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An x-ray study of coupling between acoustic and optic modes at the ferroelastic phase transition in As_2O_5

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Abstract. The intensity of the 006 reflection of As_2O_5 has been measured as a function of temperature by single-crystal x-ray diffraction across the proper ferroelastic phase transition at $T_c = 578$ K. The intensity is proportional to $|T_c - T|$ in the low-temperature ($P2_12_12_1$) phase corresponding to second-order Landau behaviour, and vanishes above T_c confirming the previously postulated high-temperature symmetry $P4_12_12$. The structure factor of the 006 reflection has been expressed in terms of the amplitude of a cooperative atomic displacement pattern arising from coupling between the critical acoustic instability and optic phonons.

1. Introduction

Arsenic pentoxide, As_2O_5, is a framework binary oxide exhibiting a pure proper ferroelastic phase transition at $T_c = 578$ K from a high-temperature tetragonal form to a low-temperature orthorhombic form, first reported by Jansen (1979). The high-temperature space group is assumed to be $P4_12_12$ (D_4^4) on the basis of Jansen's comparison of high-temperature x-ray powder diffraction intensities to a postulated high-temperature structure derived from an average of the two orientations of the low-temperature twinned structure (space group $P2_12_12_1$ or D_2^4). No further study has been carried out to test this postulated para-phase symmetry however, although Raman, morphic birefringence, and spontaneous strain behaviour are all consistent with a second-order phase transition between these two space group symmetries (Bismayer *et al* 1986, Salje *et al* 1987, Redfern and Salje 1988).

The phase transition is well described by Landau theory, the spontaneous strain, $\varepsilon_{11} - \varepsilon_{22}$, acting as the driving order parameter (Redfern and Salje 1988). The framework of corner-linked AsO_6 octahedra and AsO_4 tetrahedra (see figure 1) allows correlated distortions over long distances within the structure. This type of displacive phase transition has been considered theoretically by Cowley (1976) and results from acoustic mode softening along $\langle 110 \rangle$ in the tetragonal phase at the Brillouin zone centre as the elastic constants $C_{11} - C_{12}$ go to zero. The polarisation vector associated with these transverse phonons is perpendicular to the wavevector and within the (001) plane. In these respects the phase transition in As_2O_5 is analogous to those found in TeO_2 (Peercy and Fritz 1974) and DCN (Mackenzie and Pawley 1979). Folk *et al* (1976) and Cowley (1976) explain that the limited dimensionality of softening at such a phase transition reduces the volume of phase space in which fluctuations may occur (see figure 2).

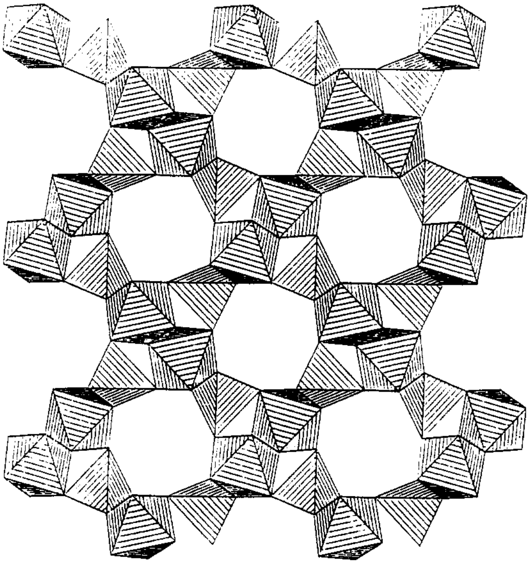

Figure 1. A projection down the z axis of the corner-linked polyhedral framework of As_2O_5, after Jansen (1979).

Together with the long length scale over which correlated ordering operates, this explains the strict adherence to a Landau model for the thermodynamic potential observed between room temperature and T_c. There is no experimental evidence for deviations from a Landau model due to either fluctuations or other coupling effects. Thus As_2O_5 may be described as an ideal 'model' ferroelastic material.

