**Acknowledgement**

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## *Dislocations and the λ-Transition in Sodium Nitrate*

An investigation of the nature of lattice dislocations in sodium nitrate merits consideration for two reasons, both of which stem from recent observations [1, 2] on a crystallographically similar solid, calcite. (Both these solids are of rhombohedral symmetry with a two-molecule unit cell, which for $NaNO_3$ has the dimensions $a_0 = 6.325$ Å and $\alpha = 47° 16'$, and for $CaCO_3$, $a_0 = 6.361$ Å and $\alpha = 46° 6'$.) In calcite, two main types of translation gliding prevail: $\{11\bar{1}\}$ $[011]$ and $\{100\}$ $[011]$. But a third type which, unlike the others, could scarcely be predicted from an examination of the crystal structure has been recently identified [3]. This type involves movement of dislocations on $\{2\bar{1}\bar{1}\}$ planes in directions parallel to $[0\bar{1}1]$; it seems to dominate when the calcite is subject to severe distortion (e.g. during the onset of solid-state thermal decomposition). One reason for studying dislocations in $NaNO_3$, therefore, is to identify the nature of the translation gliding and, in particular, to examine whether dislocations of the type $\{2\bar{1}\bar{1}\}$ $[0\bar{1}1]$ again occur, especially at temperatures approaching the λ-transition. In contrast to the situation that pertains for calcite during chemical decomposition, the lattice distortion accompanying the λ-transition of $NaNO_3$ is of the mildest kind, there being less than 2% volume change [4]. The transition takes place [5], reversibly, over the range 150 to 275° C. The $NaNO_3$ gradually changes from the calcite structure to a closely similar one, still rhombohedral, in which the nitrate ions are essentially (but not strictly [6]) disposed at random between two possible orientations, $\alpha$ and $\beta$, differing by a 60° rotation about the threefold axis. The transition may, for simplicity, be regarded as one in which the planar $NO_3^-$ ions undergo torsional oscillation.

The second reason for studying dislocations in $NaNO_3$ is to determine the influence of the thermal transformation on the dislocation content of the solid. Of especial interest from the viewpoint of the general theory of transformation in solids is the question whether dislocations originally present in the low-temperature, stable form remain locked in the lattice after thermal cycling between temperatures either side of 275° C (compare the cognate phenomenon of persistence of axes that Ubbelohde and his coworkers [7, 8] have discovered in some nitrate and other crystals).

Single crystals of both melt-grown and solution-grown $NaNO_3$ have been examined, the dislocations emergent at $(100)$ faces being revealed by etching with acetic acid in the manner developed by Di Martini [9, 10].

The dislocation content of the melt-grown crystals was relatively large (*c.* $10^7/\text{cm}^2$), a situation which is doubtless connected with the fact that melt-grown crystals traverse the λ-transition on cooling. Unambiguous evidence of the presence of dislocation "pile-ups" and the occurrence of polygonisation boundaries was afforded by micrographs such as that shown in fig. 1. Alignments of emergent dislocations, on the $(100)$ faces, in the following pairs of mutually perpendicular directions have been established: $<100>$, $<150>$; $<110>$, $<1\bar{1}0>$; $<3\bar{1}0>$, $<120>$. All these alignments may be satisfactorily interpreted in terms of the three kinds of dislocations – including the unexpected $\{2\bar{1}\bar{1}\}$ $[0\bar{1}1]$ type – identified in the calcite structure. $NaNO_3$ and calcite are therefore very similar in their dislocation behaviour.

To assess the influence of the comparatively mild solid-state transformation on the dislocation content, it was necessary to use crystals grown from aqueous solution at temperatures

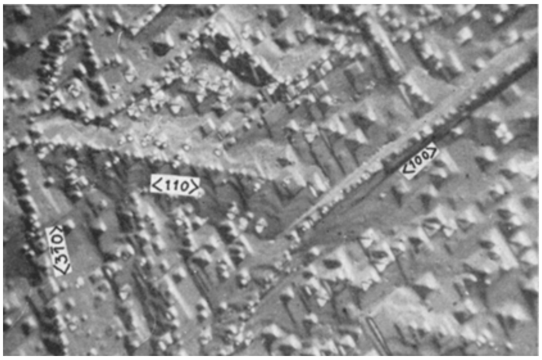


*Figure 1* Optical micrograph of melt-grown $NaNO_3$ single crystal after etching with acetic acid (×328). Dislocation etch pits on {100} face are aligned along <3$\bar{1}$0>, <110>, and <100> directions.

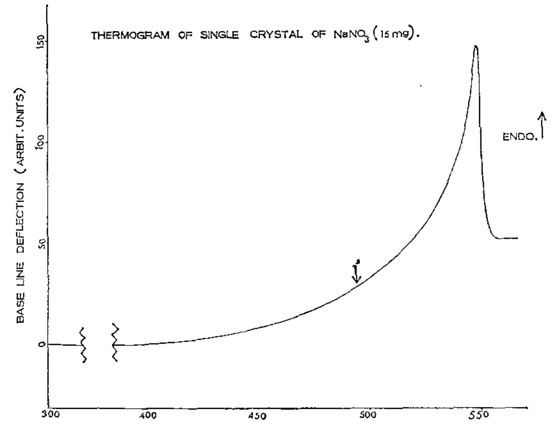


*Figure 2* Thermogram of single crystal of $NaNO_3$ over the λ-transition.

far below the onset of the λ-transition. Such crystals were found to contain relatively few dislocations ($10^4/cm^2$). The detailed course of their thermal transformation was followed accurately using a differential scanning calorimeter (Perkin-Elmer DSC-1) (see fig. 2).

