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The Dislocation Arrangement in α -Oxalic Acid Dihydrate

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Crystals of α -oxalic acid dihydrate have been examined by Lang topography. Both edge and screw dislocations are found with Burgers vectors parallel to the b axis. The dislocation density varies from zero to 10^4 lines cm^{-2} and the apparent mosaic spread varies between 10 and 50 seconds of arc. The implications of these observations for accurate structure factor determinations in molecular crystals are discussed.

Introduction

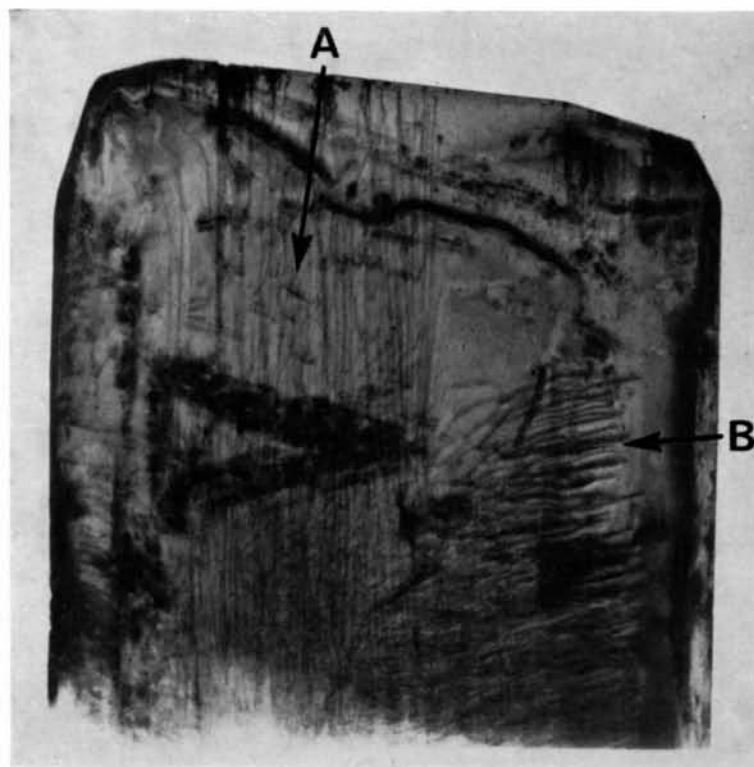
Recent crystal structure investigations with X-rays and neutrons (Coppens, 1967; Sabine, Cox & Craven, 1969; Coppens & Sabine, 1969; Delaplane & Ibers, 1969) have had as their objective the determination of physically meaningful thermal parameters from which a determination of the asphericity of electron distribution around an atom in a crystal may be obtained. Since the calculations of X-ray structure factors are carried out for spherical atoms, and since the asphericity results from a distortion of the electron distribution along a chemical bond, the apparent X-ray temperature factor is increased. Inversion of the difference between neutron and X-ray thermal parameters enables the component of displacement of the electron density to be derived.

One of the major obstacles to the accurate determination of structure factors is extinction. Zachariasen (1967) has used a model of a real crystal as one which

consists of an aggregation of perfect crystal domains separated by boundaries which interrupt the periodicity and he distinguishes between two types of crystal. In Type I the secondary extinction is controlled by the mosaic spread parameter, that is, the degree of misorientation of these domains; in Type II crystals the secondary extinction is controlled by the size of the domains. He assumes that in most real crystals this size is less than 10^{-4} cm so that primary extinction can be neglected.

Coppens & Hamilton (1969) have used a tensor form of Zachariasen's equations and from a least-squares analysis of the measured intensities have shown that extinction can be characterized by anisotropic parameters which have the physical meaning of mosaic block size and angular spread.

It is the purpose of the present work to determine, by direct observation, the arrangement of dislocations in oxalic acid dihydrate and to ascertain whether these defects provide a physical explanation for the extinc-



(a)



(b)

Fig. 1. X-ray topographs of an oxalic acid dihydrate single crystal. $\text{Cu } K\alpha_1$ radiation ($\times 40$). (a) 011 reflexion; (b) $\bar{1}0\bar{3}$ reflexion.



