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Dissociated 'a' dislocations in quartz*

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We have fully characterized by TEM the dislocations left by low temperature deformation in quartz. They are a dislocations in the basal plane with a strong preferential orientation at 60° to the Bürgers vector. Weak beam observations reveal that these dislocations are dissociated; the width of the ribbon increases under beam irradiation and reaches an equilibrium value of 250 Å. Comparisons with twins in conjunction with crystallographic and physical considerations enable a dissociation model to be proposed in terms of zonal dislocations. A slight modification to the Griggs model of hydrolytic weakening of quartz is put forward.

1. Introduction

SiO_2 quartz has a three-dimensional framework of SiO_4 tetrahedra [1]. The creation and the glide motion of dislocations in this crystal requires the breaking of the strong, partially covalent Si–O bonds and should be very difficult. Indeed, the strength of pure quartz (i.e. without dissolved water) deformed at $T < 500°$ C approaches the theoretical value. In contrast, plastic deformation becomes possible when traces of water are present in the crystal, producing the so called "hydrolytic weakening" of quartz which has been attributed to the enhanced mobility of dislocations by hydrolysis of the Si–O bonds [2, 3]. Dislocation glide (or rather climb according to [4]) would thus be partly controlled by the mobility of water molecules in the vicinity of the dislocation cores.

It has been shown by examination of the slip lines that only basal slip $(0001)\langle 11\bar{2}0\rangle$ can be activated at low temperatures, while at higher temperatures prismatic slip and perhaps low index pyramidal slip also become important. The dividing line between "low" and "high" temperature seems to be dependent on the concentration of water and on the strain-rate.

Baëta and Ashbee [5, 6] were able to deform quartz samples without confining pressure and they also found basal, prismatic and pyramidal slip with a marked preference for basal slip at low temperatures. It should be noted that in their experiments they were mainly concerned with β quartz. Quartz exhibits a displacive transition at $T = 573°$ C with only minor atomic movements and without any rupture of the strong Si–O bonds. The low temperature (α) phase is trigonal (space groupe $P3_121$) and the high temperature (β) phase is hexagonal ($P6_222$) with very small changes in the lattice parameters. With increasing pressure the temperature of this phase transition increases.

More than 40 possible glide systems have been proposed (see tables in recent papers [7] and [8]). Direct observations of dislocations by TEM should be helpful in ascertaining the slip systems and many studies on this field have been published (see reviews in [8], [9] and [10]). Unfortunately quartz is very sensitive to beam irradiation. Marked damage and even vitrification appears after a few minutes observation [11], which renders the complete characterization of the dislocations very difficult. However there is no problem of residual contrast due to anisotropic elasticity [12] and Bürgers vectors **a** and **c** have been identified [13, 14]. Furthermore several very clear preferential orientations have been observed [7, 15].

We have also observed preferred orientations for **a** dislocations in basal planes. Bürgers vector determination indicates that all these dislocations have a 60° character analogous to the case of dis-

