

Coherent Transition Between Nonhydrostatically Stressed Phases With Different Elastic Properties

M.B. Geilikman

Institute of Experimental Mineralogy, USSR Academy of Sciences,
142432 Chernogolovka, Moscow district, USSR

Abstract. The Clausius-Clapeyron equation has been derived for the coherent transition between phases with different elastic moduli. Expressions for the phase elastic moduli have been obtained for one-dimensional polymorphism, i.e., when phase structures differ in atomic layer stacking. The results are applied to the sphalerite-wurtzite transition.

The thermodynamics of nonhydrostatically stressed systems and their relevance to the theory of metamorphism present a wide range of problems (Paterson 1973; Robin 1974; Ostapenko 1977) including coherent polymorph transition under nonhydrostatic stresses. Phases with equal elastic moduli were considered by Coe and Paterson (1969). The present paper will assess the influence of nonhydrostatic stresses on the phase coherent transition where elastic moduli differ. More specifically, we consider the 'one-dimensional' polymorphism where the structure of each of the phases is obtained by packing the crystal layers of the compound in an appropriate way (Verma and Krishna 1966).

The coherent transition of first order produces a heterophase layered state, in which the elastic moduli are determined by the phase composition of the sample. Thus our primary aim is to see how the mode of packing an arbitrary mixed-layer modification affects the elastic moduli. For this, we have to isolate the largest structural units (blocks) — layers available in the compound, with which any type of layer modification can be constructed. For example, for the mixed-layer sphalerite-wurtzite modifications such blocks consist of the tetrahedron layers. For the micas, they are double silicon-oxygen layers, the upper part being displaced in relation to the lower by a third of the period in the layer plane. This arrangement results in a monoclinic rather than hexagonal symmetry for the simplest modification of the 1M mica, with a lattice period transverse to the layer plane at each structural block. For the sphalerite-wurtzite system, the cubic modification 3C is the simplest, i.e., sphalerite. Our aim is to calculate the elastic moduli for more complex modifications in a compound using the elastic moduli for the simplest modification. Considering ionic with

substantial covalent participation compounds we should not forget that the elastic properties are largely determined by rigid, directed short-range valence bonds rather than by long-range Coulomb forces with a radius of interaction greater than the thickness of the layer. Direct microscopic calculation for sphalerite (Martin 1970) which made allowance for both short-range bonds and long-range Coulomb forces showed that the latter contributed only a few per cent. Therefore, the elastic moduli of mixed-layer modifications can be calculated from elastic moduli of the simplest modification in terms of the macroscopic elasticity theory where only short range forces are considered (Landau and Lifshits 1965).

The validity of this approach was confirmed in earlier (Geilikman 1979) microscopic calculations of the elastic moduli for the sphalerite-wurtzite polytypes. There was full agreement between the results calculated on the basis of the elasticity theory and those obtained with accurate microscopic calculations. In other words, calculating elastic moduli becomes a matter of estimating the effective moduli of a sample 'put together' from layers with a similar structure and a different orientation. Thus in micas, each successive layer can be rotated by 0° , 60° , 120° , and 180° relative to the preceding layer (Bragg and Claringbull 1965). The elastic moduli of a composite layered sample were considered earlier (Lifshits and Rozentsveig 1946). However, a more compact form would seem more desirable for our purpose. We shall proceed from Hook's law for any given layer:

$$\sigma_{ij}(l) = c_{ijkm}(l) \varepsilon_{km}(l) \quad (1)$$

where $i, j, k, m = x, y, z$; $\sigma_{ij}(l)$ is the stress tensor, $\varepsilon_{km}(l)$ is the strain tensor and $c_{ijkm}(l)$ is the tensor of the elastic moduli for the simplest modification in the coordinate axes rotating about the z axis perpendicular to the plane of layers through an angle which corresponds to the orientation of a given layer. The index l indicates the number of each crystal layer. The relation between the tensors of elastic moduli of differently oriented layers can be calculated using the matrix for the rotation of the coordinate system round z axis. The matrix has the form

$$R_{ij} = \begin{vmatrix} \cos \varphi_l & \sin \varphi_l & 0 \\ -\sin \varphi_l & \cos \varphi_l & 0 \\ 0 & 0 & 1 \end{vmatrix}, \quad (2)$$

where φ_l is the rotation angle of the l th layer; the elastic moduli tensor for this layer becomes

$$c_{ijkm}(l) = R_{ip} R_{jq} R_{ks} R_{mt} c_{pqst}^0 \quad (3)$$

Here c_{pqst}^0 is the tensor of the elastic moduli for the starting orientation to which the φ_l angle is referred.

