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## ON THE MALACHITE SPIRAL CRYSTALS

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The main reason for spiral bending of malachite crystals from *Tyrol* is probably the zinc admixture. The admixture entails formation of thermodynamically stable «sandwich» structures and their curling under mechanical tension due to non-coincidence of element sizes in adjacent layers.

The finds in *Tyrol*, Austria, of spiral and curl-like crystals (Fig. 1) diagnosed as malachite are repeatedly mentioned in publications (Meixner, Paar, 1975; Brandstätter, Seemann, 1984; Jahn, 1997). The reasons for formation of exotic forms have been discussed (Jahn, 1997; Wight, 1998), but were not cleared up completely.

The reference to dislocation mechanism of growth convincingly explains the extended form of crystals (Wight, 1998). As to the curling of crystals, «environmental conditions of growth ..., in particular, unequal growth rate of fibers in a malachite bunch» (Brandstätter, Seemann, 1984), surface tension of mineral forming environment and mechanical tension near the dislocation axis (Wight, 1998), and even spiral character of dislocation growth (Jahn, 1997) were mentioned among the reasons. However, thin needles and fibers of «normal» malachite also grow under the dislocation mechanism, but do not curl. So, the dislocation growth mechanism cannot be acknowledged to be the single or main reason of the discussed phenomenon. «Unequal growth rate of fibers», in our opinion, also cannot be an explanation as it proceeds from notorious existence of a bunch of fibers (really notable in illustrations to quoted articles), which in itself requires a substantiation.

What is noticeable, that is the bluish and rather pale coloring of crystals usually indicating zinc admixture in malachite (at adequate, as a whole, color rendition in illustrations to publications by S. Jahn and Q. Wight). Really, the content of 2.7% zinc is mentioned, which is abnormally much for malachite and twice above that in normal green malachite from the same deposit. The last circumstance suggests that curling of crystals is related to this feature of their composition. S. Jahn considers the zinc admixture as a reason for dislocations (Jahn, 1997). More general assumption of the important role of zinc «inclusions» is stated by Q. Wight (1998).

The discussed phenomenon becomes understandable if one considers the crystal struc-

ture of discussed «malachite» to consist of «copper» and «zinc» (or mixed) elements of somehow different sizes and configuration. Lattice cells of malachite  $\text{Cu}_2[(\text{OH})_2]\text{CO}_3$  and rosasite  $(\text{Zn,Cu})_2[(\text{OH})_2]\text{CO}_3$  really differ from each other in linear dimensions by 0.64 — 4.7 % in different directions while angle  $\beta$  in rosasite accepts various values (Strunz, 1982), depending probably on Zn/Cu ratio.

Similar mixed structures are more stable when provided with the distant order in them, characterized by ordered arrangement of elements of one type between elements of another type, for example, separately in different layers. As is known, these «sandwich» structures have ability to bent spontaneously and even to roll into rolls. The chrysotile structure is a classical example of «sandwich» structure.

Simplifying extremely the picture, let us imagine a two-dimensional crystal structure of a mixed crystal consisting of rectangular elements of greater  $A \times B$  and smaller  $a \times b$  sizes, located separately in adjacent layers of a two-layer package (Fig. 2a). This combination of elements of different sizes in one structure results in elastic straining — rectangles turn into slanting trapezes (marked by crosses of diagonals), which is equivalent to essential increment of free energy.

Obviously, this condition of a fragment is unstable and, owing to the elastic character of deformation conditioned by forces of chemical bond, it would bent on an arch (Fig. 2b) until the sum of deformations would reach the possible minimum at this combination of elements. As a result, elements would take the form of equal, in each layer, isosceles trapeziums, in a maximum degree reduced to rectangles. The free energy would reach the possible at this conditions minimum and a fragment, having accepted an arched form, would pass into equilibrium state.

The said above is confirmed by calculations. The degree of deformation and free energy are determined by the sum of areas of shaded plots of deformations (Fig. 2a).



