

How does the nanoscale influence the structure of crystalline phases?

Understanding of crystallography is important to gain insight into various nanoscale phenomena.

Bulk crystalline matter is built up from amorphous mass to attain stability through lowering of overall energy. Crystalline matter is an ordered state made up of long range repetition of the spatial arrangement of the atoms (or molecules). There are basic seven types of crystalline structures:

1. Simple cubic
2. Tetragonal
3. Orthorhombic
4. Hexagonal
5. Trigonal
6. Monoclinic
7. Triclinic

The details about the geometry are readily available in the text books. However, bulk crystalline state is far from perfect as there are impurities and defects introduced during the crystal phase formation stage. These imperfections cause significant alterations in the properties of matter. The defects influence chemical, mechanical, optical, electrical, magnetic and thermal properties of the bulk crystalline matter. This aspect can be illustrated by the example of a diamond. The optical brilliance of diamonds is impaired by the crystal defects and accordingly its value is diminished. The fewer the number of defects, the more the diamond will sparkle and the higher will be its price!

The defects are of three types:

- Vacancy: At certain points in the crystalline phase, some atoms are absent or missing although by the geometrical order these ought to have been present.
- Dislocation: There is relative displacement of certain planes of atoms with respect to the other planes, causing a disjoint in the continuity of crystal lattice. This can be simplistically visualized as corrugated sheets of metal stacked up in a single line; but from a certain point upwards, there is an en bloc horizontal shift disturbing the order.

- Interstitials: This is the opposite of 'vacancy' where certain atoms are additionally present in the space among the ordered atoms thereby disturbing the spatial symmetry.

Therefore, the crystalline bulk state is not as pure or perfect as it should logically be. The type and population of defects and their distribution decides the properties of the bulk crystals. These defects can be removed by supplying energy, say in the form of heat. The larger the crystal, the deeper the location of the defects and higher their population. This needs higher energy for expelling the defects. This process is called annealing.

However, as we move down the length scale into the nanoscale region by slicing the bigger crystals into progressively finer crystals, more and more atoms come to the surface as compared to the number of atoms embedded inside. This process also brings the inner crystal defects to the surface. High surface energy of the nanoscale matter drives out most of these defects on the surface. Even the embedded defects are not too deep and mild heat can squeeze these out. This leads to far greater perfection and purity in the crystal structure in the nanoparticles. Obviously, the properties of these defect-free crystals are notably different from their bulk counterpart.

The second change that occurs in crystals at nanoscale is the density of packing of surface atoms. High surface energy of nanocrystals leads to surface relaxation by contraction and even rearrangement of the atoms in some cases. This leads to formation tightly packed structures. Such nanocrystals are very pure and perfect and resist any ingress of foreign atoms. This is corroborated by the fact that nanocrystals are difficult to dope.

These modifications in the crystal structure at nanoscale give rise to their novel properties.
