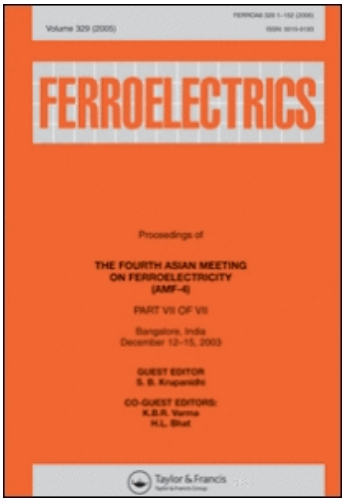

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STUDY OF THE PURELY FERROELASTIC PHASE TRANSITION IN α-Sb_5O_7I BY RAMAN SPECTROSCOPY

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The purely ferroelastic phase transition at 481 K of α-Sb_5O_7I has been investigated by Raman scattering. In the ferroelastic phase a strongly damped soft mode was observed. The temperature variation of several lines, which disappear above T_c, shows that the phase transition is weakly discontinuous. The experimental results and the structural changes of the crystal may be explained by assuming a zone boundary soft mode in the paraelastic phase.

α-Sb_5O_7I (α-SOI) belongs to the recently discovered family of Antimony (III)-oxide-iodide crystals.[1,2] α-SOI undergoes a displacive phase transition at T_c = 481 K in the course of which the space group symmetry is changed from $C_{2h}^5(P2_1/c)$ to $C_{6h}^2(P6_3/m)$. The crystal possesses a centre of inversion in both phases. In the low temperature monoclinic phase (C_{2h}^5) the crystal may exist in three different orientational states or domains. By application of a mechanical stress one state may reproducibly be converted into any other. Thus, according to the nomenclature of Aizu[3] α-SOI is a pure ferroelastic crystal belonging to the full ferroelastic species $6/mF2/m$. The crystal structure of α-SOI in both phases has been determined by Krämer.[4] The change in crystal structure during the phase transition is mainly determined by internal displacements of the iodine atoms, which couple to elastic deformations and yield the ferroelastic properties of the crystal. In the paraelastic high temperature phase the unit cell contains two formula units Sb_5O_7I where the two I-atoms are located along the sixfold hexagonal axis. Below T_c two equivalent I-atoms in neighbouring unit cells are translated alternately in opposite directions normal to the hexagonal axis. These displacements result in a doubling of the unit cell along one of the equivalent twofold axes which are perpendicular to the hexagonal c-axis. An external uniaxial stress of appropriate orientation yields a rearrangement of the I-atoms and changes the spontaneous elastic deformation of the crystal. The doubling of the elementary cell causes the Brillouin zone to be folded normal to a Σ-axis. The zone boundary M-point is reflected into the zone center.

The Raman scattering spectra of α-SOI have been determined at various temperatures. In Figure 1 the spectra below 60 cm^{-1} are shown for scattering configurations corresponding to A_g and B_g representations of C_{2h}, respectively. At 295 K there are four A_g lines: A, A', B, C and four B_g lines: D, D', E, F. At lower temperatures (100 K) the lines A, A' and D, D' are well separated.[5] Raising the temperature the intensities of the lines C, E and F decrease and vanish above T_c. The experimentally determined intensities of these lines at various temperatures up to above T_c are shown in Figure 2. At the low frequency side of the A_g spectrum a strongly damped soft mode indicated by arrows in Figure 1 can be observed in the ferroelastic phase below T_c. Above T_c the frequencies of the lines A', B and D', D coincide and become doubly degenerate modes belonging to the irr. representations E_{2g} and E_{1g} of C_{6h} respectively.

These experimental results and the doubling of the unit cell in the ferroelastic phase may be explained in a consistent manner by assuming a soft mode at the zone boundary M-point of the hexagonal structure which causes the lowering of symmetry. When the temperature drops below T_c this soft mode is translated to the center of the Brillouin zone and becomes an optical phonon of A_g symmetry being observable in the Raman spectrum. It can be shown that there exists a one dimensional little representation at the M-point of the hexagonal structure, which may induce the symmetry change from C_{6h}^2 to C_{2h}^5. The corresponding full space group representation is three dimensional because the

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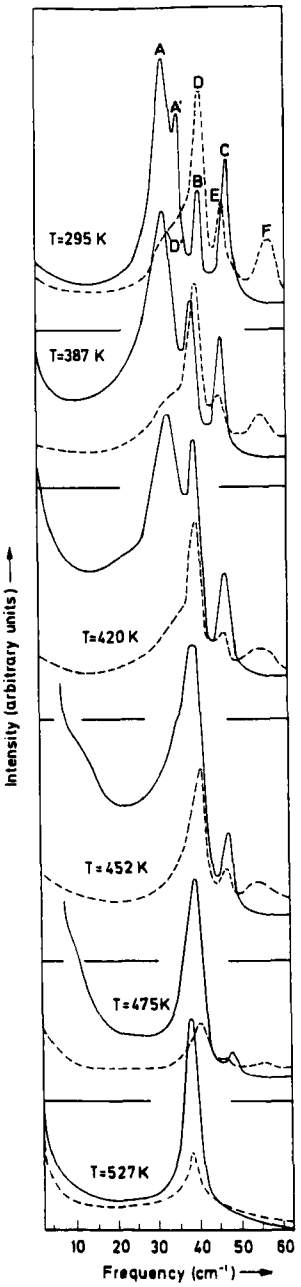

FIGURE 1 Low frequency Raman spectra of α-Sb_5O_7I at various temperatures. Full line: A_g, broken line: B_g.

