

High pressure crystal growth of superconductors and (Ga, Al)N semiconductors

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High pressure applied in the synthesis process, can change considerably the properties of the materials obtained. In general two kinds of pressure effects should be taken into account: (i) hydrostatic pressure itself, applied by an inert medium like argon, or by a solid medium, (ii) thermodynamic equilibrium between condensed phase and gas, when gas is an active component of the system. We are using these effects for the growth of single crystals of superconductors and (Ga,Al)N semiconductors.

For the investigation of intrinsic properties of strongly anisotropic superconductors such as borides or cuprates single crystals are necessary. Due to non-congruent melting of majority of these compounds crystal growth is a difficult task. The melt used for the growth of borides or cuprates contains gaseous or volatile components such as Mg, O₂, or Hg. Partial pressure of these components at melting temperature can reach values of tens or hundreds of bars. Therefore we use high pressure technique to grow single crystals of these compounds. An example of (i) is the growth of pure and substituted MgB₂ crystals in the solid state pressure apparatus (cubic anvils) at a pressure of 30 kbar at a temperature 1800-2000°C. In these experiments we have studied the influence of substitutions on the superconducting and structural properties of MgB₂. The presence of two energy bands with distinct superconducting gaps in the MgB₂ superconductor leads to several unusual properties such as high T_c of 39 K and temperature and field dependent anisotropy of the upper critical fields. The superconducting properties can be modified in a well-controlled way by partial substitution of nonmagnetic ions for Mg (e.g. Al) or B (e.g. C) or magnetic ions for Mg (Mn, Fe). Al and C substitutions influence the electronic structure, increase scattering and decrease mean free path which in the case of carbon substituted crystals leads to the strong increase of the upper critical fields. Magnetic impurities Mn and Fe cause T_c to drop rapidly already for a low substitution level.

An example of (ii) is the synthesis of the YBa₂Cu₄O₈ (Y124) compound at high oxygen pressure. Y124 is a stoichiometric, underdoped superconductor with T_c = 80 K. It does not have intrinsic oxygen nonstoichiometry, what makes it exceptional among all superconducting cuprates. Due to the stoichiometric structure and lack of twinning it is possible to investigate, if

the appearance of superconductivity is connected with any kind of phase separation or granularity of CuO_2 planes. Y124 single crystals have been grown from flux at oxygen pressure $P_{\text{O}_2}=800\text{-}1000$ bar at $T=1100^\circ\text{C}$. Other examples of superconducting crystals grown in our laboratory are Hg-based superconductors with T_c up to 130 K obtained at Ar pressure of 10 kbar at $T=1000^\circ\text{C}$ or pyrochlore superconductors XOs_2O_6 ($\text{X}=\text{K},\text{Rb}$) with triangle-based lattice and $T_c = 9.5$ and 6.5 K respectively. Another example is the crystal growth of the wide energy gap semiconductors GaN and (Ga,Al)N. At normal pressure and high temperature necessary for crystal growth, GaN is unstable and does not form. Due to the high fugacity of N_2 at high pressure it is possible to grow GaN crystals from Ga melt at high N_2 pressure of 10 kbar at $1400\text{-}1500^\circ\text{C}$.

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