Aust. J. Phys., 1983, **36**, 553–63

Structural Transformations and Their Precursors*

T. R. Finlayson

Physics Department, Monash University, Clayton, Vic. 3168.

Abstract

For a number of materials which exhibit a change of structure on being cooled below a certain temperature T_m, some physical properties display anomalous behaviour at temperatures above T_m. The particular structural transformations in mind have been broadly classified as 'martensitic' and the anomalous physical properties as 'precursive phenomena'. Some debate exists regarding the role of the precursive phenomenon in the kinetics of the structural transformation. The most direct evidence for 'martensite precursors' is obtained from electron diffraction, although various indirect evidence is contained in X-ray, neutron and γ-ray diffraction and various physical properties, for example, elastic constants and thermal expansion. In this paper current understanding of 'martensite precursors' is reviewed and examples of data from the A15 structure compounds V_3Si and Nb_3Sn, In–Tl and TiNi alloys are discussed.

1. Introduction

There are various motivations for the study of structural phase transformations ranging from an interest in the fundamentals of crystal bonding to the practical motivation of improving the mechanical properties of steel. Between these two extremes there exist studies of phase transformations stemming from their influence on related physical phenomena such as superconductivity, ferroelectricity or magnetism.

One particular set of structural transformations of interest has been broadly classified as 'martensitic', meaning 'diffusionless and proceeding by shear'. Traditionally the term 'martensite', accredited to Osmond (1894), was used in describing the plate-like microstructure obtained by quenching certain ferrous alloys (Fig. 1). The 'martensitic transformation', being from a face-centred cubic to a body-centred tetragonal structure with a large volume change associated (see last column of Table 1), was a typically first-order transition. More recently the term 'thermoelastic martensite' (Kurdyumov and Khandros 1949) has been used to describe a number of diffusionless transformations in which the associated volume changes are very small and the transitions are approaching second order. Some examples are listed in Table 1. They include the A15 compounds V_3Si and Nb_3Sn, noted for their high superconducting transition temperatures, alloys like In–Tl, which also exhibits

* Paper presented at the Seventh AIP Solid State Physics Meeting, Wagga Wagga, N.S.W., 9–11 February 1983.

0004-9506/83/040553$02.00

superconductivity, and nitinol (an ordered TiNi alloy) a notable shape-memory alloy (Buehler *et al.* 1963). A second set of materials which have been widely studied are those undergoing displacive transformations, many of which exhibit ferroelectricity. Extensive reviews of these are to be found in the recent literature (Nakanishi 1979; Bruce and Cowley 1980).

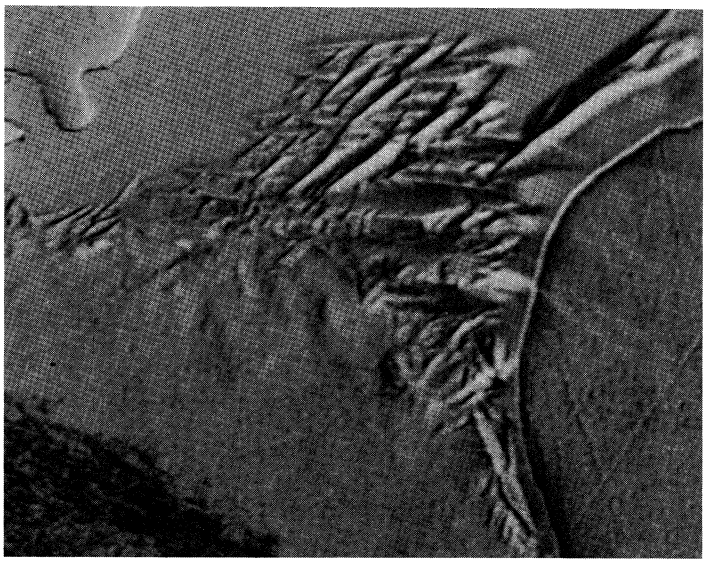


Fig. 1. Plate-like structure of martensite revealed as surface tilts in a polished section of a quenched Fe–Ni alloy. Width of section shown is 2·3 mm. [Courtesy of R. A. Jago.]

