Elastic anomalies in minerals due to structural phase transitions

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Abstract: Landau theory provides a formal basis for predicting the variations of elastic constants associated with phase transitions in minerals. These elastic constants can show substantial anomalies as a transition point is approached from both the high-symmetry side and the low-symmetry side. In the limiting case of proper ferroelastic behaviour, individual elastic constants, or some symmetry-adapted combination of them, can become very small if not actually go to zero. When the driving order parameter for the transition is a spontaneous strain, the total excess energy for the transition is purely elastic and is given by:

$$G_{\text{elastic}} = \frac{1}{2} \sum_{i,k} C_{ik} e_i e_k + \frac{1}{3!} \sum_{i,k,l} C_{ikl} e_i e_k e_l + \frac{1}{4!} \sum_{i,k,l,m} C_{iklm} e_i e_k e_l e_m + \ldots$$

which has the same form as a Landau expansion. In this case, the second-order elastic constant $C_{ik}$ softens as a linear function of temperature with a slope in the low-symmetry phase that depends on the thermodynamic character of the transition. If the driving order parameter, $Q$, is some structural feature other than strain, the excess energy is given by:

$$G = \frac{1}{2} a(T - T_c) Q^2 + \frac{1}{4} b Q^4 + \ldots + \sum_{i,m,n} \lambda_{i,m,n} e_i^{m} Q^n + \frac{1}{2} \sum_{i,k} C_{ik} e_i e_k$$

In this case, the effect of coupling, described by the term in $\lambda e^{m} Q^n$, is to cause a great diversity of elastic variations depending on the values of $m$ and $n$ (typically 1, 2 or 3), the thermodynamic character of the transition and the magnitudes of any non-symmetry-breaking strains. The elastic constants are obtained by taking the appropriate second derivatives of $G$ with respect to strain in a manner that includes the structural relaxation associated with $Q$.

The symmetry properties of second-order elastic constant matrices can be related to the symmetry rules for individual phase transitions in order to predict elastic stability limits, and to derive the correct form of Landau expansion for any symmetry change. Selected examples of "ideal" behaviour for different types of driving order parameter, coupling behaviour and thermodynamic character have been set out in full in this review. Anomalies in the elastic properties on a macroscopic scale can also be understood in terms of the properties of acoustic phonons. These microscopic processes must be considered if elastic anomalies due to dynamical effects are to be accounted for.