

ON THE DISTRIBUTION OF THE OCCURRENCE OF RIGHT- AND LEFT-HANDED CRYSTALS

CRYSTALLOGRAPHY

1965

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196501.14973>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

UDC 548.51

CRYSTALLOGRAPHY

E. D. ROGACHEVA

ON THE DISTRIBUTION OF THE OCCURRENCE OF RIGHT- AND LEFT-HANDED CRYSTALS

(Presented by Academician A. V. Shubnikov, May 3, 1965)

One of the most important questions in the problem of dissymmetry is the question of the occurrence of right- and left-handed forms of various kinds of matter. It is generally accepted that, for the organic world, either the exclusive formation or the substantial predominance of forms of one sign is characteristic. The question of dissymmetry in the inorganic world is less clear, in particular among crystals that are not the product of the activity of living nature ^(1,2). Apparently, the formation either of symmetrical forms of crystals or of dissymmetrical (enantiomorphic) forms, but in equal quantities, should be regarded as the rule. Exceptions to this rule undoubtedly exist and, possibly, are not so very few. Thus, a number of morphologically dissymmetrical inorganic crystals are known that occur only in one enantiomorphic modification ^(1,3,4). For other substances, a noticeable predominance of some forms over others has been noted ⁽⁵⁻⁸⁾.

A quantitative characteristic of the predominance of one of the forms may be the handedness index k , equal to the ratio of the number of right-handed crystals to their total number. If we are dealing with only one aggregate of the given bodies, for example with crystals obtained in one experiment, then k remains the sole characteristic. If, however, there is a series of aggregates, then, having found k for each of them, one can construct a distribution curve for the handedness index. The latter characterizes the situation more fully.

In works ^(7,8), where the presence of a sharply expressed tendency toward an excess of left-handed forms during the formation of epsomite crystals $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from an aqueous solution was shown, only the mean values of k were given. Further accumulation of experimental data made it possible to construct curves for the distribution of occurrence of right- and left-handed crystals and to draw new conclusions. To construct the curves, the handedness indices k for individual experiments were grouped into classes. (The class interval was chosen for each series of experiments individually, in accordance with the specific data.) The frequencies obtained, i.e., the numbers of occurrences of the handedness

indices in one or another class, were expressed as percentages of the total number of experiments in the given series and plotted against the midpoints of the classes. The experiments were carried out at room temperature. It may be thought that mechanical impurities served as centers of crystallization. Indeed, control experiments with a well-purified solution showed that, under the same conditions, crystallization does not occur.

The sharpest predominance of left-handed crystals ($k = 0.10 \pm 0.01$) was observed when crystallization began after the lid of the crystallizer had been slightly opened for 5–10 min after the solution had completely cooled to room temperature. The supersaturation ΔC was within the range of 50–120 g of substance per liter of solution; the temperature at which the solution was poured into the crystallizer was $t_1 = 29^\circ$. The number of experiments was $n = 57$. No dependence on supersaturation was observed. For this series of experiments, a sharply descending curve was obtained (Fig. 1, 1). The asymmetry of the distribution

can be explained, in accordance with the results of work (8), in the following way. The crystallization centers of epsomite are mechanical impurities that have a dual nature: some of them are dissymmetric, some neutral. The action of the dissymmetric impurities proves to be stronger because they either predominate quantitatively (which, however, is unlikely), or else because of their greater activity.

The next series of experiments gave a distribution curve of an entirely different character. The experimental conditions were as follows: $\Delta C = 90$ g/l, $t_1 = 29^\circ$, $n = 15$. In contrast to the preceding case, the crystallizer was not covered and cooled slowly. The cooling time of the solution to the saturation point was approximately 2.5 times greater than in the preceding experiments. The mean value of k proved to be practically equal to 0.5 ($k_{av} = 0.51 \pm 0.04$), and the curve was bell-shaped and almost symmetrical (Fig. 1, 2). The results obtained can be explained by the fact that keeping the solution at a temperature above the saturation point leads to deactivation or destruction, first of all, of those dissymmetric impurity centers that entered the solution when it was poured into the crystallizer or even earlier. As a result, the nucleation of crystals takes place on neutral impurities that are more resistant to temperature effects.

The next curve (Fig. 1, 3) characterizes crystallization in closed crystallizers under the same initial conditions, but with ordinary cooling in air ($n = 89$). The form of curve 3 reflects the simultaneous action on the nucleation process of two factors—dissymmetric and neutral. Owing to more rapid cooling than in the preceding case, deactivation of the dissymmetric impurities had time to occur only partially, but still to such an extent that, in comparison with curve 1, the relative role of the neutral impurities increased.

Obviously, depending on the cooling rate, one can obtain all intermediate types of curves between 2 and 3.