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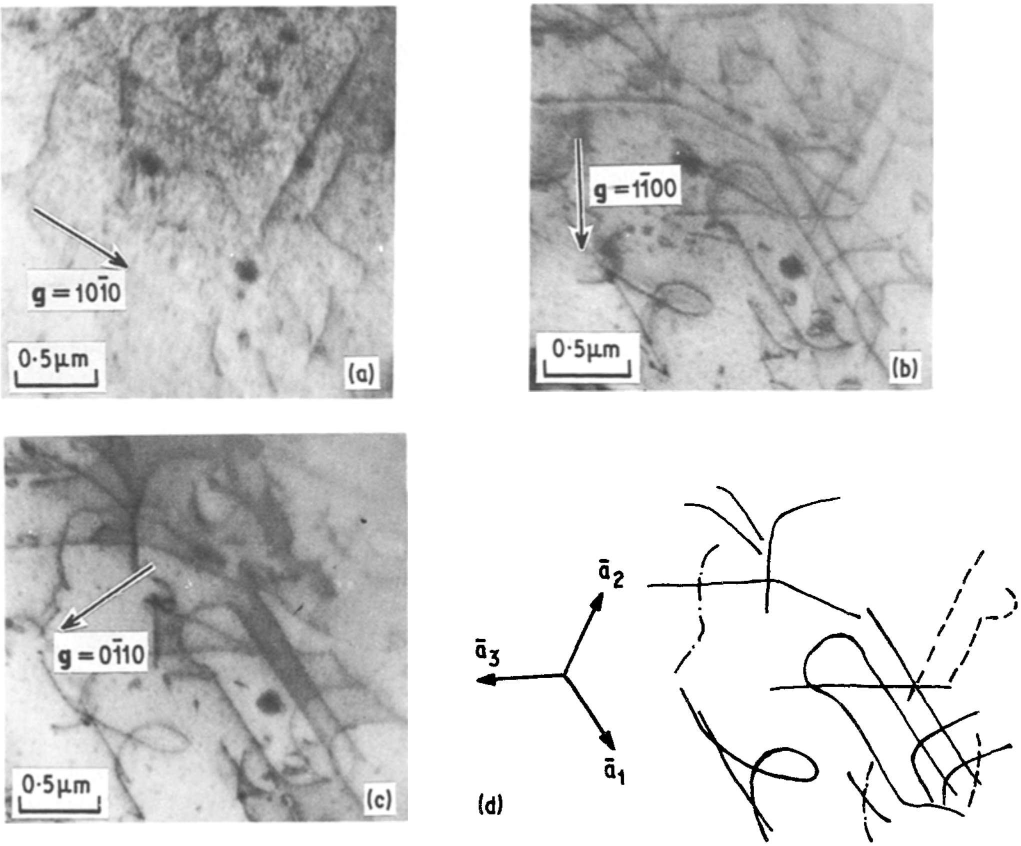

Figure 1 Micrographs of the basal lamella, (a), (b), (c), showing the three $\langle 1\,0\,\bar{1}\,0\rangle$ diffraction vectors (two beams, s large). The dislocations are unambiguously characterized (no residual contrast) as basal **a** dislocations. In (d) a diagram summarizes the various **a** Bürgers vectors: $\mathbf{a}_1$ dislocations, — —; $\mathbf{a}_2$ dislocations, ———; $\mathbf{a}_3$ dislocations, — · —.

locations in covalent diamond structures [16]. We have also been able to observe dissociations by means of weak-beam methods.

2. TEM observations

The study has been performed on a large naturally deformed single crystal. Basal thin foils were cut with a diamond saw and final thinning was achieved with an ion thinner. Samples were then observed in a 100 kV electron microscope with low intensity beam. It was possible to obtain a set of micrographs on the same area enabling the dislocations to be fully characterized, without too much irradiation damage as illustrated in Fig. 1. The configurations are characteristic of the dislocation substructure in the sample. The dislocations lie in the basal plane, with an **a** Bürgers vector and a 60° character. The density of the $\mathbf{a}_3$ dislocations is smaller than that of the $\mathbf{a}_1$ and $\mathbf{a}_2$ dislocations which have approximately the same density. The total dislocation density is of the order of $4 \times 10^8\,\mathrm{cm}^{-2}$. Twins (mainly Dauphiné type) are also observed as well as small precipitates and small bubbles which were not chemically analysed. Bubbles frequently form "negative crystals" with hexagonal shapes in the basal plane.

The preferential 60° orientation in the basal plane suggests a Peierls mechanism which could be due to dissociation. We have therefore tried to observe the fine core structure of these dislocations. It is still possible to characterize the Bürgers vectors in weak-beam conditions which roughly correspond to kinematic conditions (Fig. 2). However, except at low magnification, observations become very difficult with low beam intensity while with higher illumination irradiation damage occurs, rapidly making further observation impossible. The nature of the small defects created by irradiation has been studied by Baëta and Ashbee [11] who suggests that they are small dislocation loops in $\{1\,0\,\bar{1}\,1\}$ or $\{1\,0\,\bar{1}\,0\}$ (clusters of vacancies).

