

TABLE I [3]

Material	Carbon content		Density (% theoretical)	T_c (° K) [2]
	(wt %)	(at. %)		
NbC, as-received	10.00	46.2	91.5	7
NbC, annealed	10.90	48.6	92.5	11
TaC, as-received	6.28	50.1	83.8	10
TaC, annealed	6.50	51.1	89.3	10

rapidly penetrating across these non-superconducting regions. The annealing treatment removes these inhomogeneities and the annealed specimen does not show flux jumps. It is concluded from these results that niobium and tantalum carbides are type-II superconductors, whose critical temperature, upper critical field, and degree of irreversibility are strongly affected by carbon content and microstructure.

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References

1. B. W. ROBERTS, *Progress in Cryogenics* 4 (1964) 159.
2. A. L. GIORGI, E. G. SZKLARZ, E. K. STORMS, A. L. BOWMAN, and B. T. MATTHIAS, *Phys. Rev.* **125** (1962) 837.
3. D. J. ROWCLIFFE, (Lockheed Missile and Space Corp, Palo Alto, California), private communication.
4. A. V. NARLIKAR and D. DEW-HUGHES, *J. Matls. Sci.* **1** (1966) 317.
5. D. DEW-HUGHES, *Matls. Sci. and Eng.* **1** (1966) 2.
6. A. M. CAMPBELL, Ph.D. thesis, Cambridge (1966).
7. J. E. EVETTS, Ph.D. thesis, Cambridge (1966).

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A. V. NARLIKAR
D. DEW-HUGHES
Department of Physics
The University
Lancaster, UK

The Vertical Pulling of $MgAl_2O_4$ Single Crystals

This note describes a technique which allows single crystals of spinel, $MgAl_2O_4$ (melting point 2105°C), to be pulled from the melt, and such a crystal is shown in fig. 1. This is the first reported growth of spinel using this method. Hitherto, it has been grown by either flux or flame-fusion methods.

The main difficulties in growing high-melting-point oxides such as spinel by the vertical-pulling technique arise because iridium, which is the only suitable crucible material chemically compatible with the molten oxide, has a melting point (2410°C) only slightly higher than the oxide itself. Because of the insulating nature of oxide melts, the crucible wall must be at a considerably higher temperature than 2105°C in order to keep the material molten in the

crucible centre. As a consequence, the iridium is at a temperature approaching its own melting point, and any inhomogeneity in the crucible, such as a deviation in wall thickness or an impurity inclusion, leads to localised overheating and catastrophic failure of the crucible. In the present work, these difficulties have been overcome by using a crucible with a wall thickness of 0.125 in. (1.0 in. = 25.4 mm), twice the thickness used in the growth of sapphire [1], and by placing an iridium disc above the crucible as near to the melt surface as possible. Although a small viewing slot is necessary in the disc for the operator to see the growing crystal, this latter measure considerably reduces the radial temperature gradients.

The general arrangement of the crystal-growing apparatus is similar to that used already for sapphire [1], but, as it is the detailed changes made during the present work which

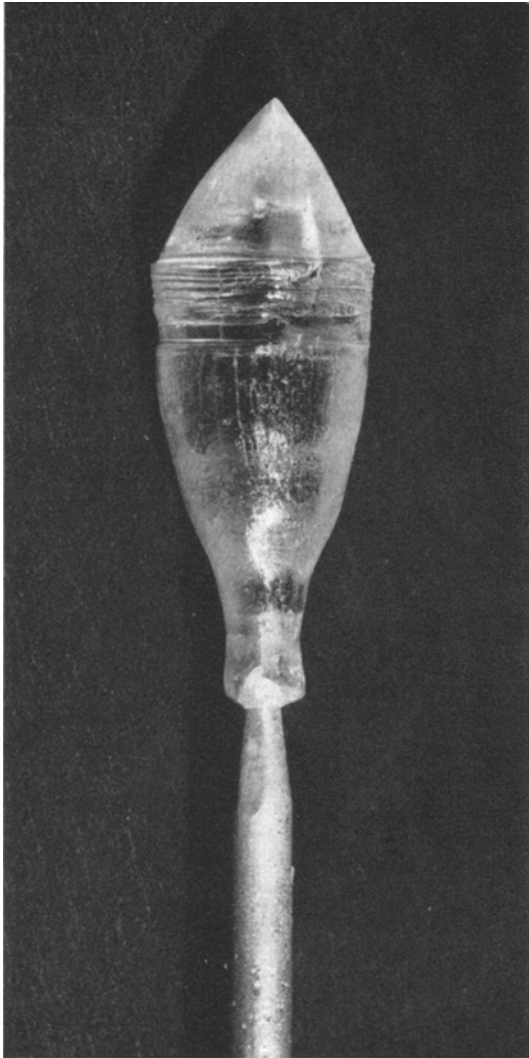


Figure 1 $MgAl_2O_4$ single crystal ($2\frac{1}{2}$ cm long \times 1 cm diameter) grown onto the end of an iridium rod.

allow spinel to be grown by the pulling technique, the essential features of the apparatus are shown in fig. 2.

