

Spontaneous strain and the ferroelastic phase transition in As_2O_5

S A T Redfern and E Salje

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

Received 11 June 1987, in final form 12 August 1987

Abstract. The tetragonal–orthorhombic phase transition in arsenic pentoxide has been studied by x-ray powder diffraction and is found to be a proper ferroelastic transition. The spontaneous strain behaves as the order parameter following Landau theory with $\epsilon_s \propto |T_c - T|^\beta$, $\beta = \frac{1}{2}$, $T_c = 578$ K. The order parameter susceptibility has been determined from line broadening and follows $|T_c - T|^{-\gamma}$, $\gamma = 1$. No deviation from Landau behaviour has been observed experimentally.

1. Introduction

Arsenic pentoxide, As_2O_5 , is a binary oxide comprising AsO_6 octahedral chains linked by AsO_4 tetrahedra (Jansen 1978, 1979). The room-temperature orthorhombic form, space group $\text{P}2_12_12_1$ (Schönflies symbol D_2^4), transforms to the tetragonal space group $\text{P}4_12_12$ (Schönflies symbol D_4^4) above 578 K. Bismayer *et al* (1986) describe the driving free energy for the transformation in terms of a Landau expansion of the order parameter, the elastic energy, and direct coupling between the order parameter and the spontaneous strain. The thermodynamic potential is

$$\Delta F = \frac{a}{2} Q^2 + \frac{b}{4} Q^4 + \dots + \lambda Q(\epsilon_2 - \epsilon_1) + \frac{1}{2} \sum_{i,k} C_{ik} \epsilon_i \epsilon_k.$$

If the behaviour at the transition is that of a pure proper ferroelastic, the structural instability would traditionally be described by critical behaviour of the strain components ϵ_i . To minimise the free energy for any value of Q the condition is

$$(\partial \Delta F / \partial Q)|_Q = 0.$$

The elastic constants would be renormalised to become explicitly temperature dependent, driving the transition. If a sublattice distortion of the polyhedral framework is the driving mechanism then Q , the order parameter itself, is used for the description of the transition with the temperature dependence of the potential arising from the prefactor a . This arises from the condition that the crystal is free of stress at any temperature

$$(\partial \Delta F / \partial \epsilon_i)|_{\epsilon_i} = 0.$$

In either case symmetry allows coupling between Q and ϵ which may itself give rise to

the transformation via an explicit temperature dependence of λ . Bismayer *et al* (1986) show that it is possible to distinguish between the third mechanism and the first two by considering the temperature dependence of the elastic constants. Furthermore their Raman observations reveal that softening of optic modes occurs without full recovery in the high-temperature phase. This may indicate that the structural phase transition shows aspects of order–disorder behaviour in addition to the pure displacive model previously considered.

The temperature evolution of the optical birefringence of As_2O_5 has been explained within the scope of Landau theory which was shown to apply over a large temperature interval between room temperature and $T_c - 5$ K, where $T_c = 578$ K (Salje *et al* 1987). There is no evidence of crossover behaviour between order–disorder and displacive behaviour. Landau theory is appropriate, therefore, for the description of this ferroelastic transition and it is suggested that this is due to long correlation lengths in framework structures which limit the temperature interval over which deviations from mean-field behaviour can occur. Although the dynamical properties and the morphic birefringence have been studied in much detail, nothing is known about the basic ferroelastic parameter—the spontaneous strain. This paper reports the results of investigations employing x-ray diffraction to study both the temperature evolution of the spontaneous strain and the variation in correlation length through the transition, and examines the role of acoustic softening as a driving force for the transition.