The overall coherence of the crystal is a critical requirement under which no layer can 'glide' in relation to another. This is a compatibility condition (Kröner 1958; Roitburd 1974) according to which the strain tensor must have the form

$$\varepsilon_{ij}(l) = \frac{1}{2}(m_i p_j(l) + m_j p_i(l)) + \langle \varepsilon_{ij} \rangle \quad (4)$$

where the average sign $\langle \dots \rangle$ denotes averaging over the sample in the direction of the z axis,

$$\langle \varepsilon_{ij} \rangle = \sum_l \lambda_l \varepsilon_{ij}(l) \quad (5)$$

where λ_l is the specific content of the layers of a given orientation in the sample. The vector m_i is the unit vector of the normal to the layer plane, i.e., $m_z = 1$, the other components being zero. The vector $p_i(l)$ is obtained from the mechanical equilibrium condition

$$m_i \sigma_{ij}(l) = m_i \langle \sigma_{ij} \rangle. \quad (6)$$

Here $\langle \sigma_{ij} \rangle$ is the macroscopic external stress tensor determined by the nonhydrostatic external load. Omitting intermediate calculations, the scheme goes like this: having found the vector $p_i(l)$ from the equilibrium condition (6), the strain tensor (4) is substituted into (1), and the two sides are averaged according to (5) to produce Hook's law for the whole sample:

$$\langle \sigma_{ij} \rangle = c_{ijkl} \langle \varepsilon_{km} \rangle \quad (7)$$

where c_{ijkl} is the required elastic moduli tensor for the layered modification obtained from

$$\begin{aligned} c_{ijkl} = & \langle c_{ijkl}(l) \rangle - \langle c_{ijnz}(l) t_{nq}(l) c_{qzkm}(l) \rangle \\ & + \langle c_{ijnz}(l) t_{nq}(l) \rangle \langle t_{qp}(l) \rangle^{-1} \langle t_{ps}(l) c_{szkm}(l) \rangle \end{aligned} \quad (8)$$

where $t_{ij}(l) = c_{ijzjz}^{-1}$. With this expression the elastic moduli for layered modification can be found for virtually any type of symmetry. For example, the elastic moduli for the mica polytypes $2O$, $2M$, $3T$, and $6H$ can be calculated using the elastic moduli for $1M$ polytype. Before we consider the sphalerite-wurtzite transition, it is essential to derive certain general thermodynamic relations for the transition of phases with different elastic moduli.

The chemical potential of the stressed system (per unit volume) is

$$\mu = \mu^0 - \varepsilon_{ij}^0 \sigma_{ij} - \frac{1}{2} s_{ijkl} \sigma_{ij} \sigma_{km}, \quad (9)$$

where μ^0 is the chemical potential of the system in the absence of external stress, ε_{ij}^0 is the inherent deformation and s_{ijkl} is the tensor of compliance coefficients calculated for a particular tensor of elastic moduli (Nye 1957).

Let us consider a heterophase state arising during the coherent $\alpha - \beta$ phase transition. Here the chemical potential for a free state contains three items:

$$\mu^0 = \lambda_\alpha \mu_\alpha + (1 - \lambda_\alpha) \mu_\beta + E_{\text{coh}} \quad (10)$$

μ_α and μ_β are chemical potentials for the individual phases, λ_α is the specific content of the α -phase layers in the sample, and E_{coh} is the elastic energy of the coherent conjugation produced by the difference in the phase inherent strains.

The β -phase inherent strain value is taken as a reference point for all other inherent strains so that

$$\varepsilon_{ij}^0 = \lambda_\alpha \mathbf{u}_{ij} \quad (11)$$

where \mathbf{u}_{ij} is the α -phase inherent strain.

For the case where the heterophase state is a phase equilibrium, the following condition

$$\partial\mu/\partial\lambda_\alpha = 0 \quad (12)$$

must be observed for the chemical potential (9). It will be noted that for the phases with different elastic moduli the tensor of compliance coefficients will depend on the phase composition of the sample.

Substituting (10) and (11) into the expression for the chemical potential (9) and using the phase equilibrium condition (12) yields

$$\mu_\alpha - \mu_\beta + \frac{\partial E_{\text{coh}}}{\partial \lambda_\alpha} - u_{ij} \sigma_{ij} - \frac{1}{2} \frac{\partial s_{ijklm}}{\partial \lambda_\alpha} \sigma_{ij} \sigma_{km} = 0. \quad (13)$$

From this we readily find the Clausius-Clapeyron equation

$$(S_\alpha - S_\beta) dT = - \left(\mathbf{u}_{ij} + \frac{\partial s_{ijklm}}{\partial \lambda_\alpha} \sigma_{km} \right) d\sigma_{ij} \quad (14)$$

where S_α and S_β are phase entropies. Equation (14) differs from preceding equations (Paterson 1973; Ostapenko 1977) by a second term in the right-hand side which stems from the difference in the phase elastic moduli.