Curve 4 was constructed from data of experiments ($n = 82$) analogous to the

preceding ones, with the only difference that higher supersaturations were used for them, $\Delta C = 130\text{--}250$ g/l (correspondingly, the temperature at which the solution was poured out was somewhat higher). These experiments are singled out as a special group for two reasons. Whereas in all the preceding cases, for which curves 1–3 were constructed, the crystalline precipitate consisted of several, sometimes of a large number of separate crystals, in the last series of experiments a multitude of needle-shaped crystallites was obtained, formed as a result of mass crystallization. Often among them one or two large crystals could be found. In addition, crystallization at high supersaturations is characterized by sharp fluctuations in the handedness index, which not infrequently assumes the extreme values 0 or 1. This suggests that here there is another mechanism of crystallization, namely, multiplication of crystals. If all subsequent crystals

Fig. 1. Distribution curves for the occurrence of right and left epsomite crystals. 1—supersaturation $\Delta C = 50\text{--}120$ g/l, number of experiments $n = 57$, crystallization with covering; 2— $\Delta C = 90$ g/l, $n = 15$, slow cooling; 3— $\Delta C = 90$ g/l, $n = 89$, ordinary cooling in air; 4— $\Delta C = 130\text{--}250$ g/l, mass crystallization, $n = 82$

owe their origin to the first, accidentally formed crystal, which, rapidly reaching, under conditions of high supersaturation, certain necessary dimensions, initiates avalanche crystallization, then one obtains $k = 0$ or $k = 1$. In the case when crystallization develops from several independently formed crystals of different sign, or when multiplication is combined with the independent formation of new crystals, k takes intermediate values, though often close to the extreme values. Naturally, a minimum should be expected in the middle part of the graph, and this is observed on curve 4. If the dissymmetric factor were absent, the curve would have a symmetric cup-shaped form. The fact that the form obtained is rather semi-cup-shaped indicates the active participation, in the phenomenon, of the nucleation of left particles. The latter is quite understandable, since no special measures were taken to suppress their activity.

Thus, the distribution curves of the chirality index k during the crystallization of epsomite depend on the relative activity of three factors: 1) symmetric mechanical impurities, 2) dissymmetric impurities, 3) multiplication of crystals. Generally speaking, along with the action of these factors, one must also bear in mind the possibility of homogeneous (spontaneous) nucleation of crystals. But its influence on the distribution of the occurrence of right and left forms will be the same as that of symmetric impurities. Therefore the bell-shaped form of the curve obtained for quartz ⁽⁹⁾ indicates that the formation of natural quartz crystals occurred either on symmetric impurities, or homogeneously, and moreover without participation of crystal multiplication.

The realization of conditions under which the action of the second and third of the factors listed would occur in pure form is more difficult. True, the literature contains data on the occurrence of some crystals in one enantiomorphic modification ^(3,4). But there is hardly any point in seeking the reason for this in the fact that all of them are formed from dissymmetric particles of one sign. It is

difficult to suppose that no random neutral particles, against the entry of which no measures were taken, were capable of inducing crystallization. Evidently, the cause of one-sided morphological dissymmetry must lie in something else. Characteristic of the action of dissymmetric impurities, rather, should be the distribution described by curve 1. It can hardly be assumed either that, following the appearance of the first crystal, all subsequent crystals will necessarily begin to appear only by multiplication. However, the possibility of a substantial predominance of the multiplication mechanism is indicated, in addition to curve 4, also by data on the crystallization of NaClO_3 in sealed ampoules⁽⁵⁾, when in 433 cases exclusively right crystals were obtained, in 411 experiments—left ones, and only in 94 cases—both simultaneously.

In conclusion, for purposes of comparison, let us consider the regularities in the distribution of right and left forms in living nature. Since there the only way new individuals arise is reproduction, the characteristic form of the distribution curve is cup-shaped or semi-cup-shaped (for example, for the so-called mollusks *Partula surutalis* or for the bacteria *Bacillus mycooides*⁽⁹⁾). In essence, these are curves of one class. Both reflect, first of all, the phenomenon of heredity, although in the second case the dissymmetry of external influences is mixed in. But in light of the data cited above, cup-shaped distributions can no longer be regarded as characteristic exclusively of the organic world, as was formerly supposed⁽⁹⁾. As for bell-shaped distributions, they are, indeed, characteristic only of the inorganic world, and precisely this difference is fundamental. On the whole, in the inorganic world, at least in that part of it which is represented by crystals, owing to the fact that multiplication and dissymmetric

factors may act or may be absent; we encounter a greater diversity of distribution curves for right- and left-handed forms than in living nature.

The author expresses gratitude to A. V. Belostin for discussion of the results.

Research Institute of Physics and Technology
at Gorky State University
named after N. I. Lobachevsky

Received
1 IV 1965

CITED LITERATURE

1. A. V. Shubnikov, *The Problem of Dissymmetry of Material Objects*, Moscow, 1961.
2. Yu. A. Urmantsev, in: *On the Essence of Life*, Moscow, 1964, p. 170.
3. V. S. Poddisoko, A. V. Shubnikov, *Proceedings of the Institute of Crystallography, Academy of Sciences of the USSR*, **11**, 212 (1955).

4. G. Wyrouboff, *Zs. Kristallogr.*, **29**, 659 (1897).
5. C. Soret, *Zs. Kristallogr.*, **34**, 630 (1901).
6. C. Eacle, *Zs. Kristallogr.*, **26**, 562 (1896).
7. A. V. Belostin, E. D. Rogacheva, in: *Growth of Crystals*, **4**, 1964.
8. E. D. Rogacheva, A. V. Belostin, in: *Growth of Crystals*, **5**, 1965.
9. V. V. Alpatov, *Bull. MOIP, Biological Section*, **58**, 5 (1953).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.