Fig. 2. X-ray topograph of an oxalic acid dihydrate single crystal showing groups of straight dislocations arranged in sheet-like arrays. Cu $K\alpha_1$ radiation ($\times 100$).

tion parameters found from analysis of diffraction data (Coppens & Sabine, 1969).

Experimental

Crystals of oxalic acid (May and Baker, 99.5%) were grown on the walls of large cylindrical glass tubes from saturated solutions of two parts acetone to one part water, by volume. The tubes of solution were maintained at a constant temperature of 35°C and many small crystals nucleated and grew over a period of several days. When the crystals were a few millimetres long, they were carefully removed and placed on filter papers to dry. Slab-like crystals, which appeared clear and free of surface irregularities, were selected from these, mounted with polyester resin on the ends of pointed wires and sealed from the air by enclosing them in small gelatin pill capsules.

The crystals were examined by X-ray topography using the Lang (1959) method. The Burgers vectors of the observed dislocations were obtained by studying the contrast of dislocations in topographs made with reflexions from various planes (Jenkinson & Lang, 1962).

A double crystal spectrometer ($n, -m$ mode) (Compton & Allison, 1935) was used to determine the rocking curves in transmission for some crystals, the primary crystal being a (111) slice of silicon of low dislocation density in reflexion.

Results

The faces of all crystals examined were (001), ($\bar{1}01$) or (101) with [010] along the major axis of the crystal.

The topograph shown in Fig. 1(a) is typical of those obtained from the large number of crystals which were examined. The observed dislocations may be divided into two groups. Those in group *A* lie generally parallel to [010] whereas those of group *B* are almost normal to [010]. In the topograph, Fig. 1(b), made from the $\bar{1}0\bar{3}$ reflexion and in fact for all topographs made with reflexions from planes lying in the [010] zone, these dislocations are all invisible. Other features which are present in both topographs can be associated with artefacts visible in the optical microscope. Thus the Burgers vectors of both groups of dislocations are parallel to [010] and dislocations in group *A* are essentially screw whilst those of group *B* are primarily edge. No dislocations were observed with Burgers vectors non-parallel to [010].

Examination of stereo pairs of topographs reveals that in some cases groups of dislocations appear to be straight and arranged in sheet-like arrays. An example is shown in Fig. 2.

Rocking curves were made on some crystals for the 001, 103, 110 and 011 reflexions with Cu $K\alpha_1$ radiation, with the use of the 111 reflexion from the silicon reference specimen.

In regions near the edges of the crystals where the dislocation density was very low or zero, the breadths

of the rocking curves at half peak intensity were about 10 seconds. In regions away from the edge where the dislocation density was still low, the half breadths increased to about 15 seconds, but in some regions where the dislocation density was 10^3 – 10^4 lines cm^{-2} , half breadths of up to 50 seconds were recorded. The silicon crystal was of commercial semiconductor quality and its contribution to the rocking curve width was probably of the order of 7–8 seconds (Bubakova, Draho-koupil & Fingerland, 1962).

By accurately traversing the crystal across the incident beam the positions of the peaks of the rocking curves were determined and in many regions of the crystal found to remain constant to within ± 1 second over distances of 1 mm.

Discussion

The lines visible in Fig. 1 may not be images of single dislocations since with the resolving power of the topograph technique each dislocation gives an image with a minimum width of 1–10 microns. However, it is unlikely that, as well as the observed dislocations, there is within the crystal a superimposed dislocation array of too high a density to be resolved by the present technique, since interaction between the two systems of dislocations would almost certainly occur and no such interactions are observed. The visible dislocations are unusually straight and show no tangles or networks similar to those visible in metals. The Pendellösung fringes clearly visible in both Figs. 1 and 2 are a consequence of dynamic diffraction effects and will only occur in a highly perfect crystal. Furthermore, the widths of the rocking curves and the constancy of the angular position of their peak heights as the crystal is traversed through the beam are consistent with the behaviour of a crystal with a low dislocation content. Thus these results, which are typical for some fifty crystals examined, indicate that oxalic acid dihydrate crystals grown under conditions similar to those used for structure determinations, have a low but variable dislocation content. Some regions appear perfect over distances of about 1 mm whilst in other regions the dislocation density is 10^3 – 10^4 lines cm^{-2} . Similar low densities in molecular crystals have been observed by Michell, Robinson & Smith (1968) in anthracene and by Belt (1964) in ammonium dihydrogen phosphate.

