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Polytypism in SiC crystals.

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An explanation of the complex polytypism in SiC crystals was recently advanced by Frank (1951), who pointed out that the existence of different structures might be due to the creation of identity periods by screw dislocations during growth. This idea was confirmed by growth spirals observed on the (0001) crystal faces of SiC by Verma (1951) and others. There are reasons which prove that, in spite of these experimental results, Frank's idea does not give the correct explanation of the observed polytypism.

X-ray photographs of SiC crystals often show the features of one-dimensional disorder (Jagodzinski, 1949 *a*, *b*, *c*). This type of disorder may be caused by edge dislocations, extending in the (0001) plane of the crystal and producing a displacement of the SiC layer into another possible position (A, B, C). The strength of such dislocations is a fraction of the unit-cell length, or a multiple of it ($\frac{1}{3}$, $\frac{2}{3}$ or $\frac{2}{3}$, $\frac{1}{3}$). Obviously, the work done to generate a screw dislocation is much larger than that to form an edge dislocation. Therefore it cannot be understood why edge dislocations should not occur in SiC crystals and destroy the order produced by the winding up growth spiral. On the other hand the plate-like habit of SiC crystals shows that the faces (0001) are not those of maximal growth, excepting, perhaps, in the last stage of crystal growth.

A total of 150 SiC crystals, randomly chosen with respect to crystallographic properties, were investigated by X-ray methods; of these crystals 62 belonged to the one-dimensionally disordered type. A special method was developed for evaluating the degree of disorder α ($\alpha = N_d/N$, N_d being the number of displaced SiC layers with respect to the special order achieved in the crystal, and N the total number of layers). The probability distribution of the average faults in all crystals shows two maxima, one at $\alpha = 0$ (completely ordered crystals), the second at $\alpha = 0{\cdot}12$ (partially disordered crystals). This complex behaviour may be explained by introducing the vibration entropy. A qualitative estimate gives largest values for it in ordered states, which have a low identity period. Disordered states will in all cases have a lower vibration entropy. Thus ordered states are favoured by vibration entropy, but disfavoured by configuration entropy. In this way the two maxima described above may occur, the first being caused by vibration entropy, the second by configuration entropy. No full account of this assumption will be given here, but it becomes clear that order in SiC crystals is merely stabilized by vibration entropy, and the long-range order commonly observed is understandable.

We can advance the explanation of the complexity of SiC structures by assuming (see Frank, 1951) that the cubic modification is the stable one. This idea is supported by the observation that a great deal of normally synthesized SiC belongs to the cubic structure (Ott, 1926), but it is generally so finely grained that it may easily be overlooked if investigated by single-crystal photographs. It may therefore be concluded that growth hindrance will prevent these cubic crystals from growing. The crystal faces of least energy in the cubic structure are the two tetrahedra (111) and $(\bar{1}\bar{1}\bar{1})$, where one (of four) covalent bond is directed into the open space. As these faces form a closed body, crystal growth will stop at a fairly high supersaturation. If any displacement is created by an edge dislocation, only two faces (e.g. 111 and $\bar{1}\bar{1}\bar{1}$) will preserve their stability—all others will be 'stepped'; that means that growth is favoured on these faces. Thus the crystals will become plate-like, especially if a fair number of displacements is present. In the cubic structure two SiC layers have to be displaced in order to obey the general law of close packing. It is quite clear that a number of stacking faults have to cooperate to lower the energy required for forming a critical two-dimensional nucleus. Vibration entropy causes the ordering effect of stacking faults. In this way the most probable structures may be derived easily from the ordered cubic structure. They are (the marked positions indicate the displacements):

$$\begin{matrix}A\,B\,C\\A\,B\,C\end{matrix}\boxed{\begin{matrix}A\,B\\B\,A\end{matrix}}\begin{matrix}C\,A\,B\\C\,A\,B\end{matrix}\boxed{\begin{matrix}C\,A\\A\,C\end{matrix}}\begin{matrix}B\,C\,A\\B\,C\,A\end{matrix}\boxed{\begin{matrix}B\,C\\C\,B\end{matrix}}\quad\begin{matrix}k\\hkkhk^*\end{matrix}\quad(15\text{ layers})$$

$$\begin{matrix}A\,B\,C\,A\\A\,B\,C\,A\end{matrix}\boxed{\begin{matrix}B\,C\\C\,B\end{matrix}}\begin{matrix}A\,B\,C\,A\\A\,B\,C\,A\end{matrix}\boxed{\begin{matrix}B\,C\\C\,B\end{matrix}}\qquad\begin{matrix}k\\hkk\end{matrix}\qquad(6\text{ layers})$$

All other actually observed structures may be derived in a similar way. It must be stressed that the observed types of SiC are ordered states favoured by crystal growth, rather than structures of genuine thermodynamical stability (the cubic modification excepted).

A full account of this study, including its theoretical foundation, will be published in *Neues Jahrbuch für Mineralogie.*

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* As Zhdanow symbols are not suited for describing disorder phenomena, we use the symbols introduced by Wyckoff (1948) and the author (Jagodzinski, 1949*a*, *b*, *c*).