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MICROPARACRYSTALS - THE BUILDING MATERIAL IN NATURE

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Abstract The positions of atoms in materials can be explored most directly by diffraction of X-rays. This was demonstrated in 1912 for crystals by Laue, Friedrich and Knipping /1/. The positions of atoms in polymers could be analysed in a similar way by transforming the intensity of scattered X-rays or neutrons into detailed structural information. Words such as short range order, medium range order, clusters, micelles, mesophases or amorphous phases, semi-crystalline or liquid-crystalline materials may be used. New definitions such as alignments, nodules, inclinations and meander-cubes appear. Another kind of research applies mathematical language: beginning with the results by Laue /2/, the reciprocal space notation by Ewald /3/ and the idea of the same a-priori probability function for all atoms in the noncrystalline state by Debye /4/, the theory of the "ideal paracrystal" was published in 1950 /5/. Laue's idea of lattices is blended with Debye's a-priori probability function: The three lattice cell vectors \( \mathbf{a}_k \) each have a priori three relative variances \( \sigma_{k1}^2 \) in the three directions \( \mathbf{a}_1 \), e.g.

\[
\sigma_{k1}^2 = \left( \frac{(\mathbf{a}_k - \mathbf{a}_k', \mathbf{a}_1)}{2} \right)^2 / a_1^2
\]

The lattice factor \( Z \) then is no longer Ewald's lattice peak function, but the three-dimensional Fourier transform of Landau's convolution polynomial /6/. The Fourier transform \( \mathbf{F}_k (b) \) of three a-priori distance statistics \( H_k(x) \) of the vectors \( \mathbf{a}_k \) define the lattice factor. In the following table all essential formula are collected:

<table>
<thead>
<tr>
<th>Author</th>
<th>Equation/Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>K. von Laue (1912)</td>
<td>( \mathbf{A}_k \cdot \mathbf{b} = h_k ) ; ( \mathbf{b} = \frac{\mathbf{g} - \mathbf{A}_k}{\lambda} )</td>
</tr>
<tr>
<td>F.R. Ewald (1940)</td>
<td>( I(h) = e^2 \frac{Z(h)}{s^2(h)} ; Z(h) = \sum_{hkl} F(h-hkl) )</td>
</tr>
<tr>
<td>P. Debye (1929)</td>
<td>The &quot;a priori probability function&quot;</td>
</tr>
<tr>
<td>L.D. Landau (1927)</td>
<td>( H(z) \rightarrow R(z) = \int H(z-x) H(z-x) dx )</td>
</tr>
<tr>
<td>F. Rinne (1933)</td>
<td>&quot;Paracrystals and Bioparacrystals&quot;</td>
</tr>
<tr>
<td>R. Hosemann (1950)</td>
<td>( Z(h) = \prod \frac{1-F_k}{1-\frac{1-F_k}{F_k}} ; F_k =</td>
</tr>
<tr>
<td></td>
<td>( Z(h) = \prod \frac{1-F_k}{1-\frac{1-F_k}{F_k}} ; F_k =</td>
</tr>
</tbody>
</table>

\[
\sigma_{k1}^2 = \frac{1}{a_1^2} \int H_k(x) \mathbf{a}_1^2 \, dx ; \quad \text{d} \mathbf{b}_k = \frac{1}{\mathbf{a}_1^2} + \mathbf{a}_1^2 \mathbf{b}_k^2 \]

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The name "paracrystal" was introduced by Rinne /7/ for liquid crystals. Laue recognized the importance of the theory of paracrystals for all materials intermediate between crystalline and liquid state. Nevertheless, the new theory is still applied merely in USA and the U.K. preferably to promoted catalysts /8,9/. The caution of most scientists may be due to the new mathematical language and the fact that ideal paracrystals consist of lattice cells shaped like paralleloepipeds. On this account their lattices contain particular irrational statistical correlations. Recently it was proved that in all paracrystals only certain partial correlations exist which, on account of the so called $\alpha^*$-relation, affect the intensity function of the ideal paracrystal by less than $1.5\%$ and hence can be neglected /10/. The theory of paracrystals offers fundamental equations by which most substances can be deciphered as microparacrystals /11/ by measuring their integral widths $\delta b$ of reflections. These widths increase linearly with $h^2$ (order of reflection). From the slope of this straight line and from its intersection with the ordinate, $g_{kk}$, and the number, $N_k$, of netplanes can be calculated. All materials investigated by us until now are submitted to the $\alpha^*$-relation which connects $N_k$ with the $g_{kk}$-value of the bearing netplanes $k$ (see below).

$$g_{kk} \sqrt{N_k} = \alpha^*; \quad \alpha^* = 0.15 \pm 0.05.$$

Figure 1 gives some examples of organic and inorganic materials in a plot $\sqrt{N}$ against $1/g$. There is no doubt that this $\alpha^*$-relation conceals a law in nature which is of fundamental importance for most noncrystalline materials. The model of Figure 2 shows all essentials of a two-dimensional paracrystal in equilibrium state. Some larger coins are statistically mixed with smaller ones and represent atoms with four orthogonal valences.