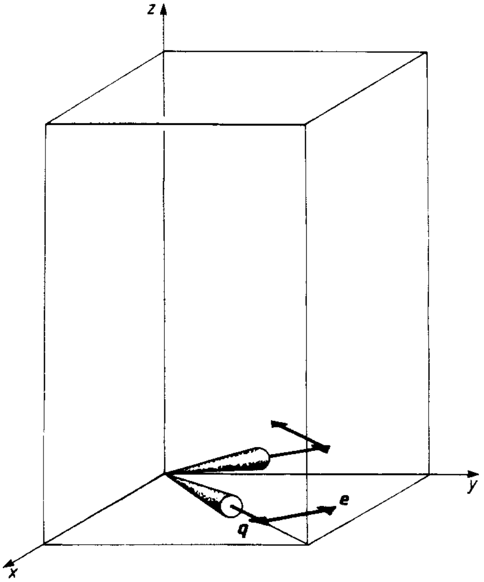

Figure 2. The wavevectors (q) and polarisation vectors (e) of the critical transverse acoustic mode in As_2O_5. Cones indicate regions of critical fluctuations.

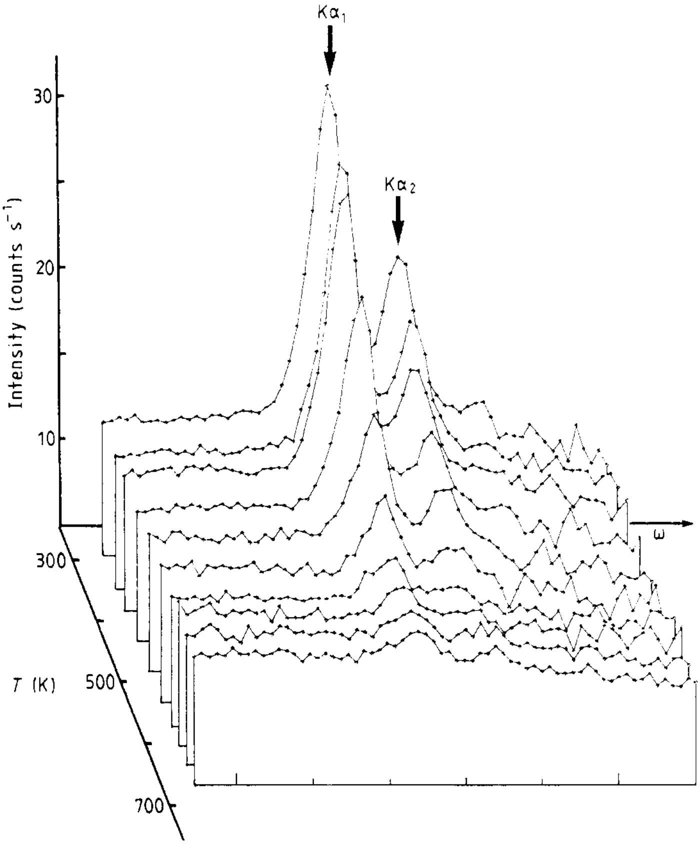

Figure 3. The temperature evolution of typical ω–2θ scan profiles between 26.9°ω and 28.2°ω.

Consideration of the symmetry change $P4_12_12$–$P2_12_12_1$ indicates that Bragg reflections $00l$, $l = 4n + 2$, are prohibited in the high-symmetry phase but may appear in the low-symmetry distorted structure as a result of conversion of the 4_1 axis to 2_1. This paper presents the results of x-ray critical scattering studies of the 006 reflection which further probe the nature of the phase transition and test the validity of the proposed high-temperature space group, upon which all previous work has rested.