2. Experimental details

Extremely hygroscopic As_2O_5 powder was loaded into 0.3 mm diameter silica glass capillaries, and sealed under argon. Diffraction experiments were carried out using a Huber 632 heating Guinier powder camera configured to record transmission powder patterns. $\text{Cu K}\alpha_1$ was selected from a bent quartz monochromator. A Huber 633

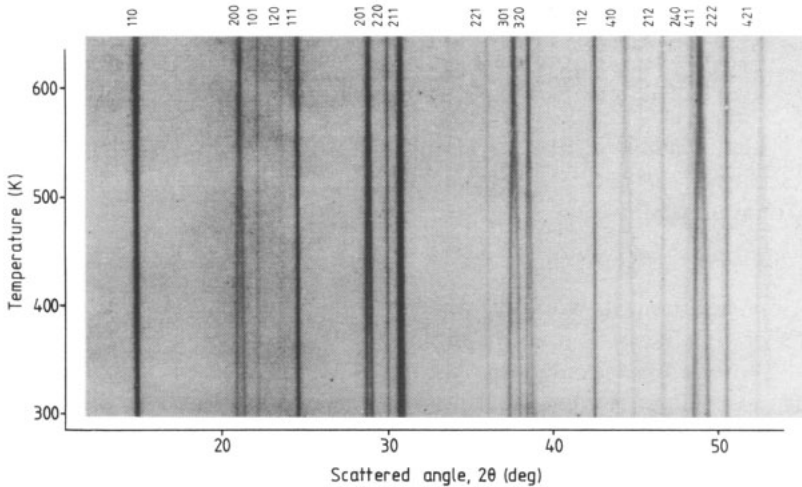


Figure 1. The continuous movement heating Guinier diffraction pattern of As_2O_5 . Reflections in the tetragonal phase have been indexed.

temperature controller allowed relative temperature stability better than 1 K, as measured by a chromal–alumel thermocouple. Exposures were made under isothermal conditions, the controller allowing automatic isothermal conditions, the controller allowing automatic film movement and temperature variation between exposures. The absolute temperature scale was calculated and correction facilitated by measuring known transitions in the temperature range 370 to 700 K. Care was taken to avoid errors arising from fluctuations in thermal gradient through the furnace.

Figure 1 shows a photograph obtained from a continuous heating experiment, which is effectively a plot of line position with temperature. The large spontaneous strain is evident from the obvious peak splitting of pairs of reflections in the orthorhombic phase. Lines showing no peak splitting correspond to those with equal multiplicities in the orthorhombic and tetragonal phases.

Cell parameters were calculated by least-squares refinement of about 20 measured reflections at each temperature, giving one standard deviation error of around 0.0014 \AA in a and b and 0.0007 \AA in c . The temperature evolution of these lattice parameters is shown in figure 2. Line profiles were obtained from scans of exposed films by a Joyce–Loebl microdensitometer. Five densitometer scans were made for the exposure at each temperature and averaged to reduce statistical effects arising from film grain. The densitometer traces shown in figure 3 demonstrate the splitting of the tetragonal 411 reflection into the orthorhombic 411 and 141 reflections through the transition, and show the behaviour of the 222 reflection, which is unaffected by the transition.