We heated the sample during the observations to enhance the rate of recombination of Frenkel pairs. We observed that below the $\alpha \rightarrow \beta$ transition

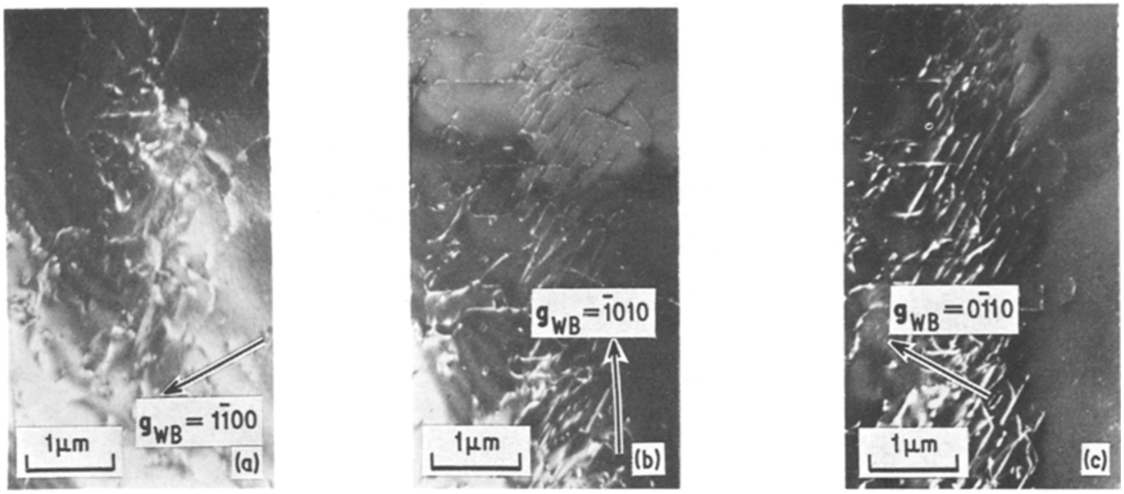

Figure 2 Basal lamella; weak beam images on the same area with the three $\langle 10\bar{1}0\rangle$ diffraction vectors. Dislocations can be characterized as straight 60° **a** dislocations with mostly $\mathbf{a}_1$ and $\mathbf{a}_2$.

temperature, the production rate of small defects was considerably reduced but the material became amorphous. This was also noted in [11]. In contrast, at $T > 573°$ C, there are neither small defects nor vitrification even for high intensity electron beams. This is a convenient observation condition, but the heating stage has only one rotation facility, and it is more difficult to reach the required diffraction conditions for weak beam images, for example.

It should be noted that dislocations are not affected when passing the transition in both senses. We also observed that dislocations become more and more widely dissociated with increasing irradiation, reaching a maximum disssociation width of the order of 250 Å. In Fig. 3, the three weak beams have been photographed at 600° C and under exactly the same diffraction conditions with a few minutes irradiation between successive images. The ribbon widens, one of the partials slowly moves towards the external surface, and gradually escapes from the foil.

A subsequent annealing without irradiation at the same temperature $T = 600°$ C does not modify the dissociation width of 250 Å which can thus be assumed to be the equilibrium distance, at least for the β quartz structure stable at this temperature. For comparison, we performed the same kind of experiments on α quartz without heating (and thus without annealing). Irradiation also increases the dissociation width and this can be imaged in weak-beam conditions because irradiation damage is less visible and does not obscure the dislocation ribbon (Fig. 4). The maximum distance between partials is again of the order of 250 to 300 Å. We also tried to evaluate the minimum dissociation width at the beginning of irradiation in α quartz as well as in β quartz. We found a value of about 60

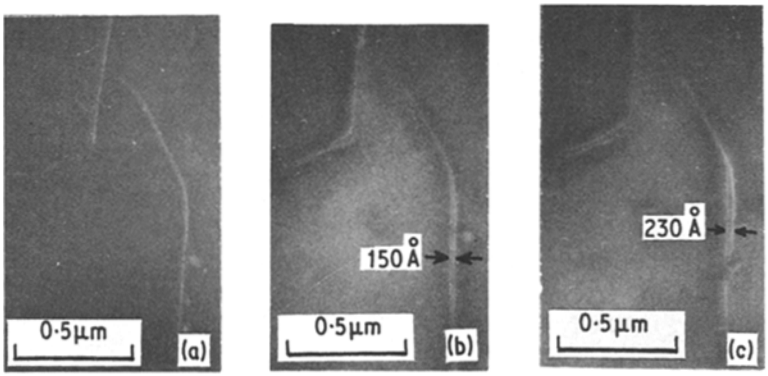

Figure 3 Basal lamella at 600° C (β quartz); series of weak-beam images on the same region for increasing irradiation. Dislocations are dissociated and the width of the ribbon increases. It can be seen that one of the partials slowly moves toward the external surface of the thin foil and partially disappears.

