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Thermodynamics of a ferroelastic phase transition

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The elastic-strain-energy contribution to the thermodynamic potential of a crystal in the close vicinity of a ferroelastic transition has been determined for a fcc indium-23-at.%-thallium alloy from elastic stiffness tensor data. The potential plotted as a function of the strain order parameter has a second minimum at $\eta_{\min}=+0.012$, predicting a c/a ratio ($\simeq\eta_{\min}+1$) for the fct form below T_c close to that (1.017 ± 0.004) measured, validating treatment of this transition as purely ferroelastic. dT_c/dP has been measured as $+11.8\pm1.3$ K/10^8 Pa, and the effect of hydrostatic pressure in stabilizing the fct phase has been established. The volume ($\Delta V/V=-2.7\times10^{-5}$) and entropy ($+230$ N m^{-2}K^{-1}) differences between the two phases are very small.

Symmetry breaking at a ferroelastic phase transition occurs as a homogeneous deformation of the crystal. The soft mode is a zone-center acoustic phonon. The order parameter is a strain tensor component, and experimentally the mode softening is manifested by a reduction of the corresponding second-order elastic stiffness. Thus, as T_c is approached, the quadratic term in the strain free energy decreases and higher-order terms become increasingly important. Thus, a pure ferroelastic transition is driven by the vibrational anharmonicity of the softening acoustic mode. Schematic plots of the thermodynamic potential comprise a regular feature of phenomenological Landau treatments of a wide variety of phase transitions. The present objective has been to use measured values of the second- and higher-order elastic constants to provide a quantitative assessment of soft-mode anharmonicity by obtaining the thermodynamic potential of a crystal in the close vicinity of a ferroelastic transition. Comparison between the predicted value of the symmetry-breaking strain induced at the transition with that which actually occurs can then be used to assess the degree of confidence which can be placed in the thermodynamic potential developed in the Landau formalism[1] for a soft-acoustic-mode transition. The vehicle used for the study has been a fcc indium–23-at.%-thallium alloy which at room temperature is close to undergoing a ferroelastic transition driven by softening of $\langle 1\bar{1}0\rangle$ polarized long-wavelength shear acoustic vibrations propagating in a $\langle 110\rangle$ direction. Landau argument predicts first order for this transition — there is a cubic term in the order parameter[2–5] — but the theory can be misleading in this aspect.[6,7] A direct test of first-order character would be to measure changes in entropy ΔS or volume ΔV associated with the structural change. However, such measurements have proved difficult for the fcc-to-fct phase transition in the indium-thallium alloys. Therefore, the thermodynamic potential obtained from the elastic constant measurements has been used to assess the values of ΔS and ΔV to be expected at the transition. To estimate ΔV, the effect of hydrostatic pressure P on the phase-transition temperature T_c is needed: Measurement of dT_c/dP is reported here. This particular measurement resolves another controversial question: Which phase is stabilized by the application of pressure?

Near a phase-transition point, Landau[1] assumed that the thermodynamic potential Φ is a smooth function of thermodynamic parameters and can be expanded as a Taylor series in the order parameter η (a generalized coordinate describing the amplitude of the mean displacements of the atoms from their high symmetry positions):

$$\Phi(P,T,\eta)=\Phi_0+A(P,T)\eta^2+B(P,T)\eta^3+C(P,T)\eta^4+\cdots . \tag{1}$$

For all intents and purposes the transition occurs at constant volume, so the Gibbs and Helmholtz energies may be used interchangeably. Although the theory was constructed for second-order phase transitions, it should also apply to a first-order transition (except in the critical region very close to T_c) which involves small displacements η, i.e., when the third-order invariant B is small. Symmetry adaptation can be achieved by transformation of the elastic strain free energy Φ from finite strain tensor space to an irreducible strain space spanned by six strain tensor components which act as eigenvectors. For this fcc-to-fct phase transition, the appropriate strain free-energy expansion up to fourth order in the order parameter η_1 is[8]

$$\Phi=\Phi_0+\tfrac{1}{4}(C_{11}-C_{12})\eta_1^2+\frac{1}{24\sqrt{3}}(C_{111}-3C_{112}+2C_{123})\eta_1^3 + \tfrac{1}{192}(C_{1111}-4C_{1112}+3C_{1122})\eta_1^4 . \tag{2}$$