FIG. 1. Spiral crystal of malachite. Tirol, Austria. Photo Rainer Bode. Under the permission of «Mineralien Welt»

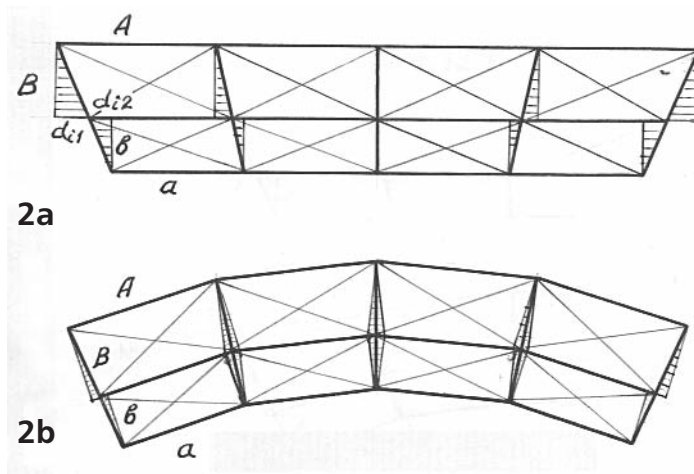


FIG. 2. Fragment of mixed crystal structure (explanation in text)



FIG. 3. Crystal of the manganous calcite, width 12 cm; Dalnegorsk, Primorski Krai. Photo of the author

The area of  $i$  (from the middle) deformed plot in the first option is equal to the strained area  $S_i = B d_{i_1}/2 + b d_{i_2}/2$ ,

where  $d_{i_1}$  and  $d_{i_2}$ —displacements of borders of big and small elements along their common border.

As in isomorphism conditions these elements only slightly differ in sizes, it is possible to accept to be

$$d_{i_1} \approx d_{i_2} = i(A-a)/2,$$

and then

$$S_i = i/4 \cdot (B+b)(A-a),$$

while the total area of  $n$  strained plots is

$$S_{total} = 1/4 \cdot (B+b)(A-a) \sum_{i=1}^n i = 1/8 \cdot n(n+1)(B+b)(A-a)$$

In the arched structure all shaded areas are equal and the total area of  $n$  strained plots is

$$S'_{total} = n/2 (B+b)(A-a)$$

The ratio of areas expressing the deformation degree of the structure is

$$S_{total} \cdot S'_{total} = (n+1)/4$$

$S'_{total}$  is i.e. always less than  $S_{total}$ ,

as expected.

It is easy to see that other ratio of element numbers (for example, as in the considered case, 2.7 % of «zinc» elements) would not change the picture, but only increase the curvature radius.

Thus, sorting of elements during the growth enables, under other conditions being equal, decrease of free energy, whereas chaotic arrangement of elements excludes this possibility. Hence, sorting of elements is motivated and is ruled by a natural process towards the decrease of free energy.

Passing from a two-layer package to a structure of a set of packages, where elements of both types are separately packed, it is necessary to assume the origination of tangential shift tension accompanying bending between packages of layers. It is these tensions that cause the longitudinal splitting of a growing crystal into fibers, but also support the process of their curling. The stated reasons also remain

in force for more realistic model of structure of unequal three-dimensional monoclinic elements, as lattice cells of malachite and roasite actually are. This model results in crystal curling by a spiral, which really occurs.

Summarizing, it is necessary to draw a conclusion that origination of sandwich structures is a necessary and sufficient condition for minimization of that part of free energy, which is conditioned by the presence of two types of elements, and curling of a crystal is nothing other than a method and morphological expression of free energy minimization. The curled form of «malachite» from Tyrol is paradoxically closer to equilibrium than hypothetical flat-face form of the same mineral. At the same time, on the background of the considered main reason, it is natural to assume the influence of other factors — unequal growth rates at different sides of a crystal, as at growth of gypsum antolites (Maleev, 1971), the surface phenomena, tension near the axis of dislocation, etc.

Analogous ordering of structure probably explains the origination of curled and curved forms of other mixed crystals, for example, manganous calcite from Dalnegorsk (Fig. 3).

## References

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