Table 1. Materials showing martensitic transformations with their measured transformation strains

	Martensite		
	Thermoelastic		Ferrous
Material	V_3Si, Nb_3Sn	TiNi, AuCd	Fe–Ni
	In–Tl	AgCd, Cu_3Al	Fe–C
	Mn–Cu	Cu–Au–Zn, Au–Ag–Cd	Fe–Mn
	Mn–Ni	Cu–Al–Ni	Fe–Pt
Trans. strain	10^{-4}	$\sim 10^{-3}$–10^{-2}	10^{-1}

Irrespective of one's particular motivation in the study of these phase transformations, one is inevitably led to the questions of how, why and where in the crystal the transformation is initiated, i.e. what happens in the crystal prior to the appearance of the plate-like microstructure which signals the transformation. It is in endeavouring to answer these questions that various physical properties have been studied as a function of temperature. Anomalies in such properties at temperatures in the neighbourhood of the transformation temperature are commonly called 'precursive' or 'premartensite' phenomena. On the basis of the knowledge of such phenomena various theories have been advanced to account for the kinetics of the structural transformations (see Section 3).

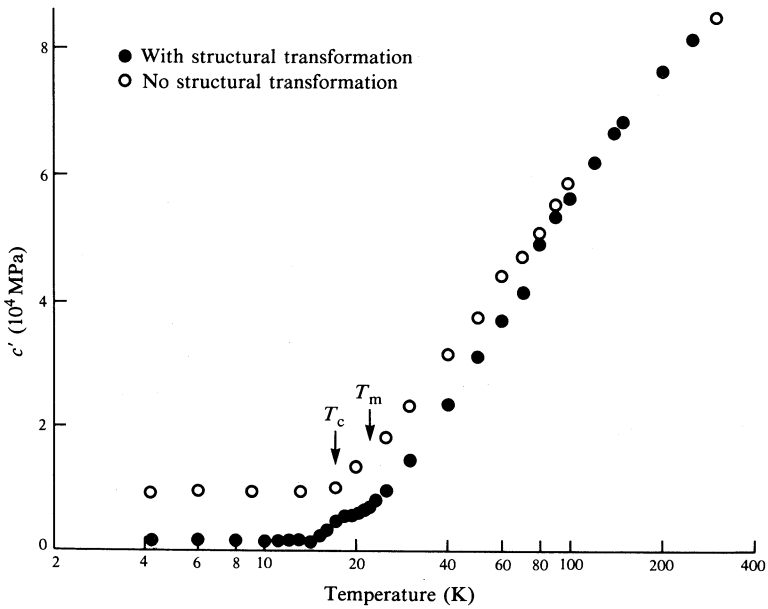


Fig. 2. Temperature dependence of the elastic modulus $c' = \frac{1}{2}(c_{11} - c_{12})$ for transforming (solid circles) and non-transforming (open circles) V_3Si, where T_m and T_c are the structural and superconducting transition temperatures. [From Testardi (1973).]