2. Experimental details

The single-crystal of extremely hygroscopic As_2O_5 used for x-ray diffraction experiments was relatively large (about 1.5 mm long) and irregularly shaped. This crystal was mounted in a glass capillary of diameter 1.0 mm sealed under dry nitrogen. Diffraction intensities were measured on a Philips PW1100 four-circle diffractometer, using graphite-monochromated Mo Kα radiation with a 0.8 mm beam collimator, and horizontal and vertical detector apertures of 2.0° and 1.5° respectively.

A resistance heater rotating with the χ-circle was centred in the Eulerian cradle giving temperatures between 293 and 665 K at the specimen. A Eurotherm temperature controller allowed a relative temperature stability better than 1 K to be achieved (at a fixed setting of the χ-circle) as measured by a chromel/alumel thermocouple set 1 mm from the specimen. At each temperature the profile of the 006 reflection was measured with continuous ω–2θ scans, recording the integrated intensity at every 0.02° ω. Each profile was obtained by combining a single scan of total width 4° ω and scan speed $0.0005° \mathrm{s}^{-1}$ with several scans of width 1° ω and speed $0.0001° \mathrm{s}^{-1}$—this minimised statistical counting fluctuations. Typical profiles are shown in figure 3.

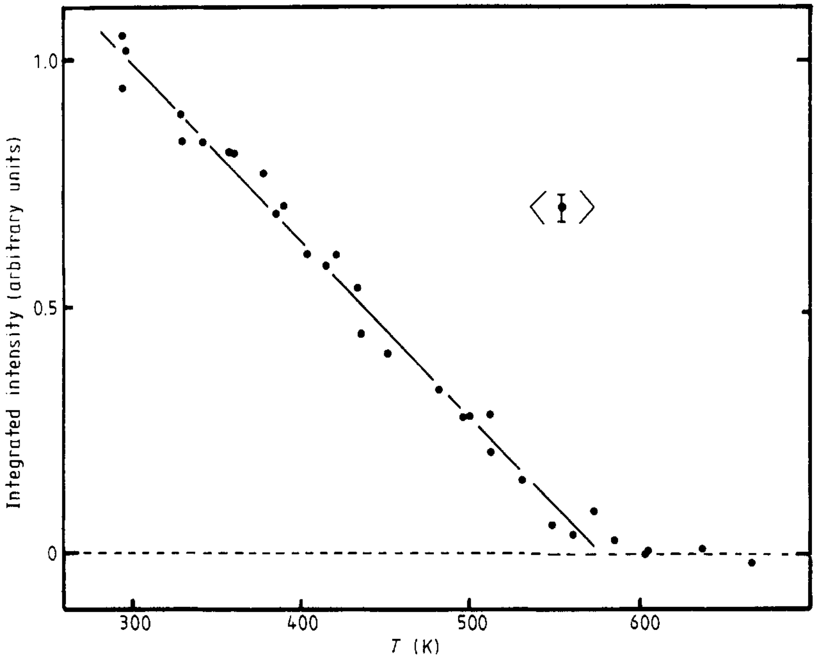

Figure 4. The temperature dependence for As_2O_5 of the integrated intensity of the $K\alpha_1$–$K\alpha_2$ doublet of the 006 reflection. The typical error bar shown indicates estimated 95% confidence limits.

Systematic variations in integrated intensity arose from the instability of the x-ray source as well as slight movements of the crystal inside the capillary (due to the temperature-dependent ferroelastic shape deformation). These errors were eliminated by normalising the background counts for each peak profile with a simple scale factor applied to the whole profile. This simple procedure considerably reduced the scatter of the integrated intensity data, which are shown in figure 4. The temperature dependence of the Bragg intensity below T_c was obtained after the baseline—the averaged background of the four high-temperature measurements (more than 20 K above T_c)—was subtracted from all peak profiles. Profiles were integrated between 27.2° and 27.9° ω to give the results presented in figure 4. Error bars indicate the maximal observed variation of the integrated intensity of single scans at each temperature. Integration of the peak profiles without any correction for background intensity gave practically the same scatter in the data for excess Bragg scattering below T_c when plotted as a function of temperature.