star of the M-point consists of three k-vectors. We denote the normal coordinates being basis functions of this representation by Q_1, Q_2, Q_3, where the indices refer to the three different vectors of the star of the M-point. The free energy, which is determined by the symmetry of the crystal, contains an interaction term $F_I(u_{ij}, Q_\alpha)$ as a function of the elastic strain tensor and the Q_α. Minimizing the free energy with respect to u_{ij}, F_I leads to the relations

$$u_{xx} - u_{yy} \propto 2Q_1^2 - Q_2^2 - Q_3^2, u_{xy} \propto \sqrt{3}(Q_2^2 - Q_3^2) \quad (1)$$

at zero external stress. Below T_c the thermal average of only one component of Q_α, which we term Q_α^s, differs from zero depending on which M-point is actually shifted to the Γ-point or which domain is realized. The other components remain zero. Inserting Q_α^s successively for $\alpha = 1, 2$ and 3 in (1), we obtain the different irreducible components of the spontaneous deformation $u_{xx}^s - u_{ys}^s$ and u_{xy}^s for the three orientational states of the ferroelastic phase.

The Raman lines C, E and F, which disappear above T_c result either from zone boundary modes, which are shifted to the Γ-point and become Raman active in the ferroelastic phase, or from zone center B_g modes of C_{6h}, which are Raman inactive in the hexagonal structure and will be activated by the spontaneous strain. The temperature variation of the intensities may

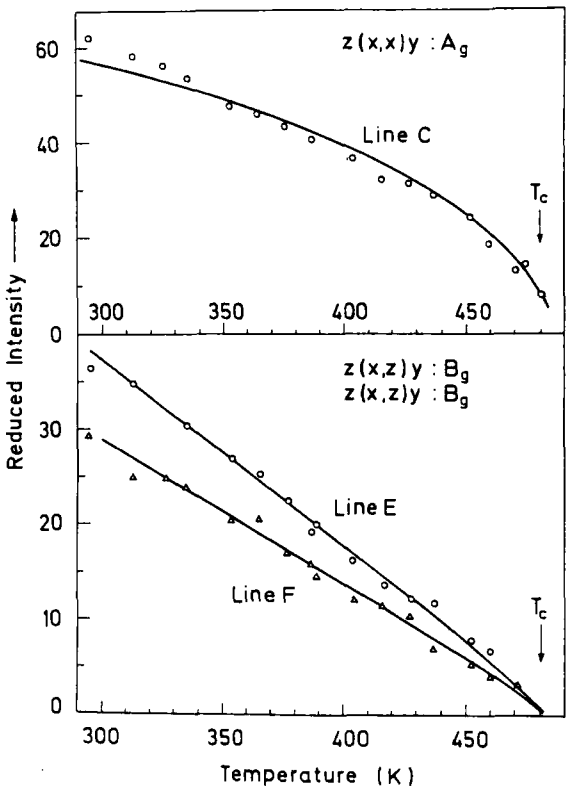

FIGURE 2 Temperature dependence of the reduced intensity $I_{red} = I/(n(\omega) + 1)$ for the lines C, E and F.

be determined by expanding the Raman polarizability P in terms of u_{ij}^S and Q_α^S, respectively. We assume that the expansion coefficients are independent of temperature. Bearing in mind that according to (1) u_{ij}^S is proportional to $(Q_\alpha^S)^2$ we obtain for zone center B_g-phonons $P(\omega) \propto (Q_\alpha^S)^2 Q(\omega)$ and for zone boundary modes $P(\omega) \propto Q_\alpha^S Q(\omega)$, where the $Q(\omega)$ is the dynamical coordinate of the respective phonon. Therefore the reduced intensity $I_{red} = I/(n(\omega) + 1)$ turns out to be proportional to the second or fourth power of the order parameter

$$I_{red} \propto \left\{ \begin{array}{l} (Q_\alpha^S)^4 \text{ for zone center } B_g \\ \\ (Q_\alpha^S)^2 \text{ for zone boundary} \end{array} \right\} \begin{array}{l} \text{phonons being} \\ \text{Raman inactive in} \\ \text{the high tempera-} \\ \text{ture phase.} \end{array} \qquad (2)$$

$I \propto |\mathbf{P}|^2$ is the intensity and $n(\omega)$ the Bose population factor.

Approaching T_c the experimentally determined intensities (circles and triangles in Figure 2) decrease almost continuously. However, the intensity of line C is definitely non-zero at T_c, though it is very small. This shows that the phase transition of α-SOI is of first order with a very small discontinuity of the order parameter at the transition temperature.

Therefore we have fitted the intensity curves to the temperature variation of Q_α^S as it results from the Landau theory for discontinuous phase transitions:

$$(Q_\alpha^S(T))^2 = (Q_\alpha^S(T_1))^2 \{1 + [(T_1 - T)/(T_1 - T_0)]^{1/2}\} \qquad (3)$$

where T_1 and T_0 are the boundaries of metastability of the low temperature and high temperature phases respectively. The results are shown by the solid lines in Figure 2 and agree rather well with the experimental points. The A_g line E is proportional to $(Q_\alpha^S)^2$ and results from a zone boundary phonon of the hexagonal phase, whereas both B_g lines E and F, being proportional to $(Q_\alpha^S)^4$, are Raman inactive optical phonons at the Γ-point above T_c. The temperature interval $\Delta T = T_1 - T_0$, which is a measure of the discontinuity of the phase transition, turns out to be as small as 1 K.

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