The spinel melt was prepared from the component oxides MgO and Al_2O_3 which were supplied as high-purity powders by BDH Ltd*. Polycrystalline growth was initiated on the end of a pointed iridium rod, and single-crystal growth was achieved in the normal manner by reducing the crystal diameter. Attempts to seed onto flame-fusion crystals were unsuccessful, as these are generally non-stoichiometric and have a

*British Drug Houses Ltd, Poole, Dorset, UK

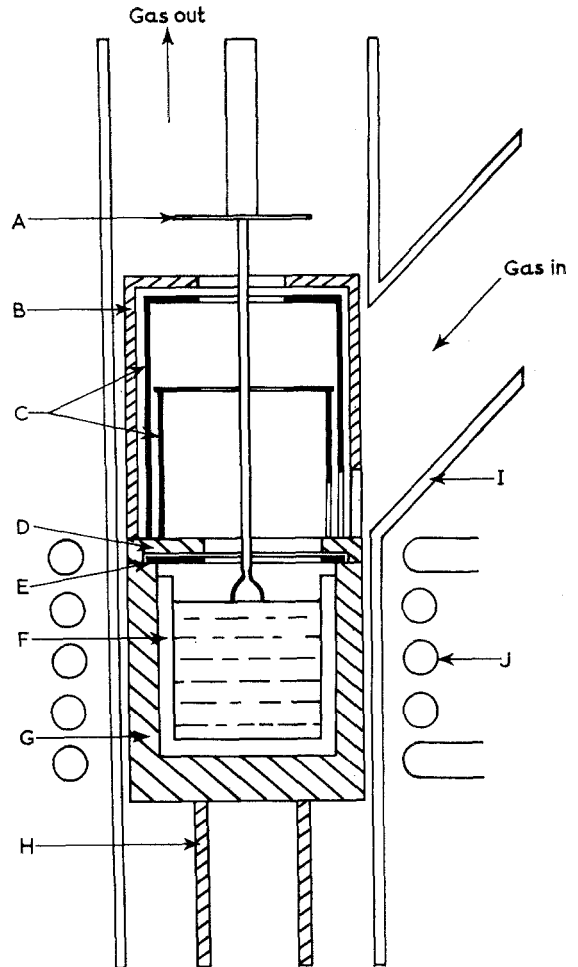


Figure 2 Vertical-pulling apparatus used for spinel single-crystal growth: A, Pt/20% Rh heat shield; B, alumina jacket; C, iridium liners; D, magnesia spacer; E, iridium annulus; F, iridium crucible; G, magnesia jacket; H, alumina pedestal; I, silica envelope; J, rf coil.

melting point below $2105^\circ C$. As a consequence, such seeds melt before they can be inserted into the molten spinel.

The present crystals were grown in an atmosphere of nitrogen containing 0.5 vol % oxygen and flowing at a rate of $300\text{ cm}^3/\text{min}$. Respective pull and rotation rates of 6 mm/h and 50 rev/min were found to yield transparent crystals.

The crystals develop facets on the central region of the growing interface, similar to those already reported in yttrium aluminium garnet [2]. The crystals also exhibit surface roughness, similar to that observed on sapphire grown in pure nitrogen, and which was shown to be due to oxygen deficiency [3].

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References

1. B. COCKAYNE, M. CHESSWAS, and D. B. GASSON, *J. Matls. Sci.* 2 (1967) 7.
2. W. BARDSLEY and B. COCKAYNE, "Crystal Growth", Proceedings of International Conference on Crystal Growth, Boston, 1966 (Pergamon Press, 1967), p. 109.

3. M. CHESSWAS and B. COCKAYNE, unpublished work.

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B. COCKAYNE
M. CHESSWAS
Royal Radar Establishment
Malvern, Worcs, UK

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 $a_0 = 6.325 \text{ \AA}$ and $\alpha = 47^\circ 16'$, and for CaCO_3 , $a_0 = 6.361 \text{ \AA}$ and $\alpha = 46^\circ 6'$.) 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, α and β , 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: $\langle 100 \rangle$, $\langle 150 \rangle$; $\langle 110 \rangle$, $\langle 1\bar{1}0 \rangle$; $\langle 3\bar{1}0 \rangle$, $\langle 120 \rangle$. 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