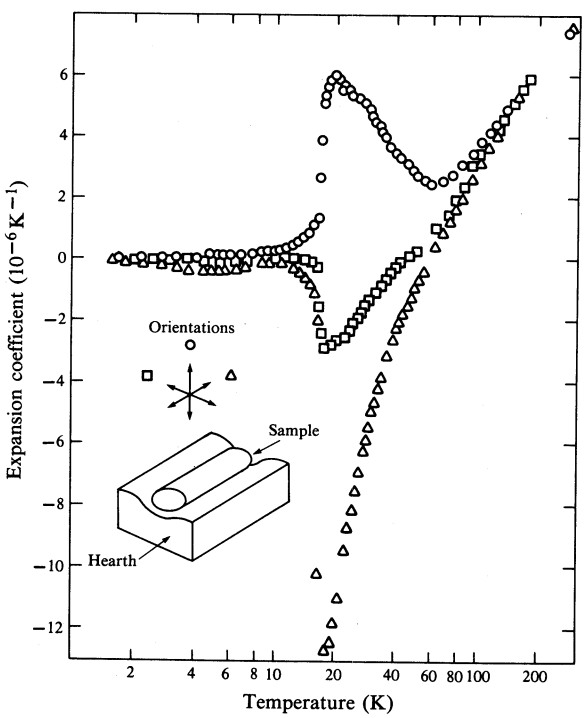


Fig. 3. Linear thermal expansion coefficients for a polycrystalline sample of composition V 25·75 at.% Si measured along the three mutually orthogonal axes indicated.

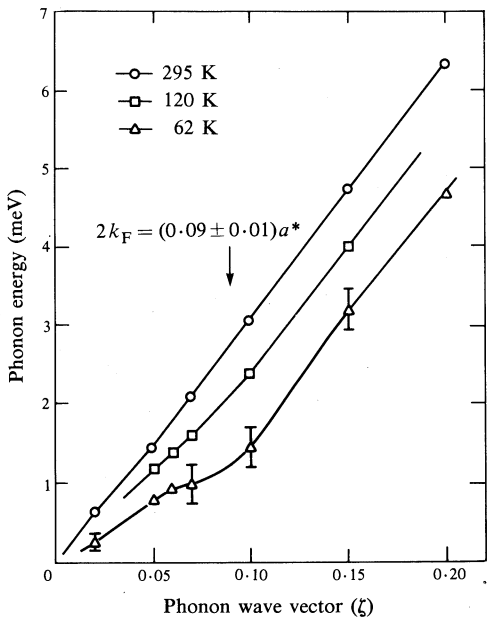


Fig. 4. Phonon dispersion in the [ζζ0] TA_1 mode for Nb_3Sn at three different temperatures. [From Axe and Shirane (1973).]

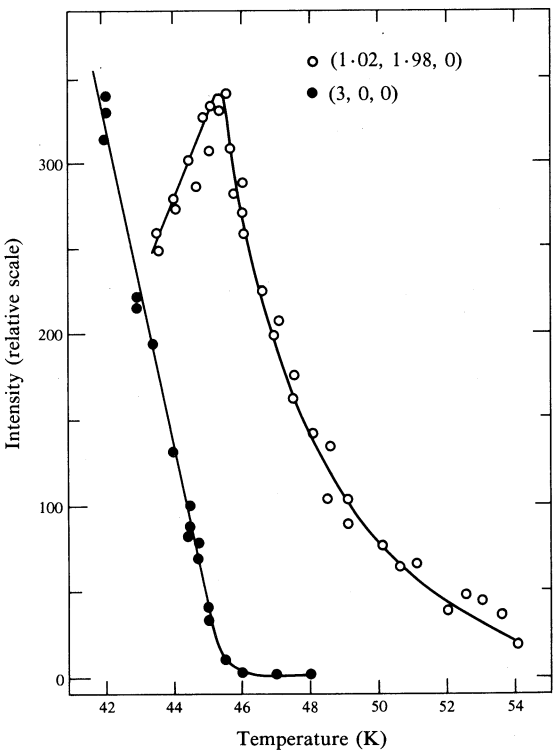


Fig. 5. Temperature dependences of the central peak in the [ζζ0] TA_1 energy spectra (open circles) and the (300) Bragg reflection (solid circles) for Nb_3Sn. [From Axe and Shirane (1973).]

