Equilibrium

Equilibrium of a Si crystal is a somewhat subtle concept. It means the crystal is not subjected to any net increase or decrease of energy and that the temperature is constant and doesn't vary throughout the crystal. In addition, the entropy of the system will be a maximum. Entropy is a measure of disorder in a system - it increases with increasing disorder. For example, the entropy of water in the form of ice is less than the entropy of the same amount of water when it is a liquid, since the atoms in a liquid are not as ordered as the atoms in an ice crystal. In statistical terms entropy can be expressed as $S = -k \Sigma p_n \log(p_n)$, where p_n is the probability the system will be in the nth energy state. As the order increases and the number of states shrinks, the p_n vanish except for one of them, which approaches unity and S vanishes, that is, as the number of states shrinks, $n \rightarrow 0, n \ln (n) \rightarrow 0$. As the number of states increases, increasing numbers of the p_n are non-zero, and S increases. From thermodynamics we have (First Law) $dU = TdS - dW$ where U = energy, S = entropy and W is the work done (by the system). If the volume of the crystal is constant and the temperature is constant, $dU = TdS$. Since S = maximum, $dS = 0$ and hence $dU = 0$. This is the condition of thermodynamic equilibrium.