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**Fig. 1** - The $\alpha^*$-relation (Eq. 1).

**Fig. 2** - Coin model as an example for a two-dimensional paracrystalline lattice in equilibrium state.
Their radial potentials are responsible for the size of adjacent distances from center to center. Their tangential potentials on the other hand become active, because the coins lie in statistically curved lines and rows. These deviations resulting from straight lines reach maximal $360^\circ \alpha^*/2\pi$ and influence the diffraction by less than $1/2\alpha^*/2\pi$. Those rows where atoms directly touch each other are called "bearing netplanes" because tangential strains are transferred by them. The consequently arising distortions of the valence angles require a new kind of energy which in crystalline lattices is unknown. This leads to a new term of free enthalpy $\Delta G$ which for cubic paracrystals with $N^*$-lattice cells is given by $1/12$:  
$$\Delta G_p = 3/2 \sum_k N^3 N_k A_0 \varepsilon_{kk}^2$$  

A depends on the form of the tangential potentials and determines the value of $\alpha^*$. Figure 3 shows a characteristic example with a particular value of the surface free energy $\sigma$ and volume enthalpy $\Delta G_v$, $g = 0$ % for crystals, $g = 4.2$ % for polymer blends and $g = 7.5$ % for melts. After attaining the critical size, the paracrystals grow to a minimum of enthalpy where $N_k = (A/\varepsilon_{kk})^2$.

Fig. 3 - Free enthalpy of crystals ($g = 0$ %), polymers ($g = 4.2$ %), melts and glasses ($g \approx 7.5$ %).

As an example of a glassy noncrystalline material the analysis of SiO$_2$-glass /13/ is briefly described: The observed intensity function was divided by the product of atom form amplitudes. Its Fourier transform, the so called reduced radial density function (RRDF) then shows a sharp peak at $1.61 \AA$ (Fig. 4). The truncation effect of a peak function is drawn above. Reconvolution leads to a distribution width of $0.06 \AA$ of the SiO-distance. Taking into account the sharp peak of the intensity function at $0.23 \AA^{-1}$ and the atom and mass density and following the Einstein-principle of plainness one finds straightforward the paracrystalline structure which according to the sharp $0.24 \AA^{-1}$-peak of the intensity function must be cubic. Two SiO$_2$-motive most conveniently can be packed together to a common lattice cell if the O-atoms build a fcc-lattice where two Si-atoms are included as a bcc-lattice cell shifted by $1/4$, $1/4$, $1/4$ (Fig. 5a).
The thus constructed crystal has a much too large density. It becomes somewhat too small by using the lattice cell of Figure 5a as the brick of a two times larger fcc-lattice (Fig. 5b). An alternating 11'-twist of the SiO₂-tetrahedra (Fig. 5c) leads to the correct density and introduces paracrystalline distortions for simplicity not drawn in Fig. 5. Nevertheless, one obtains herefrom all the positions of the pair-distribution function and their weights. The residual electron density distribution at the Si-Si- and O-O-peaks are negligible. Now the RRDF depends only on the pair-distribution of atom positions. One has to adapt solely the widths of the single pair-peaks to the observed RRDF and one finds automatically the paracrystalline distortions of g - 10%. It is interesting to note that the 11'-twists of the SiO₄-tetrahedra are observable in the RRDF, because some of the O-O-maxima cleave into two parts (Fig. 4). After introducing paracrystalline distortions, four interpenetrating families of rings with six SiO₄-tetrahedra of Figure 5 still build up a three-dimensional network: The paracrystalline lattice factor Z(b) of the table describes the structure of the microparacrystalline powder diagram similar as the conventional lattice factor averaged over all directions in a Debye-diagram, including the atoms in the grain boundaries. In melts and glasses this is performed by bimodal statistics which in the case of SiO₂ build up the "amorphous network".

Fig. 4 - Radial density function of SiO₂ reduced to SiO (RRDF).
Fig. 5 - Undistorted lattice cell of the SiO₂-structure. The arrows indicate the 11'-twists around the Z-axis. The dotted lines represent the "bearing netplanes".

Figure 6 shows schematically the Si-atoms of one SiO₂-microparacrystal of ~12 Å diameter. The "bearing netplanes" of the fcc-crystal are the (111)-netplanes which define the surfaces of the paracrystalline octahedra and produce the above mentioned 0,24 Å reflection. The prolongation of the netplanes outside the microparacrystal are not drawn for convenience. The structure has some similarities to
that of β-cristobalit but shows as well some remarkable differences and corresponds to the regions of higher order discussed by Valenkov et al. /14/, Zachariasen /15/, and the recently mentioned "clusters" by Phillips /16/.

Fig. 6 - Schematic drawing of an undistorted octahedral microparacrystal of SiO$_2$-glass.

REFERENCES

/14/ Valenkov, N. and Porai-Koshitz, Z. Kristallogr., 91 (1936), 195.