2. Physical Properties

A15 Compounds (V_3Si and Nb_3Sn)

The most dramatic behaviour for the A15 compounds is shown by the shear modulus c' $[= \frac{1}{2}(c_{11}-c_{12})]$, measuring the stiffness of the crystal to $\{110\}\langle 1\bar{1}0\rangle$ shear. As illustrated in Fig. 2 (solid circles), for V_3Si, c' decreases with decreasing temperature towards a temperature T_m ($\sim$21 K) at which a distortion from the cubic to a tetragonal structure has been detected by lattice constant measurements. Surface examination at a temperature below T_m has revealed striations introduced by the transformation and analogous to the plate-like martensite structure (Batterman and Barrett 1966). Pertinent to the debate on precursor effects is the second result shown in Fig. 2 (open circles), which is c' for a non-transforming crystal. For this specimen the lattice softening is said to be arrested by the onset of superconductivity at $T_c = 17$ K. The anomalous mechanical behaviour is not confined to long-wavelength transverse elastic waves, since a marked softening of much of the transverse acoustic phonon branch TA_1 ($\boldsymbol{q} \parallel [110]$, $\boldsymbol{e} \parallel [1\bar{1}0]$) with decreasing temperature has been observed using inelastic neutron scattering measurements (Shirane *et al.* 1971).

Precursive effects have also been found in thermal expansion behaviour of V_3Si (Fig. 3). The data, in this case from a polycrystalline sample (Gibbs *et al.* 1980), show strong anisotropy in thermal expansion at temperatures well above 21 K for measurements made along the three mutually perpendicular directions through the ingot illustrated. Related effects above T_m have also been found in single crystal data (Milewits and Williamson 1978), and have been ascribed to microdomains of tetragonality in the crystal. X-ray diffraction studies on V_3Si by Hastings *et al.* (1979) have revealed anomalous precursive line broadening, which these authors believe to be evidence for 'd-spacing fluctuations' near the surface of the sample.

For Nb_3Sn, which is more favourable for study by neutron scattering than V_3Si (on account of the large incoherent scattering cross section for vanadium), the inelastic scattering results (Axe and Shirane 1973) are most interesting (see Fig. 4). In addition to the overall softening of much of the TA_1 branch one finds a distinct kink at $\boldsymbol{q} \sim (0{\cdot}09 \pm 0{\cdot}01)\boldsymbol{a}^*$ and the emergence of a central peak in the TA_1 mode energy spectra, the intensity of which increases rapidly with decreasing temperature as shown in Fig. 5. The intensity of this central peak reaches a maximum at T_m, indicated here by the appearance of the (300) reflection which is forbidden in the A15 (cubic) structure.

It would not be possible to measure such a precursive central peak for V_3Si. However, a result which seems to be related to this is the anomalous temperature dependence of elastic γ-ray scattering reported recently by Ti *et al.* (1983).

In–Tl

This is one of a series of indium alloys which exhibit 'thermoelastic martensite' behaviour. Alloys in the composition range 15·5–31 at.% Tl form disordered solid solutions which undergo a martensitic transformation from face-centred cubic to face-centred tetragonal structures as the temperature is lowered. The temperature T_m decreases from 425 K at 15·5 at.% to 0 K at $\sim$31 at.% Tl. The geometry of this transformation involves two $\{110\}\langle 1\bar{1}0\rangle$ shears and, as might be expected, c' exhibits a precursive softening (Fig. 6).