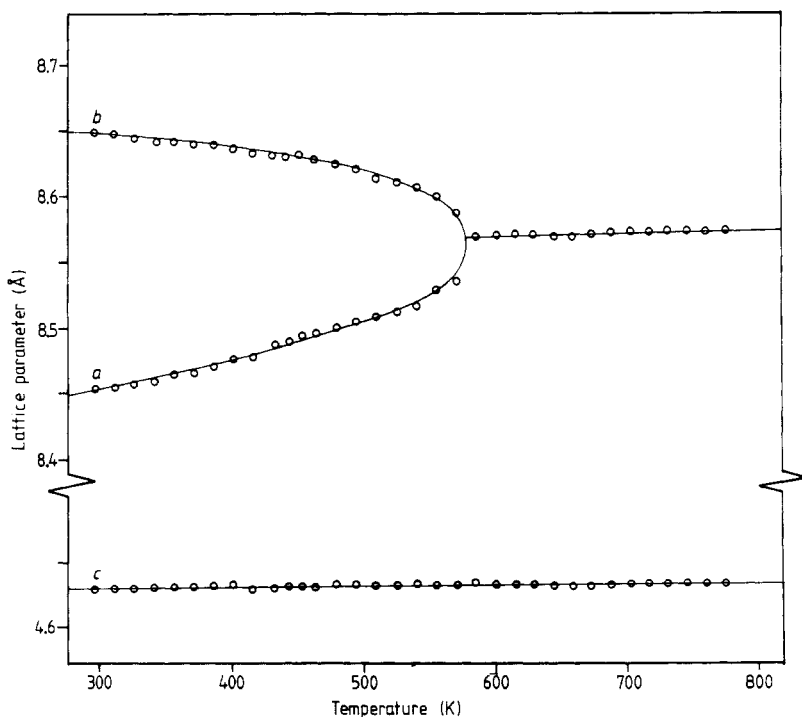


Figure 2. Lattice parameters of As_2O_5 from room temperature to 770 K. The size of each data point indicates the average standard error.

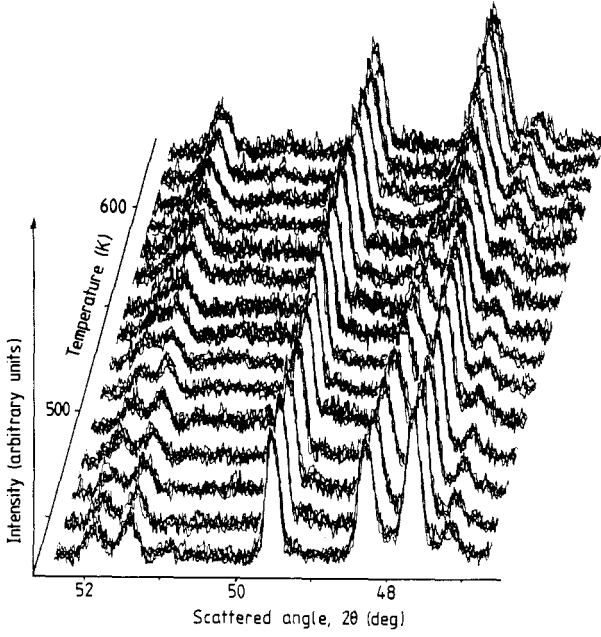


Figure 3. Densitometer traces of As_2O_5 powder x-ray patterns showing peak splitting of the 411 reflection.

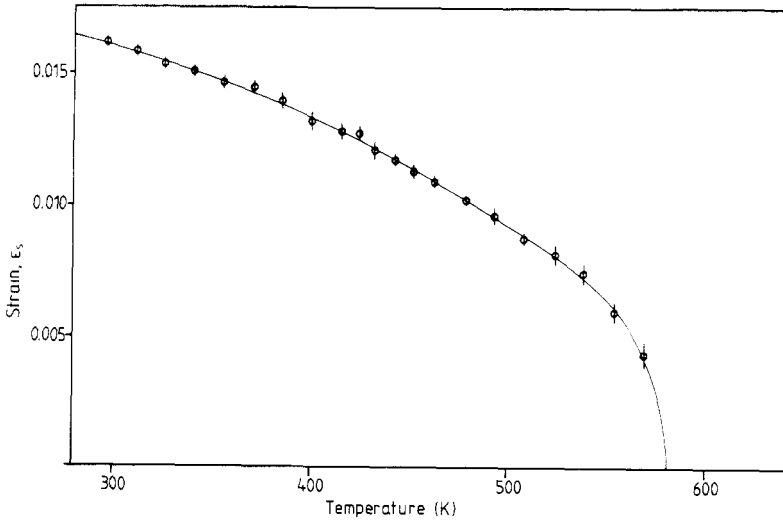


Figure 4. The spontaneous strain of As_2O_5 from room temperature to T_c . Error bars indicate two standard deviations. The full curve shows the strain predicted by Landau theory.

