The Hall constant, measured at room temperature in 6400 Oe magnetic fields had a value of only 5×10^{-4} cm^3 C^{-1}.

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Martensitic or deformational transformations and molecular crystals

Studies of structure-transformations in crystals containing more than 8 atoms per unit cell suggest that the displacements possible in martensitic transformations should be further examined. It has been claimed that lattice deformations need not be considered for molecular crystals and that a similar view can probably be taken of other crystals [1, 2]: in mineralogy the aragonite-calcite transformation, in which the oxygen atoms which are components of an anion must be disengaged from their cation co-ordination, has been taken as a typical example of a reconstructive transformation [3]. General theory of lattice deformations is available [4]. In compounds, however, it is not always obvious whether the atomic displacements occurring during the proposed lattice deformation will allow the lattice correspondence to be maintained.

The term martensitic in this note implies that during the appropriate deformation which interconverts the lattices the structural units fall into their sites in the new cell through consequential displacements which do not require any units to exchange neighbours (even by passage of rows of atoms over one another by partial dislocations); and that the resulting misregistry between the lattices, unless zero, is accommodated by dislocations or by transformation twinning. More generally the structural relationship and the corresponding mechanism can be described as "deformational". Except in stress induced transformations in polymers [5] the structural units considered have been atoms or diatomic molecules [6] or simple ions [7]. The structures can then snap over into the new configuration in unconstrained regions.

A deformational relationship is evidently maintained in the transformation in the molecular crystal of *p*-di-iodobenzene. It is not a continuous order-disorder change since there is a discontinuous change of lattice parameter (about 1 %) and of birefringence, accompanied by marked superheating and supercooling, yet growth is not random, since a reproducible orientation relation was shown by the optical extinction direction [8]. Here the lattice deformation is small.

In general, molecules pack densely with the humps (atoms) of one fitting the hollows of a neighbour [9] unless held in a less dense configuration by directional interactions such as hydrogen bonding. In inorganic crystals modification of such directional interactions by thermal motion commonly results in transformation accompanied by lattice deformation: in crystals of near-planar molecules it may permit some relative displacement of molecules. Similarly when increasing oscillation of molecules would bring side-groups of neighbours into too close proximity some relative displacement of the molecules may result. Again when a particular polymorph does not correspond to the hump-hollow combination of lowest free energy, an increase in thermal motion of the whole molecule within these crystals of rather low lattice energy may permit relative translation to another hump-hollow combination. Such translation involves a shift of the atoms of each molecule past or around atoms of adjacent molecules. Thus atom neighbours are exchanged but not structural units, which are the molecules. This is, nevertheless, an activated process.

Such an activated process in a martensitic transformation has been shown in rubidium nitrate [10]. Transformation from the calcite-related [11] form II in which the flat NO_3^- ions are co-planar to the cubic NaCl-related form I requires the anions to tilt and the oxygen atoms to be disengaged by thermal motion from their co-ordination by cations Yet this transformation

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is martensitic for it shows a clear and reproducible shape-change and interface (with lamellar twinning in the reverse change), maintains an orientation relation and can occur suddenly in small crystals Detailed results will be reported later. In the calcite-like structure the disengagement of the oxygen atoms is a reconstructive component of the total mechanism, and is activated, as is required for the change of hump-hollow combination in molecular crystals.

On the other hand, interconversion of the polymorphs of some molecular crystals would require the molecules to move completely past one another. This is true of *p*-dichlorobenzene [12] which provided the most extensive evidence for reconstructive growth [2, 13]. In general even if points representing the centres of molecules could be taken to their new sites without interchange, the thermal motion needed to slide the interlocking molecules over one another, usually with tilting, would also permit motion in the interface. This motion could wipe out the energy-absorbing dislocation and twinning processes at an interface, rendering the martensitic mechanism irrelevant. Intermolecular attractions would still operate across the interface and expedite transformation. Use of measurements of kinetics to support a specific mechanism such as ledge growth, however, requires detailed agreement between theory and experiment, because any mechanism involving a driving force and an activation energy will produce a peak in the graph of rate versus temperature [14].

Williams has reported a deformational transformation in 1,8 dichloro-10-methyl-anthracene [15], an example of a large molecule with side groups. The structure is already densely packed [16]. Displacements of less than molecular dimensions are to be expected. The further work on this [17] should help to clarify the conditions for deformational transformations.

It appears that the arguments of Mnykh and Panfilova [2] especially as illustrated by their models, apply to transformations involving either interchange of molecules, or large variations of the co-ordination of molecules by molecules. The present arguments suggest that deformational transformations in crystals of rather large molecules will involve displacements (possibly associated with tilts) which are appreciably less than molecular dimensions.

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