Measurement of the hydrostatic and uniaxial pressure dependences of the velocities of ultrasonic modes propagated in monocrystalline In–23-at.%-Tl alloy[5] gives the following values of the required elastic constant combinations at room temperature 291 K, just above T_c (=286 K):

$$\begin{aligned} A&=(C_{11}-C_{12})/4=0.195\times10^9\ \mathrm{N\,m^{-2}} ,\\ B&=(C_{111}-3C_{112}+2C_{123})/24\sqrt{3}\\ &=-19.7\times10^9\ \mathrm{N\,m^{-2}} ,\\ C&=(C_{1111}-4C_{1112}+3C_{1122})/192=5\times10^{11}\ \mathrm{N\,m^{-2}} . \end{aligned} \tag{3}$$

Measurement of these elastic stiffnesses enables exploitation of the Landau approach to develop the thermodynamics of a soft-acoustic-mode transition by calculating first

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the dependence of the strain free energy upon the order parameter $\eta_1[\simeq(c/a-1)$ to first order], which carries the cubic into a tetragonal structure. The potential ϕ as a function of η_1 (Fig. 1) is an asymmetric double well with the lower minimum at $\eta=0$. In the Landau approach, extrema in the invariant under G_0 (the crystallographic group of the higher symmetry phase) are sought. The fct structure should be established with a value of $\eta_{\min}$ determined from the condition of equilibrium (i.e., when the thermodynamic potential Φ is a minimum):

$$\eta_{\text{extrema}}=[-3B\pm(9B^2-32AC)^{1/2}]/8C\ . \tag{4}$$

As T_c is approached, the second-order invariant $\frac{1}{2}(C_{11}-C_{12})$ is found experimentally to decrease with temperature with $\partial[\frac{1}{2}(C_{11}-C_{12})]/\partial T=-1.2\times10^6$ N m^{-2} K^{-1}: the asymmetry of ϕ reduces with the second minimum $\eta_{\min}$ decreasing toward that at $\eta=0$. Immediately below T_c, $\phi(T,\eta_{\min})<\phi(T,\eta=0)$, so that the material jumps discontinuously from the minimum at $\eta=0$ to that at $\eta_{\min}$, i.e., from the fcc to the fct state, this symmetry-breaking Thom catastrophe being driven by the vibrational anharmonicity of the soft mode. In the fct phase close to T_c, the c/a ratio obtained from Debye-Scherrer powder photography is 1.017 ± 0.004; agreement with the calculated value of $\eta_1=\eta_{\min}$ of $+0.0196(\equiv c/a=1.0196)$ near T_c provides some justification for the use of mean field theory.