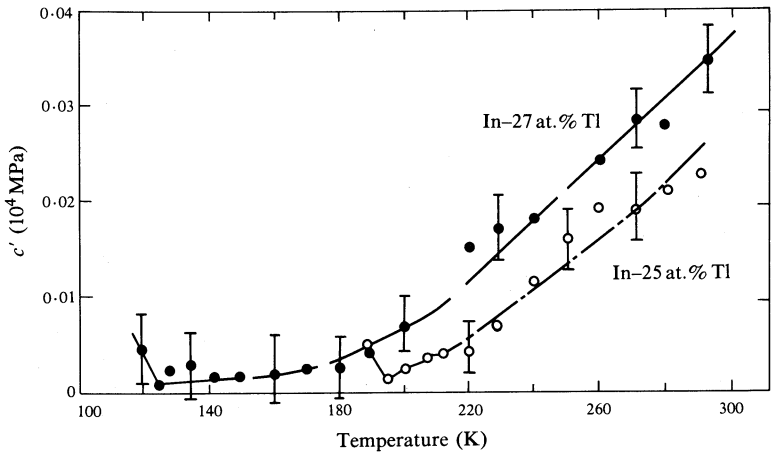
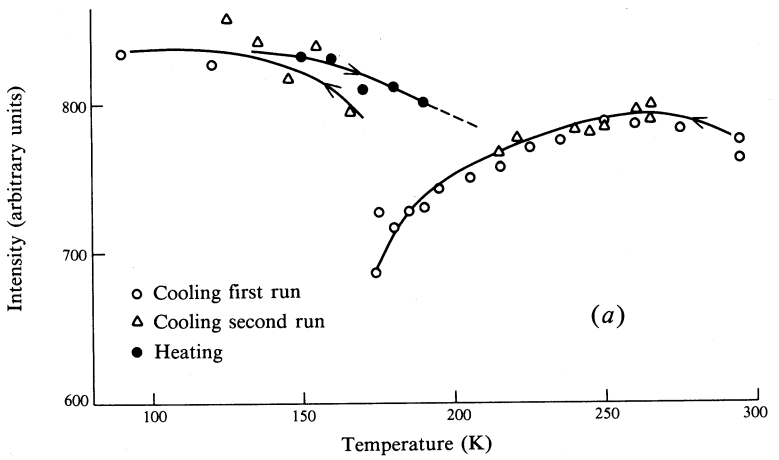


Fig. 6. Temperature dependence of $c' = \frac{1}{2}(c_{11} - c_{12})$ near the transformation temperature in each of two In–Tl alloys. [From Gunton and Saunders (1973).]



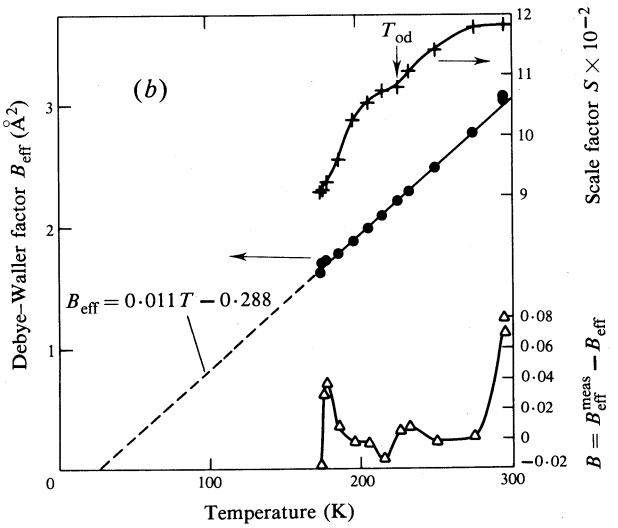


Fig. 7. Neutron scattering data for In–25 at.% Tl: (*a*) Integrated intensity versus temperature for (200) peak; (*b*) Temperature dependences of scale factor S and effective Debye–Waller factor B_{eff}.

Elastic neutron scattering from an In–25 at.% Tl single crystal (Wilkins *et al.* 1983) has revealed an anomalous decrease in scattered intensity with decreasing temperature in the cubic phase, as shown in Fig. 7*a* where the transformation is indicated by the marked discontinuity in intensity. This precursive decrease is also seen in the temperature dependence of the scale factor S shown in Fig. 7*b*, which gives a measure of the amount of material scattering into the Bragg peaks for the cubic phase. An additional anomaly indicated in Fig. 7*b* by T_{od} and believed to indicate an ordering reaction was also discovered. However, because a related anomaly was found for a non-transforming In–33 at.% Tl alloy, this reaction seems not to be a 'martensite precursor'. An anomaly in the vicinity of the temperature T_{od} had been observed in the thermal expansion data for a range of In–Tl crystals by Pahlman and Smith (1968); however, these authors offered no explanation for this additional anomaly. It is noteworthy that it was also found for alloys which did not exhibit the structural transformation indicated by a discontinuity in the expansion coefficient. The effective Debye–Waller factor B_{eff}, shown in Fig. 7*b*, also provides evidence of precursive behaviour above T_m and an anomaly at T_{od}. This behaviour is emphasized in the plot showing the deviation of the measured values B_{eff}^{meas} from the straight line fit of B_{eff} as a function of temperature given in the figure.