3. Spontaneous strain

The transition from the high-temperature space group $P4_12_12$ to the low-symmetry subgroup $P2_12_12_1$ involves no loss of translational symmetry and is due solely to the critical behaviour of phonons associated with the centre (Γ point) of the Brillouin zone. Bismayer *et al* (1986) give the correlation table between these two space groups showing that the active representation of the order parameter corresponds to the representation B_1 in the supergroup $P4_12_12$. The spontaneous strain must also transform according to this active representation, in other words the symmetry-adapted strain is proportional to $x^2 - y^2$. Hence the form of the spontaneous strain (in Voigt notation) is $\epsilon_s \propto (\epsilon_2 - \epsilon_1)$ or, in the nomenclature of Aizu (1970), $\epsilon_s = 2^{-1/2}|\epsilon_2 - \epsilon_1|$. There are two orientational states of the ferroelastic $P2_12_12_1$ structure with respect to the high-symmetry para-elastic phase. These are denoted S and S' by Aizu, and correspond to the two possible twin domains observed in As_2O_5 with equal and opposite resultant strains.

Applying the approach of Salje *et al* (1985a) it is now possible to determine the twin law for ferroelastic domains in As_2O_5 . The spontaneous strains for the two adjacent twin domains are given by

$$\mathbf{S} = \begin{bmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix} = (\epsilon_1 \ \epsilon_2 \ 0 \ 0 \ 0 \ 0)$$

$$\mathbf{S}' = \begin{bmatrix} -\epsilon_{xx} & 0 & 0 \\ 0 & -\epsilon_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix} = (-\epsilon_1 \ -\epsilon_2 \ 0 \ 0 \ 0 \ 0).$$

At the domain boundary all strain components must be equal. Adopting the arguments of Sapriel (1975) the domain wall is the plane defined by

$$(S_{ij} - S'_{ij})x_i x_j = 0$$

which leads to the condition that $x = y$ or $x = -y$ at the domain boundary. The twin planes are therefore of the form $\{110\}$. According to David (1983) this implies that the soft acoustic modes associated with the transition propagate in the $\langle 110 \rangle$ directions.

The spontaneous strain may be calculated from the lattice parameters measured by x-ray powder diffraction (figure 2). The strains ϵ_1 and ϵ_2 are given by

$$\epsilon_1 = a/a_0 - 1$$

$$\epsilon_2 = b/b_0 - 1$$

where the subscript 0 refers to those parameters expected by extrapolation from the high-symmetry para-phase to the ferroelastic phase. For the transition considered here $a_0 = b_0 = (a + b)/2$; hence ϵ_s is given by

$$\epsilon_s = |(a - b)/(a + b)|.$$

The variation of the spontaneous strain, ϵ_s , with temperature is shown in figure 4. The full curve shows the strain predicted by a Landau potential with critical exponent $\beta = \frac{1}{2}$. We see that the spontaneous strain follows Landau behaviour within the limit or error.

4. Discussion

The temperature dependence of the spontaneous strain in As_2O_5 is in agreement with that expected from Landau theory of the structural phase transition. The good agreement with theory may be related to the restricted directions of propagation of the critical acoustic phonons. The softening is limited to waves in the $\langle 110 \rangle$ directions only. Cowley (1976) points out that in such cases (which he denotes as type I) a continuous phase transition may be expected to occur. Deviations from Landau behaviour result from fluctuations in the order parameter near T_c . As fluctuations become more pronounced and comparable with the value of Q itself and if they extend over distances corresponding to the correlation range ξ then the Ginzburg criterion is no longer fulfilled and Landau theory breaks down. In the case of type I structural instabilities, however, fluctuations of the acoustic phonons are restricted to cones around the two perpendicular directions of wave propagation in k -space, and thus Landau theory will be obeyed even at temperatures close to T_c .