Dislocation multiplication occurs as soon as the λ-transition commences (figs. 3a and 3b), there being a marked tendency for helical dislocations (see fig. 4), and dislocation loops lying on {100} planes, to be introduced to the lattice. We have found no evidence to suggest that any of the above-mentioned types of dislocations originally present in the lattice at the lower temperatures remain locked in the lattice during a single thermal excursion to beyond the λ-transition. However, twin bands, which, by analogy with calcite, involve twin gliding on {110} planes in the [001] directions, do tend

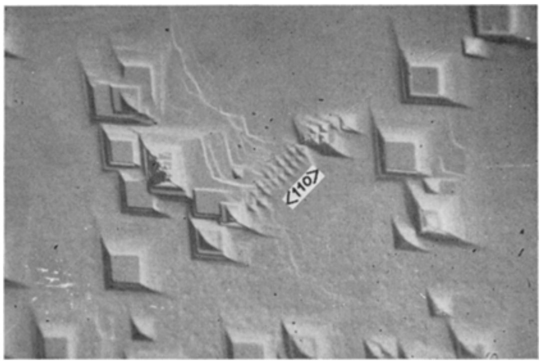
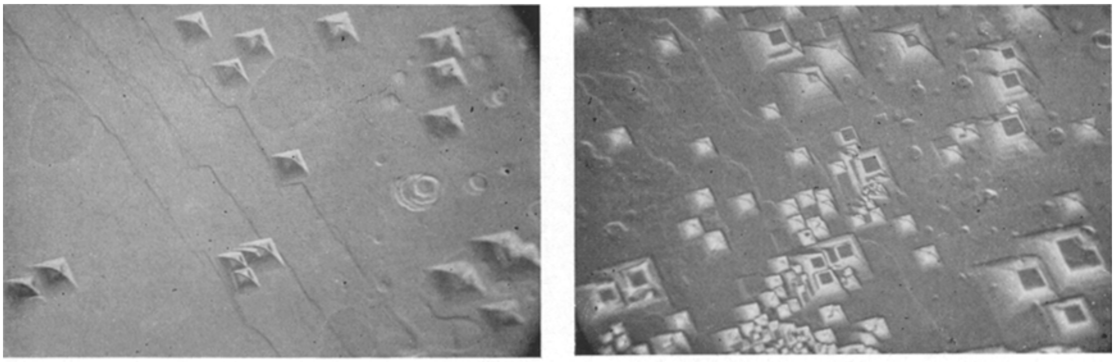


*Figure 4* Micrograph showing sequence of half-loops arising from a helical dislocation which, along its length, intersects the {100} surface (×263).



(a)

(b)

*Figure 3* (a) Micrograph of solution-grown $NaNO_3$ showing a few dislocation etch pits and surface steps (×175). (b) Micrograph of same region after crystal had been taken to the point P (fig. 2), slowly cooled and re-etched (×175). Note appearance of new dislocations and movement of original ones (as evidenced by flat-bottomed pits).

to remain locked in the $NaNO_3$ during thermal cycling. Other solids which undergo reversible thermal transformations (e.g. quartz [11] at 575° C) would be expected to behave in a manner similar to $NaNO_3$.

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## *The Number of Components Required in a Composite Material*

One of the aims of research in composite materials is to reduce or eliminate the empirical approach, in order to design a composite material, the physical properties of which have been specified in advance, from a knowledge of the physical properties of available individual components; for example, to specify values for properties such as specific gravity, moduli of elasticity, and thermal conductivity in the final composite, and to calculate how these may be obtained by combining individual components, and what will be the effect of the geometrical arrangement of the latter upon these properties. The question to which we direct our attention is: what is the minimum number of components required to achieve the desired result?

This question is only concerned with "relevant" physical properties. This distinction between "relevant" and "irrelevant" physical properties in a given application is of great importance in materials science. It is obvious that, under any given circumstances, certain properties are relevant and the remainder irrelevant. Thus, in a milk bottle, certain mechanical properties like impact strength are important in use, whilst others such as dielectric constant are unimportant. It follows that, in the selection of materials for the design of composites, attention need only be focused on a relatively small number of properties.

We define a composite material as a solid which is made by physically combining two or more existing materials to produce a multiphase system with different physical properties from the starting materials. A chemical reaction may occur during or after the process of manufacture, so that in certain cases a phase in a composite material may differ from the starting material (for example, the rubber phase in high impact polystyrene has different mechanical properties from the original rubber; another example is the matrix in concrete). However, this point is not central to the argument, since we are concerned with the finished composite and hence the relationship between: (i) the physical properties of the finished composite; (ii) the geometrical structure of the composite; and (iii) the physical properties of the constituent phases. For the purpose of this discussion, the individual phases are assumed to be uniform and isotropic.

We wish to deal with the problem: if it is desired to specify $n$ properties in a composite material (this will usually be a small number – say $<6$), how many single materials or components are required to attain the desired result? (This is an idealised form of the problem, since it states that a given property in the composite should have a specific value; for example, a Young's modulus $E$ of 100 000 lbf/in.$^2$ (1 lbf/in.$^2$ = $7 \times 10^4$ dyn/cm$^2$). In practice, a range of 100 000 to 120 000 lbf/in.$^2$ may be satisfactory, or $E$ should be $>100\,000$ lbf/in$^2$.)