's quotations above, regarding low interfacial energy at «rational» composition planes. The foregoing discussion points out some of the features that a thermoelastic theory accounting for surface energies should seemingly exhibit. This makes it possible to draw a scheme that roughly takes into account the role played by such energies. It is a first attempt to complement the classification of growth twins envisaged by Zanzotto 1990. To summarize, we have:

1) Formations with low original interfacial energy, probably originated by the simultaneous growth of the composing individuals, and whose boundary energy is furthermore *maintained* low no matter how the environment changes during the growth process and after. The environmental conditions play in this case a definite «selective» role and these polycrystals can hence exhibit all the features generally attributed to genuine twins, as discussed above. They are hence the most common and frequent, and indeed, among these are Type 1 and compound twins.

2) Polycrystals that, in spite of probably high boundary energies, exhibit a structrure such that these energies are not increased by the possible environmental changes (*i.e.* they are stable formations exhibiting stress-free joints). As shown above, the alum twin of sect. 2 and Note I is an example, together with some other of the twins formed by oriented agglutination of pre-existing crystals reported for instance by Zyndel 1914, Friedel 1933 or Dana 1962, vol. 3, pp. 96-8. The common Type 2 (not compound) twins belong to this class. They are rarer than the formations of class 1), but it is likely that they have a greater chance to occur than those of the following class, in that for instance, if they are formed at high temperature, they are unlikely to fracture in cooling.

3) Formations whose origin is analogous to those of class 2) but for which the probably high original boundary energy is even possibly increased by environmental changes, owing to a «wrong» morphology which does not satisfy the conditions of stability. They exist but they are rare: again see some of the examples reported for quartz by Zyndel 1914, Friedel 1933 or Dana 1962, vol. 3, pp. 96-8.

As emerges from the discussion in the preceding sections, in the case of growth twinning the theoretical analysis does not seem to deliver a definite twinning condition that the orientations must satisfy, as is the case with mechanical twinning. What is more likely to be the results of such an investigation, is an evaluation of the likelihood of occurrence of polycrystals with given morphologies, resulting in a rather complex picture where «genuine» twins are the formations holding the «most probable» positions.

We finally mention that, as perhaps is already clear from the discussion above, growth twins exhibit a much greater variety of twin laws and shapes than mechanical twins. While even in this case Type 1 twins are the most frequent, many other orientations are observed. A great number of interesting examples can be found in the treatises by Friedel 1926 and by Dana 1962, Vols. 1 and 2, but see also Cahn 1954, Curien and Kern 1957, Donnay 1952, Friedel 1923, 1933, Takeda *et al.* 1967, Zyndel 1914, and of course many others.

APPENDIX

Friedel 1926, pp. 489-90, reports a leucite twin which has a clear mechanical origin («... les macles se multiplient par échauffement et par pression ...») and that Mügge interpreted as a usual Type 1 twin. Friedel prefers to describe the twin law rather as a four-fold operation, and claims that this is an example of twinning mode that cannot possibly be obtained through a simple shearing movement of lattice points. By this example he also seems to conclude the existence of mechanical twins not of order two. It is proved here that this is not correct.

Lattice vectors are $\boldsymbol{e}_a$, with

$$\boldsymbol{e}_a \cdot \boldsymbol{e}_b = \begin{bmatrix} a^2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

where a is a rational number, and the indicated twinning operation is the rotation $\boldsymbol{Q}$ such that

$$\text{(A1.1)} \qquad \boldsymbol{Q}\boldsymbol{e}_a = Q_a{}^b \boldsymbol{e}_b, \qquad \text{with} \quad Q_a{}^b = \begin{bmatrix} 0 & a & 0 \\ -1/a & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

With this choice of the twin law, we have $\boldsymbol{Q}^4 = \mathbf{1}$. However, it is not difficult to see that, taking into account the possibilities of Remark I in sect. 2 of Note I, the *same* twin structure can also be described by means of a two-fold operation. Hence, this does not seem to be a proper example of a mechanical twin not of order two. The existence of a period two operation then readily delivers the existence of a possible twinning shear; nevertheless, since the two-fold operation might not restore the motif, we give here a direct proof that the twinning equation can be solved with the given $\boldsymbol{Q}$.

We need to find a matrix of integers m belonging to $GL(3, \mathbb{Z})$, and a simple shear

$\boldsymbol{S} = \mathbf{1} + \boldsymbol{A} \otimes \boldsymbol{N}$ such that the equation

$$QS\boldsymbol{e}_a = m_a^{\ b}\boldsymbol{e}_b \tag{A1.2}$$

(which is substantially the same as (I 2.2)) is solved for the given rotation $\boldsymbol{Q}$.

Take integral numbers p and q such $a = p/q$, with $p \neq q$ and $GCD(p,q) = 1$, and take integers r and s such that

$$rq + sp = 2. \tag{A1.3}$$

Such r and s always exist in $\boldsymbol{Z}$ when p and q are relative prime as supposed.

Then define $\boldsymbol{A} = A^i\boldsymbol{e}_i$ with: $A^1 = (sp-1)(q^2/p^2)$, $A^2 = (sp-1)(q/p)$, $A^3 = 0$. Furthermore, take $\boldsymbol{N} = (p/q)\boldsymbol{e}_2 - \boldsymbol{e}_1$, because this is the normal direction to the observed interface. Since $sp \neq 1$ because both s and p are integral numbers different from 1, it is $\boldsymbol{A} \neq 0$. Defining $\boldsymbol{S}$ by means of the above $\boldsymbol{A}$ and $\boldsymbol{N}$, and using equation (A1.3), we immediately get

$$S\boldsymbol{e}_1 = rq\boldsymbol{e}_1 - (sp-1)(p/q)\boldsymbol{e}_2\,, \qquad S\boldsymbol{e}_2 = (sp-1)(q/p)\boldsymbol{e}_1 + sp\boldsymbol{e}_2\,, \qquad S\boldsymbol{e}_3 = \boldsymbol{e}_3\,, \tag{A1.4}$$

whence

$$QS\boldsymbol{e}_1 = (sp-1)\boldsymbol{e}_1 + rp\boldsymbol{e}_2\,, \qquad QS\boldsymbol{e}_1 = -sq\boldsymbol{e}_1 + (sp-1)\boldsymbol{e}_2\,, \qquad QS\boldsymbol{e}_3 = \boldsymbol{e}_3\,, \tag{A1.5}$$

so that equation (A1.3) is solved with

$$m_a^{\ b} = \begin{bmatrix} sp-1 & rp & 0 \\ -sq & sp-1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

which is in $GL(3,\boldsymbol{Z})$ because it has integral entries and determinant 1, as can be checked directly using equation (A1.3).

Hence, there is at least the theoretical possibility, excluded by Friedel, that this mode be activated, as is usual in mechanical twins, by a homogeneous twinning shear involving all the lattice points.

The phenomenon observed by Friedel could probably have been misleading, in that he mentions how the twins multiply themselves more and more in heating, giving a twinning pattern so fine that «its detailed study is impossible». This feature might have led to choose the particular movements of lattice points Friedel 1926, p. 490. Fig. 524, proposed, and to conclude that no shear was present. Rather, this phenomenon is most likely to be related to what is discussed by Ball and James 1987.

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