Let us take the sphalerite-wurtzite transition as an example. Here structural layers formed by the tetrahedra can only be right or twin oriented. For convenience, we introduce $n_i = \pm 1$ where ‘plus’ is for right, and ‘minus’ for the twin orientation. These notations correspond to Hägg’s definition describing polytype structures (Verma and Krishna 1966). If the layer packing is such that $n_i = 1$ for each layer pure sphalerite is formed, in which the trigonal axis normal to the layer plane coincides with the cubic [111] direction. The elastic moduli for the polytype modifications sphalerite-wurtzite were calculated earlier (Geilikman 1979). It is not difficult to see that the general expression (8) obtained in this paper leads to the same results, so we can move straight to the expressions for the compliance coefficients in the Clausius-Clapeyron Eq. (14). The s_{14} and s_{44} coefficients appear to depend on the mode of stacking and are thus different for wurtzite and sphalerite:

$$s_{14} = -n c_{44}/c |c_{14}|; \quad s_{44} = c_{44}^{-1} + 2n^2/c, \quad (15)$$

where $c_{44} [c_{44}(c_{11} - c_{12}) - 2c_{14}^2]/c_{14}^2$. $c_{\lambda\mu}$ are the sphalerite elastic moduli in the trigonal arrangement ($\lambda, \mu = 1, 2, \dots, 6$ according to Voigt’s notation), and the x axis is perpendicular to the vertical plane of the mirror reflection. The structural parameter n is the average value n_i , calculated from (5), i.e.,

$$n = \frac{1}{L} \sum_{l=1}^{l=L} n_l, \quad (16)$$

where L is the number of layers in the crystal. For the wurtzite (β -phase) $n=0$, and for sphalerite $n = \pm 1$, depending on a right or a twin crystal orientation.

The strain of the phase transformation \mathbf{u}_{ij} in (11) depends generally on two factors one of which is the change in the crystal volume during transition. Using the numerical evidence for the constant lattices (Sternberg 1977) gives us:

$$\begin{aligned} \mathbf{u}_{xx} = \mathbf{u}_{yy} &\simeq 10^{-3} \\ \mathbf{u}_{zz} &\simeq 3,2 \cdot 10^{-4}. \end{aligned} \quad (17)$$

The tensor of this strain is diagonal owing to the threefold symmetry axis in the crystal and persists during the transition so that this strain works only against σ_{xx} , σ_{yy} , and σ_{zz} stresses.

Apart from the strain which results from volume jumps there may be a 'packing' deformation as a result of the repacking involved in sphalerite-wurtzite transition. So far, no comprehensible theory has been suggested to explain the mechanism and kinetics of the sphalerite-wurtzite or any other fcc-hcp transitions. However, structural considerations suggest that sphalerite can be converted to wurtzite (and vice versa) simply by displacing every second layer along the y axis by $a/\sqrt{3}$, where a is the lattice constant in the layer plane. Though this strain does not affect the crystal volume, it does change its form. However, owing to the threefold symmetry axis, there are three and not one equivalent displacement directions in the layer plane which form an angle of 120° . The crystal will retain its macroscopic form if the number of shears along each of these three directions are the same and if they are evenly distributed across the crystal (along the z axis).

The repacking deformation is a so called deformation with an invariant plane and so it does not produce incompatibility during the phase coherent conjugation. The elastic energy of the coherent conjugation results from the strain itself (17). In an earlier paper (Roitburd 1974) the elastic energy of the conjugation was calculated for the phases with equal elastic moduli. In our example the whole problem has to be solved over again, using the elastic moduli from a previous paper (Geilikman 1979). This is, however, no real problem, and we will give the final result

$$E_{\text{coh}} = (\mathbf{c}_{11} + \mathbf{c}_{12} - \mathbf{c}_{13}^2/\mathbf{c}_{33}) \mathbf{u}_{xx}^2 \lambda_\alpha (1 - \lambda_\alpha) \quad (18)$$

where λ_α is the part of sphalerite, and $1 - \lambda_\alpha$ is the part of wurtzite in the sample. So (9), (10), and (15) yield the chemical potential for the nonhydrostatic stress field of the sphalerite-wurtzite coherent conjugation

$$\begin{aligned} \mu = E_0 + E_{\text{coh}} + \lambda_\alpha \mu_\alpha(T) + (1 - \lambda_\alpha) \mu_\beta(T) - \lambda_\alpha \mathbf{u}_{ij} \sigma_{ij} \\ + \frac{1}{c} \left\{ n \frac{\mathbf{c}_{44}}{|\mathbf{c}_{14}|} [\sigma_{yz}(\sigma_{xx} - \sigma_{yy}) + 2\sigma_{xy}\sigma_{xz}] - n^2(\sigma_{xz}^2 + \sigma_{yz}^2) \right\}. \end{aligned} \quad (19)$$