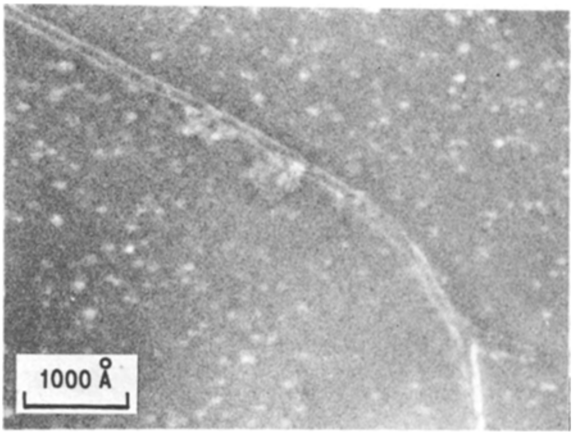

Figure 4 Weak beam image on α quartz (not heated). Irradiation has increased the dissociation width. Irradiation damage is visible but does not hide the dissociation. Note the shape of the extended node.

to 80 Å but it is not possible to be sure that there is no increase during the short time necessary to obtain the correct diffraction conditions.*

One can assume the following mechanism for the effect of electron irradiation: the **a** dislocations are dissociated but the partials cannot reach their equilibrium distance because this glide motion implies the rupture of strong Si–O bonds. Irradiation can therefore help the dislocations to dissociate by breaking these bonds. It can also produce point defects giving rise to climb motion at high temperatures, which is perhaps observed in Fig. 3c, where one of the partials moves toward the external surface. This last phenomenon has never been observed without heating. There are two simple hypotheses for the dissociation reaction of basal **a** dislocations:

(1) dissociation in two collinear partials such as $\mathbf{a} \rightarrow \alpha\mathbf{a} + (1-\alpha)\mathbf{a}$ with $0 < \alpha < 1$,

(2) dissociation in two Shockleys which gives in Miller–Bravais indices;

$$1/3[2\bar{1}\bar{1}0] \rightarrow 1/3[10\bar{1}0] + 1/3[1\bar{1}00].$$

In the latter case one can expect extended or constricted nodes at junctions of three **a** dislocations and all the partials would be visible with $\mathbf{g} = \langle 10\bar{1}0\rangle$, while one of them would be out of contrast for each of the diffraction vectors $\mathbf{g} = \langle 11\bar{2}0\rangle$. We performed weak-beam observations in both diffraction conditions without conclusive results. Nodes have a very particular shape (Fig. 4). Up until the present we could not positively identify the Bürgers vector of the partials, but geometrical and physical considerations of the nature of the fault enable us to propose an entirely different dissociation model.

3. Discussion

The crystal structure of α and β quartz are rather complicated. Fig. 5 represents a simplified drawing with only Si atoms of α quartz projected on the basal plane (0001). The strong Si–O–Si bonds are represented by straight bars. In fact these bonds, projected on (0001), are almost but not quite straight. The simplified drawing is obtained as follows: one places one Si atom in $u\mathbf{a}_1$ ($u = 0.465$ for α quartz); repeated lattice translations give all the equivalent atoms at level zero (open circles); using any of the 3_1 screw axes, one generates all the atoms at levels $c/3$ (half filled circles) and $2c/3$ (filled circles).

It is now possible to depict a perfect 60° dislocation lying in the basal plane. The configuration is best seen (Fig. 6a) in a plane perpendicular to the dislocation line i.e. in $(2\bar{1}\bar{1}0)$ for a dislocation line parallel to $[2\bar{1}\bar{1}0]$ with a Bürgers vector $1/3[1\bar{2}10]$. It can be seen that two strong bonds per a length along the dislocation line are broken; one Si valence and one SiO valence cannot be saturated if it is assumed that these bonds are strongly directed, i.e. have a strong covalent character. The atomic configuration is comparable to the case of 60° dislocations in Si or Ge [16] and the origin of the 60° preferred orientation is certainly the same in both cases. It corresponds to a minimum mobility of the dislocations because a maximum density of strong bonds has to be broken for their propagation. A high Peierls friction

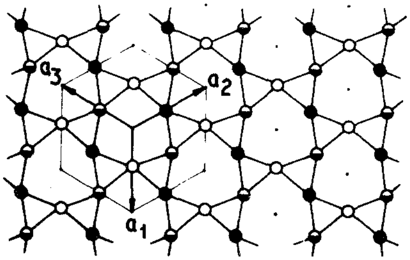

Figure 5 Simplified representation of the crystal structure of α quartz projected on the basal plane (0001). Si atoms only are noted. ○ Si atoms at level 0; ◐ Si atoms at $c/3$; ● Si atoms at $2c/3$. The strong Si–O–Si bonds are represented by bars.