The Burgers vectors of all dislocations observed were parallel to the *b* axis and consequently the displacement of atoms from their lattice positions is a maximum in this direction and a minimum in directions normal to the *b* axis. Thus it is to be expected that extinction will be anisotropic in oxalic acid dihydrate since the perfection of the crystal to X-rays will be a function of orientation. This is consistent with the work of Sabine, Cox & Craven (1969) who observed anisotropic extinction in α -oxalic acid dihydrate and suggested that the layers of atoms appeared rumped in the *ac* plane but showed little rotation about the *b* axis.

It is well known that sub-boundaries in metals are formed from dislocation arrays. It is likely that similar boundaries in molecular crystals are also arrays of dislocations although other defects such as vacancies, interstitial atoms and stacking faults may have some influence on the size of the blocks (Hirsch, 1956).

Coppens & Sabine (1969) have used the tensor formulation of the Zachariasen formulae (Coppens & Hamilton, 1969) to analyse neutron diffraction data from oxalic acid crystals grown under similar conditions to those here. In that analysis the average block size was found to be 10^{-4} cm. If these domains are to be attributed to dislocations, a density of at least 10^8 lines cm^{-2} would be required. The present results indicate that these densities do not seem reasonable even for the most imperfect regions of the crystals. Furthermore, most crystals have relatively large regions free of dislocations. Although these crystals are not those used for the X-ray and neutron structure analyses, it is unlikely that the dislocation densities differ significantly since both sets of crystals were prepared in a similar way.

Thus there is a real discrepancy between the results of Coppens & Sabine and the defects revealed in topographs made by the Lang method. It appears that the application of Zachariasen's treatment to crystals containing this type of perfection will yield parameters which are physically unrealistic. Additional work is required to establish the relationship between defects and extinction with a view to enabling corrections to be applied which are directly related to the physical state of the crystal.

Note added in proof: – Ikeno, Maruyama & Kato (1968) have suggested that the low dislocation densities observed by them in crystals of sodium chloride grown from aqueous solutions are characteristic of the growth method. They have also pointed out that sodium chloride is usually assumed to have an ideal mosaic structure and that this is not consistent with their results.

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Die Kristallstruktur des Dimethylnitrosaminkupfer(II)-chlorids, $(\text{CH}_3)_2\text{NNO}\cdot\text{CuCl}_2$

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The structure of dimethylnitrosamine copper(II) chloride, $(\text{CH}_3)_2\text{NNO}\cdot\text{CuCl}_2$, has been determined from three-dimensional X-ray data using Patterson and difference Fourier syntheses. Full-matrix least-squares refinement resulted in $R=11.8\%$. 4 formula units are contained in the orthorhombic cell (space group $Pnam$) with $a=6.376$, $b=14.685$, $c=7.265$ Å. All atoms except Cl are situated in the mirror plane $xy\frac{1}{2}$. The structure consists of slightly folded CuCl_2 chains parallel to [100]. The Cl surround the Cu in an almost perfect square ($\text{Cu}-\text{Cl}$ 2.295 Å). Perpendicular to the Cl plane two adjacent Cu in the chain are connected by the O and the nitroso N of one dimethylnitrosamine alternating on both sides of the CuCl_2 chain. The Cu is surrounded by a distorted tetragonal bipyramid of 4 Cl, 1 O, and 1 N ($\text{Cu}-\text{O}$ 2.29, $\text{Cu}-\text{N}$ 3.02 Å).

Einleitung

Nitrosamine bilden mit den Halogeniden der Metalle und Nichtmetalle Additionsverbindungen $\text{Hal}\cdot\text{R}_2\text{N}_2\text{O}$ und $\text{Hal}\cdot(\text{R}_2\text{N}_2\text{O})_2$. Da beim Nitrosamin-Molekül alle Atome seines Grundgerüsts Koordinationsbindungen ausbilden können, sind schon mehrere Versuche un-

ternommen worden, die Koordinationsstellen zu suchen.

Bei den Nichtmetallhalogeniden wurde eine Koordination am Aminstickstoff angenommen (Goubeau, 1961), aber spätere Protonenresonanzmessungen sprechen für eine Bindung über den Sauerstoff (Schmidpeter, 1963; Brown & Coates 1962).