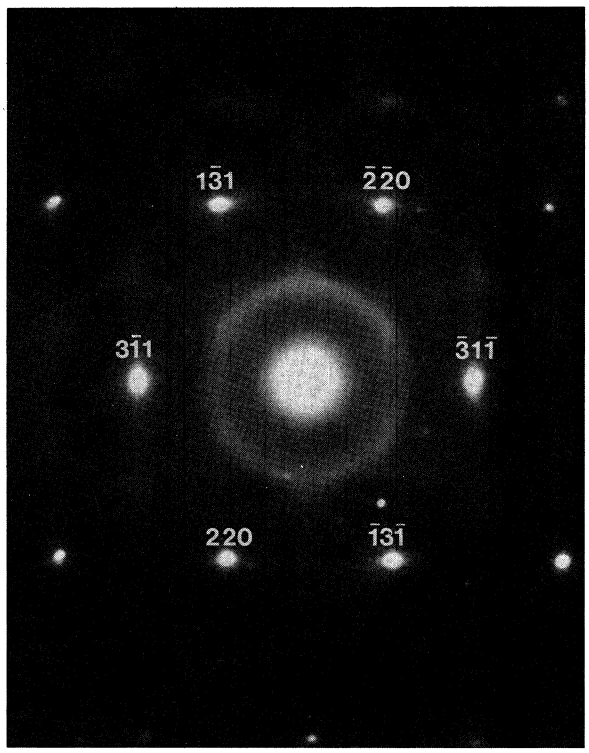


Fig. 8. Electron diffraction pattern from an In–24 at.% Tl crystal showing the two features of diffuse scattering near fundamental Bragg peaks and {110} sheets away from these.

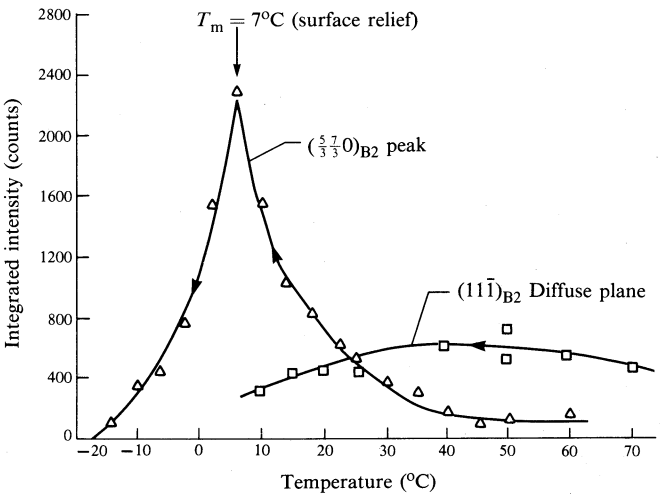


Fig. 9. Temperature dependence of intensities of {111} diffuse scattering (squares) and one-third 110 reflection (triangles) for a TiNi alloy. [From Sandrock *et al.* (1971).]