In addition to the onset of spontaneous strain, the phase transition is also reflected by a singularity in the width of those powder diffraction lines that split in the orthorhombic phase. Figure 5 shows the temperature evolution of the linewidth Γ of such reflections, namely the orthorhombic 141 and 411 reflections, which merge to 411 in the tetragonal phase. The observed increase in Γ does not occur for reflections whose Bragg angle does not depend on the order parameter, for example 222, as can be seen in figure 3. Above T_c we observe significant but decreasing line broadening of the tetragonal 411 peak, corresponding to the increasing correlation length of fluctuations beyond that seen by x-rays. The linewidth of the 411 peak falls to that of the original low-temperature orthorhombic peaks. The possible order-disorder behaviour inferred from the non-recovery of the softened Raman mode observed by

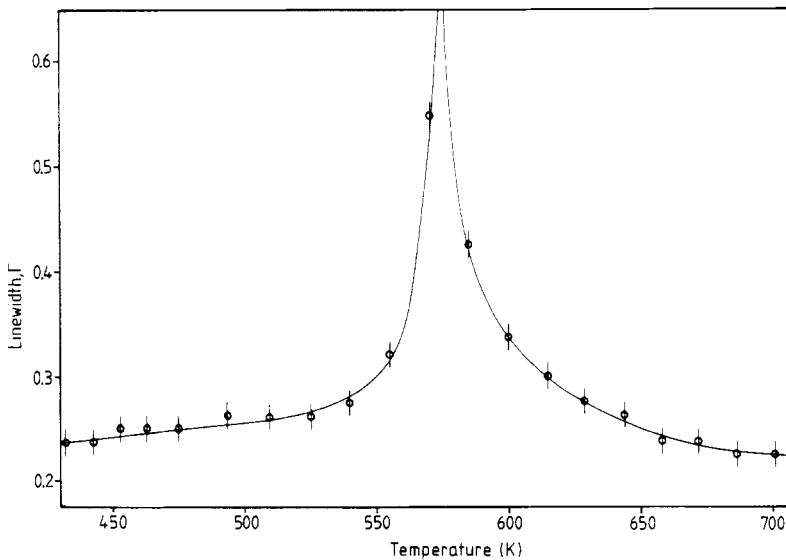


Figure 5. The absolute linewidth, Γ , of the 411 reflection through the transition. Γ is in units of 2θ degrees.

Bismayer *et al* (1986) should lead to broadening of lines in the tetragonal phase, which do we not observe. The broadening may be explained solely in terms of order parameter fluctuations near T_c : the linewidth increases due to inhomogeneous variations of the spontaneous strain, and lines that are independent of the order parameter remain sharp. The correlation length of the fluctuations increases as T_c is approached from below, and becomes comparable with and then greater than the correlation length of the x-rays. The linewidth is therefore directly proportional to the susceptibility χ of the order parameter. Landau theory predicts that the susceptibility shows the temperature dependence

$$\chi \propto |T - T_c|^{-\gamma}$$

and the slope of χ^{-1} against T below T_c is twice that above T_c . The data have been plotted in figure 6 for Γ^{-1} close to T_c and it can be seen that this relationship between the slopes above and below T_c is followed. This corresponds to the critical exponent $\gamma = 1$ as expected for a phase transition following Landau theory. Hence the line broadening is entirely consistent with Landau theory, and results from the expected fluctuations of the order parameter near T_c .

Softening of the $\langle 110 \rangle$ transverse acoustic phonons at the zone centre might be expected to lead to dynamical broadening of the powder lines, but this diffuse scattering would affect all Bragg peaks and we have not been able to observe such an effect. Nevertheless such a phonon instability, resulting in softening of the mode near $q = 0$ as T_c is approached, may be used to describe the driving order parameter. The softening of the acoustic mode may be considered in terms of the elastic constants in the tetragonal form; the transition arises from an instability in the quantity $C_{11} - C_{12}$. In this respect the transition is similar to that observed in DCN (MacKenzie and Pawley 1979), where the phonon dispersion curves have been measured by neutron scattering and are observed to soften. Similar acoustic softening has been observed in s-triazine