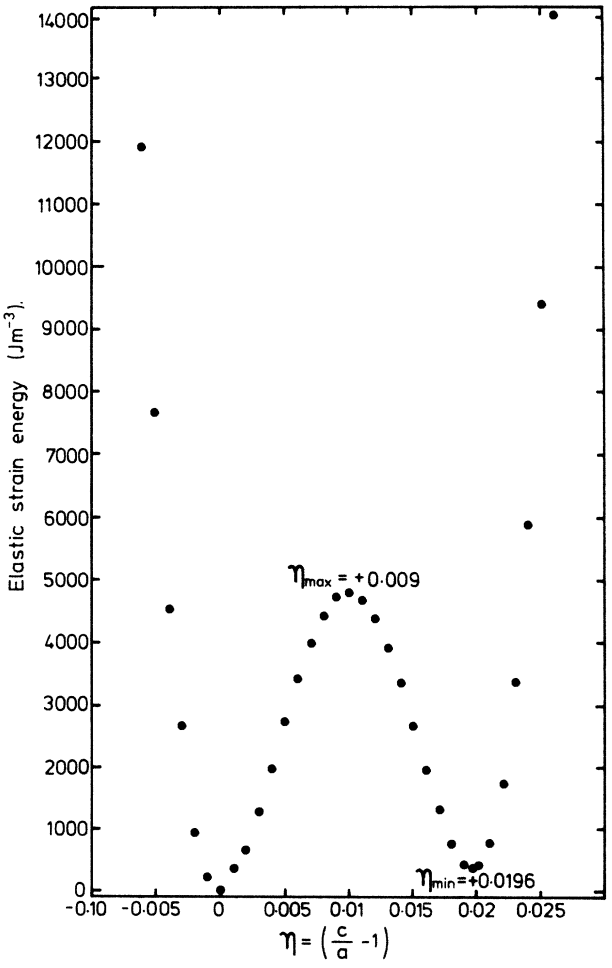

FIG. 1. Variation of elastic strain energy with the order parameter, namely, the strain tensor component which corresponds to the soft-mode eigenvector.

This agreement between the experimental c/a ratio and $(\eta_{\min}+1)$ establishes that the elastic strain energy involved in the anharmonic soft long-wavelength acoustic phonons determines the transition thermodynamics. Hence, neglecting higher powers, the entropy difference per unit mass between the two phases at T_c can be written as

$$\Delta S'=\frac{1}{\rho}\left[\left(\frac{\partial\phi}{\partial T}\right)_{\mu_{\min}}-\left(\frac{\partial\phi}{\partial T}\right)_{\mu=0}\right]$$
$$=+\frac{1}{\rho}\left(\frac{\partial A}{\partial T}\right)\mu_{\min}^2=\frac{1}{4\rho}\left(\frac{B^2}{C^2}\right)\frac{\partial A}{\partial T}\ . \tag{5}$$

Insertion of 0.02 for $\mu_{\min}$ calculated from the values of A, B, and C obtained at 291 K, which is near $T_c(\simeq286$ K), leads to 0.027 K^{-1} for $\Delta S'$. This will be a reasonable approximation to the true transition entropy. The latent heat $T\Delta S'$ is 7.8 J kg^{-1} where $\rho=8449$ kg m^{-3} is the density of the In–23-at.%-Tl alloy. Comparison with the latent heat of melting for ice (22.5×10^5 J kg^{-1}) shows how very small the entropy change is for this transition. Indeed, it is extremely close to the zero value expected for a second-order transition.

To extend the thermodynamic treatment to find the change in volume at the transition, it is necessary to measure the effect of hydrostatic pressure on the transition temperature. Therefore, dT_c/dP has been measured for the 23-at.%-thallium alloy. Ultrasonic wave velocity measurements have been made as a function of temperature and pressure for several modes. After each cycle through the transition was completed, the crystals were annealed at 400 K for 10 h. Hysteresis adds weight to the indications that the transition may be first order.[4,5] A change in slope observed in measurements of hydrostatic pressure dependences of the velocity of the [001] polarized shear mode propagated in the [110] direction at fixed temperatures between 286 and 295 K has been used to obtain P_c (under increasing pressure) at different temperatures (Fig. 2). A straight line least-mean-squares fit gives $+11.8\pm1.3$ K/10^8 Pa (10^8 Pa = 1 kbar) for dT_c/dP. An alloy of similar composition had a T_c of 272 K, and a value of P_c of 1.3×10^8 Pa at 291 K,[5] enabling an estimate of dT_c/dP of about $+14$ K/10^8 Pa. Whether the application of hydrostatic pressure raises or lowers, the transition temperature has caused contention. Does the fcc phase go to the fct phase under pressure, or does the reverse happen? The observation that it is the fcc phase which transforms under pressure[5] is quantified by the data presented here in Fig. 2. However, the results conflict with a sparsely supported indication that the application of pressure has no effect on the transformation temperature, i.e., $dT_c/dP=(0.0\pm0.5$ K/10^8 Pa).[9]

Combination of the values of ΔS and dT_c/dP enables an estimate of the change in volume ΔV at the transition by