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*The illuminating time of the photographic plate was systematically shortened to prevent fuzzy images due to possible motion of the partials during exposure.

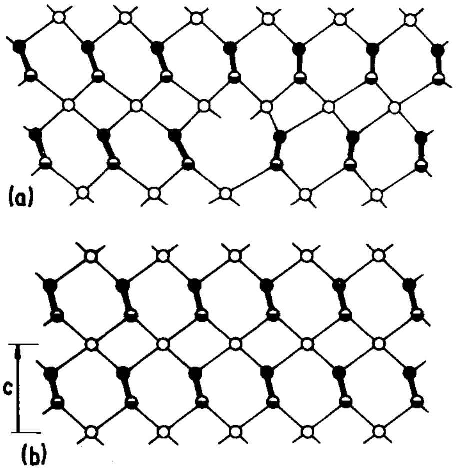

Figure 6 (a) Dislocation viewed in the $(2\bar{1}\bar{1}0)$ plane perpendicular to the dislocation line. The almost vertical thick bars represent two Si–O–Si strong bonds. The view represents a crystal layer of thickness *a*; (b) Perfect crystal, same view.

results in both cases* which is confirmed by the large decrease of the elastic limit with increasing temperature.

We also note that water molecules in the vicinity of the dislocation core would immediately saturate the free valences giving rise to two Si–OH and this would not enhance the dislocation mobility as proposed in the Griggs model [2, 3] which considers an unrealistic case with only one free valence. For a dissociated dislocation, the two free valences are far apart and the Griggs model is then valid. Such a situation is depicted in Fig. 7 for a dissociation into two collinear partials **a**/2. The corresponding fault energy is probably high because the strong bonds Si–O–Si are highly distorted. This cannot correspond to the observed large dissociation. The other simple possibility, i.e. the dissociation into two Shockleys also distorts the bonds, giving rise to a high energy fault.

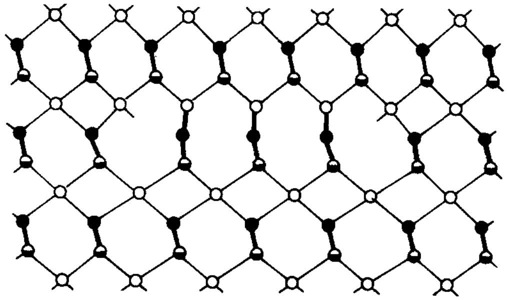

Figure 7 Dissociated 60° dislocation in two collinear partials *a*/2. Projection on $(2\bar{1}\bar{1}0)$ perpendicular to the dislocation.

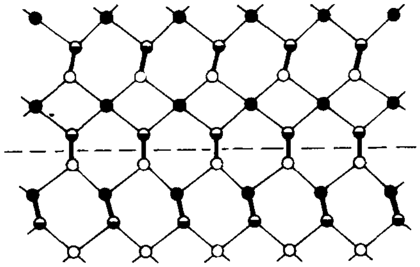

Figure 8 Brazil twin in the basal plane

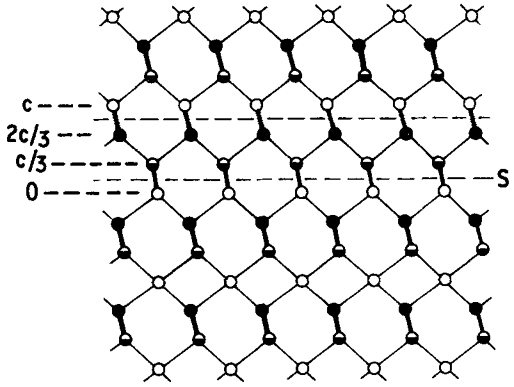

Figure 9 Model of fault which does not modify the nearest neighbours nor the length and the orientation of the bonds.