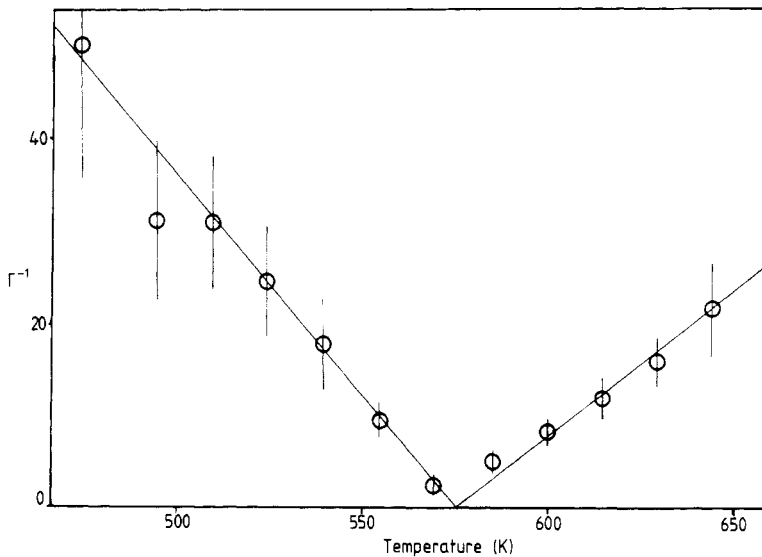


Figure 6. The inverse linewidth, Γ , (corrected for instrumental broadening) for the 411 reflection versus temperature. Γ is in units of 2θ degrees.

(Dove *et al* 1983), where the ferroelastic transition at 198 K is accompanied by significant changes in the dispersion curves above T_c .

The softening of the hard-mode Raman lines observed by Bismayer *et al* (1986) arises from direct coupling between the acoustically driven spontaneous strain and the optic modes. The spontaneous strain behaves as the order parameter, and is proportional to the shift in the hard-mode frequency ($\Delta\omega$):

$$\Delta\omega^2 \propto \varepsilon_s^2 \propto Q^2 \propto (T_c - T)^{2\beta} \quad \beta = \frac{1}{2}.$$

These dependences obviously violate the Grüneisen relation:

$$\Delta\omega/\omega = \gamma_i \Delta V/V$$

where V is the molar volume and ω is the hard-mode frequency. In the orthorhombic phase the cell volume is given by $a \times b \times c$, and the lattice parameters a and b can be expressed in terms of the extrapolated tetragonal parameters a_0 and b_0 ($a_0 = b_0$) as

$$\begin{aligned} a &= a_0 - \alpha(T_c - T)^{1/2} \\ b &= b_0 + \alpha(T_c - T)^{1/2} \\ \Rightarrow V &= c_0[a_0 b_0 - \alpha^2(T_c - T)] \\ \Rightarrow \Delta\omega &\propto \Delta V \propto (T_c - T) \propto \varepsilon_s^2 \end{aligned}$$

which conflicts with the observed result, $\Delta\omega \propto \varepsilon_s$. Hence the Grüneisen relation is not obeyed in the ferroelastic phase of As_2O_5 , where the dilation along b counteracts the contraction along a in the expression for volume.

In conclusion, the x-ray scattering experiments described here imply a transition mechanism in which the spontaneous strain directly reflects the order parameter, and which can be understood as being driven by acoustic mode softening. The transition is correctly described by a Landau model for the free energy with the distortion of the polyhedral framework playing the major role in the transition. In this respect As_2O_5 is a model ferroelastic. Landau theory has also been successfully applied to a number of framework silicates to describe the behaviour of the spontaneous strain (Salje *et al* 1985b, Redfern and Salje 1987). It seems that for displacive transitions in framework structures, Landau theory accurately describes the observed behaviour over most of the range of the reduced temperature scale. This is attributed to the long length scales over which correlated ordering may occur.

Acknowledgments

The authors wish to thank U Bismayer for providing powdered samples of As_2O_5 . SATR acknowledges financial support from the Natural Environmental Research Council. This is Cambridge Earth Sciences contribution number 1024.

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