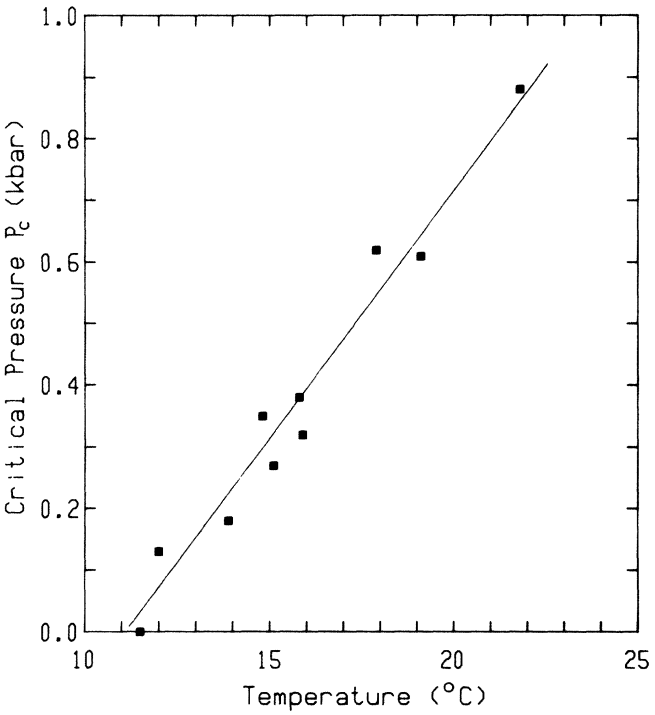

FIG. 2. The effect of hydrostatic pressure on the ferroelastic-phase-transition temperature for an indium–23-at.%-thallium alloy.

using the Clausius-Clapeyron equation

$$\left(\frac{\Delta T_c}{\Delta P}\right)=\left(\frac{\Delta V}{\Delta S}\right)=\frac{\Delta V/V}{\rho\Delta S'} . \tag{6}$$

$\Delta V/V$ is found to be -2.7×10^{-5} on going from the fcc-to-fct modification, a volume decrease which corresponds to length changes of only about 1 part in 10^5: The same magnitude as that expected for the thermal expansion over a temperature range of only a few degrees. The work done per unit mass $(P\Delta V)/\rho V$ in undergoing the phase change at atmospheric pressure is $-3.3\times10^{-4}\,\mathrm{J\,kg^{-1}}$, which may be compared instructively with that $(+1.7\times10^{5}\,\mathrm{J\,kg^{-1}})$ for the ice-water transition. The change in specific internal energy Δu $(=T\Delta S-w)$ is dominated by $T\Delta S$, which accounts for 99.995% of the heat of transformation.

Phase transitions depend upon the phenomenological parameters in a very sensitive manner. Measurements of the invariants of the second-, third-, and fourth-order terms in the order parameter have been used to quantify the thermodynamic potential for this ferroelastic phase transition. The prediction of the correct c/a ratio in the fct phase is evidence that it is sufficient to consider the elastic strain energy alone in treatment of the thermodynamics of the transition. Landau symmetry arguments predict that the transition should be first order because there is a cubic term in the order parameter. However, fluctuations associated with the anisotropy of the tensor for transitions having a second-rank-tensor order parameter (as strain, the order parameter for a ferroelastic transition, is) can result in renormalization of the cubic term.[6,7] The transition can be continuous if the coefficient B of the bare term is small compared with that C of the quartic term. For this crystal B is only 0.039 of the coefficient C, so that fluctuations could induce a continuous transition. In principle, a first-order character for the transition could be firmly established from measurements of ΔS and ΔV. However, a latent heat could not be detected in specific heat measurements made on a 28-at.%-Tl alloy,[10] and a negligible change in volume $(\Delta V/V=0\pm0.003\%)$ has been reported for the transition in a 20-at.%-Tl alloy.[9] The values of ΔS and ΔV predicted here are so small that in reality they may not be measurable with sufficient accuracy to provide a conclusive test of first order. Thus, this transition is so close to having a second-order character that for practical purposes it can be assumed to be so. To prove it to be second order would necessitate the unfeasible determination of zero quantities: $\frac{1}{2}(C_{11}-C_{12})\rightarrow0$ at T_c, $\Delta S=0$, $\Delta V=0$. The observed hysteresis does indicate a slight first-order character, as would the measurement[5] of the coefficient $(C_{111}-3C_{112}+2C_{123})/8$ of -102 ± 8 GPa in this 23-at.%-Tl alloy near T_c, although the proviso mentioned above concerning fluctuations precludes making a definitive statement to this effect on the basis of the existence of a third-order invariant.

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