3. Discussion

The theory of x-ray scattering intensities of critical superlattice reflections at displacive phase transitions is well established and was considered by Bruce and Cowley (1981). For soft-mode transitions the structure factor can be expanded in terms of the normal-mode mean amplitudes $\langle Q_j \rangle$ which become non-zero below the transition temperature. In As_2O_5, however, the phase transition is driven by acoustic mode softening along $\langle 110 \rangle$ for $|\boldsymbol{q}|$ tending to the Brillouin zone centre. These acoustic phonons with vanishing small wavevector correspond to a homogeneous deformation of the crystal and the phase factors, $\exp(\mathrm{i}\boldsymbol{S} \cdot \boldsymbol{r}_k)$, for waves scattered from atoms at $\boldsymbol{r}_k$ to the reciprocal-lattice point with scattering vector $\boldsymbol{S}$, are invariant. Hence the pattern of systematic extinctions is not affected by the acoustic mode softening, and critical superlattice reflections are not expected to arise, since in itself a $\boldsymbol{q} = 0$ (Γ-point) instability does not lead to broken translational symmetry.

The symmetry change in arsenic pentoxide, however, implies that there is a change in the screw periodicity of the structure along the z axis (due to the loss of the 4_1 axis) at the phase transition. Atoms within one unit cell are displaced 'out of phase' parallel to the z axis in the low-temperature structure, breaking the $\frac{1}{4}c$ periodicity and giving rise to reflections of the type $00l$, $l = 4n + 2$, below T_c. Thus the cooperative $\boldsymbol{q} = 0$ atomic displacement pattern responsible for the temperature evolution of the 006 reflection described here is of optic character rather than acoustic. Jansen (1979) discussed the relationship between the high- and low-temperature structures, and consideration of the differences between twin-related orthorhombic cells suggests the displacement pattern that is shown in stylised form in figure 5. Octahedral tilts around axes within the $\{110\}$ planes lead to atomic displacements with a component parallel to z, and we can see from figure 5 that these are of optic character, breaking the 4_1 symmetry. The irreducible representation of the symmetry-breaking process is B_1 (Bismayer *et al* 1986).

The mean amplitude of the cooperative atomic displacement pattern $j0$ for wavevector $\boldsymbol{q} = 0$, $\langle Q_{j0} \rangle$, is non-zero in the low-temperature distorted phase. The struc-

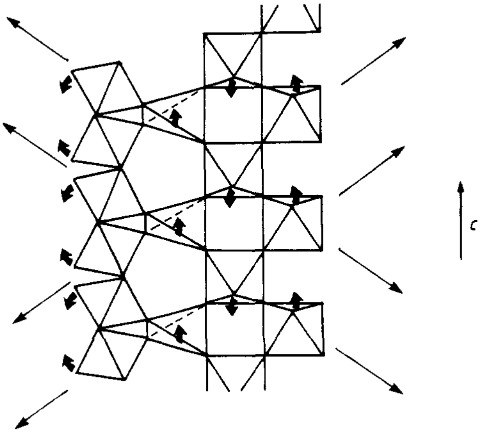

Figure 5. A schematic diagram showing the atomic displacements in the orthorhombic phase of As_2O_5 away from the positions in the tetragonal para-phase. Fine arrows indicate the projections of the polyhedral tilt axes which lie in the $\{110\}$ planes.