Here, E_0 is the part of the elastic energy of external stresses which does not depend on the phase composition of the sample, the last term being the difference between the phase compliance coefficients according to (15). Assuming a minimal chemical potential and knowing $|n|=1$ for sphalerite, we will find that sphalerite must be right oriented if the term in brackets of (19) is negative, and twin-oriented ($n = -1$) if it is positive. There is a simple relation between the sphalerite specific content and the structural parameter

$$\lambda_x = |n| \quad (20)$$

because of $n=0$ for wurtzite. Consequently, for the transition between the phases with different elastic moduli, nonhydrostatic stresses alter the phase equilibrium temperature, and more than that, they determine the orientation of the formed phase.

Let us consider the case where only shear stresses σ_{xz} and σ_{yz} act upon the sample. Here the dominant term for the transformation strain in Clausius-Clapeyron Eq. (14) will become naught because the tensor \mathbf{u}_{ij} is diagonal (17) so that the second term formed by the difference between the phase elastic moduli becomes dominant. Introducing the shear load $\sigma = (\sigma_{xz}^2 + \sigma_{yz}^2)^{1/2}$ and using formulae (13), (14), and (19) yield

$$\frac{dT}{d\sigma} = \frac{4\lambda_x}{c\Delta S} \sigma, \quad (21)$$

where $\Delta S = S_\alpha - S_\beta$. For the latent heat of the sphalerite-wurtzite transition of 13.4 kJ/mol (Landolt-Börnstein 1961), the elastic moduli from a previous paper (Geilikman 1979), the coefficient in (21) will be $4/c\Delta S \approx 0.3$ deg/kbar².

The major inference from (21) is that the phase composition dependence of the elastic moduli may result in a quadratic rather than a linear load dependence of the phase equilibrium temperature. Notably, even for equal elastic but with nonuniform state of new phase (for example, polysynthetic twins), the tensor of the elastic moduli (8) will depend, as a result of anisotropy, on the orientation ratio of phases.

Consequently, the phase equilibrium Eqs. (13) and (14) show that the coherent transition between the non-hydrostatically stressed phases has certain characteristic features resulting from the difference in the phase elastic moduli.

Acknowledgements. The author is grateful to Dr. Yu.E. Gorbaty, Dr. G.V. Novikov and Professor V.A. Zharikov for interesting discussions.

References

- Bragg, L., Claringbull, G.F.: Crystal structures of minerals. London: G. Bell and sons Ltd 1965
 Coe, R.S., Paterson, M.S.: The α - β inversion in quartz: a coherent phase transition under non hydrostatic stress. J. Geophys. Res. **74**, 4921-4948 (1969)
 Geilikman, M.B.: Elastic properties of polytypes. Phys. Status Solidi B: **91**, 725-733 (1979)
 Kröner, E.: Kontinuumstheorie der Versetzungen und Eigenspannungen. Berlin, Heidelberg, New York: Springer 1958

- Landau, L.D., Lifshits, E.M.: Theory of elasticity (in Russian). Moscow: Nauka 1965
- Landolt-Börnstein: Zahlenwerte und Funktionen aus Physik, Chemie, Geophysik, Astronomie, Technik. 4 Teil. Berlin, Heidelberg, New York: Springer 1961
- Lifshits, I.M., Rozentsveig, L.N.: On theory of elastic properties of polycrystals (in Russian). Zh. Eksp. Teor. Fiz. **16**, 967-978 (1946)
- Martin, R.M.: Elastic properties of ZnS-structures semiconductors. Phys. Rev. **B1**, 4005-4011 (1970)
- Nye, J.F.: Physical properties of crystals. Oxford: Clarendon Press, 1957
- Ostapenko, T.G.: Thermodynamics of nonhydrostatic systems and its application to the theory of metamorphism (in Russian). Kiev: Naukova Dumka 1977
- Paterson, M.S.: Nonhydrostatic thermodynamics and its geologic application. Rev. Geophys. Space Phys. **73**, 355-389 (1973)
- Robin, P.-Y.F.: Thermodynamics equilibrium across a coherent interface in stressed crystal. Am. Mineral. **59**, 1286-1299 (1974)
- Roitburd, A.L.: Theory of heterophase structures at phase transformations in solid state (in Russian). Usp. Fiz. Nauk **113**, 69-104 (1974)
- Sternberg, A.A.: Temperature atomic approach and polytypism. In: Protessy realnogo kristalloobrazovaniya (in Russian). Moscow: Nauka 1977
- Verma, A.R., Krishna, P.: Polymorphism and polytypism in crystals. New York: John-Wiley 1966

Received December 10, 1979