Before looking for different dissociations, it is useful to examine other well known planar defects. α quartz exhibits at least two twins which have been seen and characterized in TEM; Dauphiné twins [17] which can occur on any plane, and Brazil twins [15, 18] which generally occur on $\{10\bar{1}1\}$ but which can also occur on (0001). The Brazil twin is depicted in Fig. 8 in terms of our simplified model. It should be noted that there is a displacement vector **R** ~ **a**/2 in the boundary (**R** is exactly **a**/2 for β quartz when $u = 0.500$).

Our simplified crystallographic model for quartz is based on the assumption that Si atoms are covalently bonded by means of the oxygen

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*The two possible configurations called "glide set" and "shuffle set" in Si or Ge are not found in the case of quartz. There are always in the latter case two unsaturated valences Si and SiO whatever the level of the glide plane. However some other differences in double kink nucleation for instance could occur and could select a preferred level for the glide plane. These possibilities have not been studied here.

atoms. We thus obtain a special lattice with only Si atoms. Their pseudo-covalent bonds (Si–Si) correspond to a sp^3 hybridization type. Any possible extended defect with a low fault energy will have to preserve the length and the orientation of these pseudo-covalent bonds. In this model, the nearest neighbours of each Si or O atom remain unchanged. All these conditions help to reduce the fault energy and are fulfilled for the twins. This allows an extension of our model to the fault associated with the dissociated dislocations to be proposed with some confidence. The corresponding configuration is shown in Fig. 9. This fault has a thickness equal to one c parameter, i.e. the dislocation is a zonal dislocation [19, 20] with atomic rearrangements in several layers. From a geometrical point of view the fault is obtained as follows: on the $(2\bar{1}\bar{1}0)$ projection, the crystal is cut along the basal section S between the levels 0 and $c/3$. The lower block is fixed while the upper block is moved by $\mathbf{a}_2/2 = 1/6[\bar{1}2\bar{1}0]$. This operation produces misoriented bonds in S as in Fig. 7. It is therefore necessary to displace the atoms in some layers around S to again find the sp^3 orientations of the bonds. This rearrangement can only be achieved as follows; (1) the atoms of the layer at level $c/3$, just above the S surface, are moved by $1/6[\bar{1}\bar{1}20] = \mathbf{a}_3/2$, (2) the atoms of the layer at level $2c/3$, just above the preceding layer are moved by $1/6[11\bar{2}0] = -\mathbf{a}_3/2$. Alternatively the fault can be generated by three successive shears on the basal plane; (1) shear vector $\mathbf{a}_2/2 = 1/6[\bar{1}2\bar{1}0]$ on the plane between levels 0 and $c/3$, (2) shear vector $\mathbf{a}_3/2 = 1/6[\bar{1}\bar{1}20]$ on the plane between levels $c/3$ and $2c/3$, (3) shear vector $-\mathbf{a}_3/2 = 1/6[11\bar{2}0]$ on the plane between levels $2c/3$ and c. The resulting displacement of the upper block is only $1/6[\bar{1}2\bar{1}0]$ but the fault between this block and the fixed one extends over a thickness c.

In fact this description is true only for β quartz where the parameter u is exactly 0.500. For α quartz the shear vectors are modulated by the parameter u ($u = 0.465$ at room temperature and increases with T, reaching the value 0.500 at the transition temperature $T = 573°$ C). In the absence of precise energy fault calculations, one cannot know the exact positions of the shifted atoms inside the layer of thickness c. The shear vectors can become $u\mathbf{a}$ or $(1-u)\mathbf{a}$ or any intermediate value without qualitative change in the fault energy.

The partials limiting such a fault will be studied in a future paper as well as the problems of triple nodes and of attractive junctions.

4. Conclusion

Basal **a** glide in quartz at low temperatures exhibits preferential 60° orientations analogous to those observed in covalent crystals Si and Ge. The model of unsaturated valences or dangling bonds can be transposed to quartz. Furthermore the 60° dislocations in quartz are dissociated but the partials do not normally reach their large equilibrium distance because this necessitates the breaking of strong bonds.

At higher temperatures, quartz exhibits plastic deformation on other slip planes (prismatic slip – **a** and **c** – and pyramidal slip). For the **a** dislocations this has been described by cross-slip of the screws and pencil glide mechanisms would result [21]. However in that case dangling bonds also occur, which should give rise to preferential orientations; dissociation is expected because the length of the Bürgers vectors and the energy of the dislocations are still very large.

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