ture factor $\langle F(\boldsymbol{S})\rangle$ for elastic scattering at a reciprocal-lattice vector $\boldsymbol{S}$ may be expanded in terms of this (small) amplitude $\langle Q_{j0}\rangle$ of the cooperative distortion mode (Bruce and Cowley 1981):

$$\langle F(\boldsymbol{S})\rangle = F^0(\boldsymbol{S}) + (F_{j0}(\boldsymbol{S})\langle Q_{j0}\rangle + \ldots) \tag{1}$$

where F^0 is the structure factor of the undistorted para-phase. The coefficient $F_{j0}(\boldsymbol{S})$ is given by

$$F_{j0}(\boldsymbol{S}) = \sum_k f_k(\boldsymbol{S} \cdot \boldsymbol{U}_k(\boldsymbol{q}_{j0} = 0)) \exp(\mathrm{i}\boldsymbol{S} \cdot \boldsymbol{r}_k) \tag{2}$$

where the atomic scattering factor f_k is attenuted by the Debye–Waller factor. $\boldsymbol{U}_k$ is the displacement vector of atom k for unit amplitude Q; such that $\boldsymbol{u}_{lk}$, the displacement away from $\boldsymbol{r}_{lk}$ of atom k in unit cell l due to the distortion mode j, is given by

$$\boldsymbol{u}_{lk} = Q_j(\boldsymbol{q}_j)\boldsymbol{U}_k(\boldsymbol{q}_j) \exp(\mathrm{i}\boldsymbol{q}_j \cdot \boldsymbol{r}_l). \tag{3}$$

At reciprocal-lattice points, where $F^0(\boldsymbol{S}) = 0$, the form of the structure factor in equations (1) and (2) implies that new reflections in the distorted phase have an intensity dependent on

$$|F_{j0}(\boldsymbol{S})|^2\langle Q_{j0}\rangle^2. \tag{4}$$

This is the intensity of the reflections of the type $00l$, $l = 4n + 2$, in the low-temperature distorted phase.

The Raman-active optic phonons in arsenic pentoxide have been studied by Bismayer *et al* (1986)—their observations of optic modes of irreducible representation B_1 show that although these modes soften appreciably as T_c is approached from below they do not recover above T_c and none of them is a true soft mode with $\omega^2 \rightarrow 0$ at T_c; the primary order parameter of the transition (η) is not therefore an optic phonon. The atomic displacement pattern considered here results from a combination of the acoustic and optic modes associated with the transition. Rae (1982) has described the proper ferroelastic transition in *s*-triazine similarly. The eigenvectors of the displacement pattern $\langle Q_{j0}\rangle$ do not, therefore, correspond to those of the soft acoustic mode or any optic mode, but to a combination of them all. Because of their low frequency the acoustic modes make only a small contribution to the free energy available to drive the transition, but the incomplete softening of the optic distortions coupling to them is more significant energetically. In this sense although the driving order parameter itself is the acoustic shear (the softening of $C_{11} - C_{12}$), the synergetic influence of the acoustic–optic coupling is most important.

The incompletely softened optic modes and the cooperative distortion $\langle Q_{j0}\rangle$ have the same irreducible representation as the spontaneous strain, and the lowest-order coupling between the optic distortion and η is linear. This linear coupling is responsible for the observation by Bismayer *et al* (1986) that the low-temperature excess frequency, $\Delta\omega^2$, is proportional to $|T_c - T|$. We also expect $\langle Q_{j0}\rangle \propto \eta$ which leads to a predicted dependence for I_{006} of $I_{006} \propto \eta^2$. Indeed the temperature dependence of I_{006} (figure 4) does follow $I \propto |T_c - T|$ below T_c, which is in agreement with the previously reported behaviour of η: $\eta \propto |T_c - T|^\beta$, $\beta = \frac{1}{2}$. There is no significant deviation from this behaviour over the whole temperature range studied. Above T_c the 006 reflection does not appear to be completely absent (figure 3). Because of the lack of profile broadening for this weak residual intensity, we attribute this effect to the persistence of low-temperature domains trapped due to the wedging of the crystal within the capillary rather than dynamical fluctuations of order. These intensity measurements are consistent with all previous measurements of the order parameter behaviour in As_2O_5. Furthermore, the observed temperature dependence of the 006 reflection confirms the postulated high-temperature symmetry (4_12_12).

Acknowledgments

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