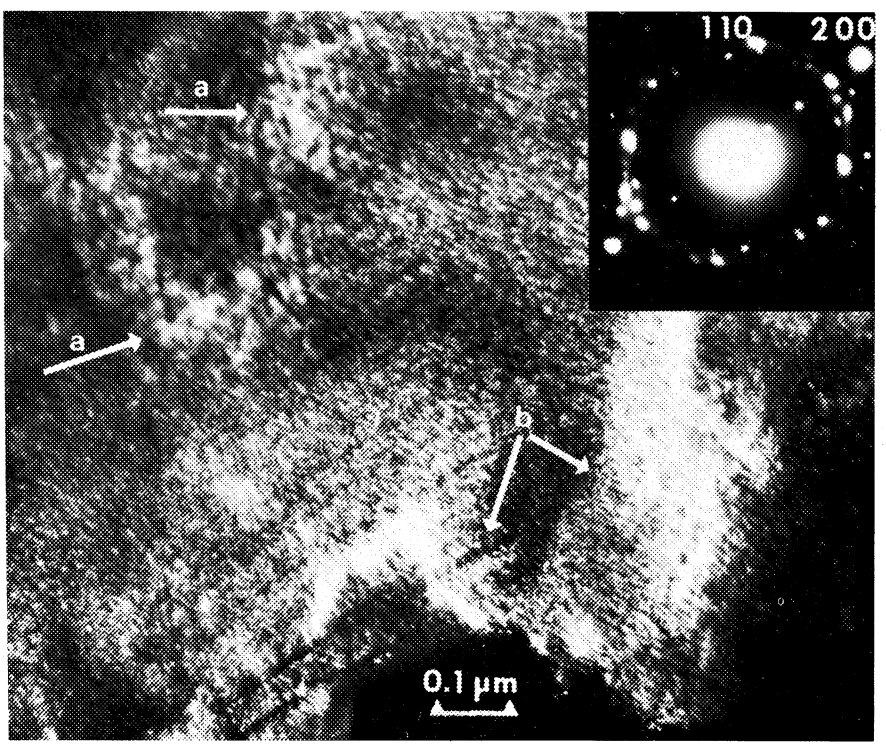


Fig. 10. Dark field image taken using five premartensite reflections. The larger particles correspond to one-third 110 (a) and one-half 100 (b) type reflections, while the smaller particles correspond to the one-half 110 type reflections. [From Moine *et al.* (1982).]

Preliminary electron diffraction data from an In–24 at.% Tl crystal (Norman 1982) indicate two apparently independent features in the premartensite temperature range (see Fig. 8). These are (*a*) diffuse streaks through Bragg peak positions and (*b*) sheets of diffuse scattering away from face-centred cubic reflections and passing through 110 reciprocal lattice positions. There is reason to suggest that feature (*b*) is related to the additional anomalous behaviour at T_{od} in the neutron scattering data, although it has yet to be shown that it is a feature common to the electron scattering from non-transforming alloys. Meanwhile, the feature (*a*) appears to be the real precursive phenomenon in that it is explainable in terms of thermal diffuse scattering arising from the softening of the TA_1 phonon branch.

TiNi

Diffuse streaks are well known in the premartensite range for a number of alloy systems, a most notable one of which is TiNi of approximately equiatomic composition. It has an ordered B2 (CsCl) structure that distorts to monoclinic on cooling below T_m, which is close to room temperature (Sandrock *et al.* 1971). In both X-ray and electron diffraction patterns abnormal diffuse scattering was found lying parallel to {111} B2 planes and passing through fundamental Bragg reflections. This diffuse intensity peaked at ~40°C. At the same time one-third 110 superlattice reflections grew in intensity and peaked at T_m (see Fig. 9). Sandrock *et al.* (1971) interpreted these findings as resulting from oscillations of ⟨111⟩ rows of atoms giving the {111} planes a diffuse intensity. As the temperature is lowered these uncoordinated oscillations become coordinated into plane waves, thus accounting for the discrete superlattice reflections. At a certain value of the strain accompanying these discrete lattice displacements, the discontinuous formation of martensite plates is initiated. Subsequent electron diffraction studies by Sinclair and co-workers indicated that there can be many such extra premartensite reflections (Moine *et al.* 1982) which in general can be accounted for by various lattice displacement waves (Michal *et al.* 1982). They have argued, however, that not all of these waves can be directly associated with atomic movements in the martensite reaction. Dark field imaging using the extra reflections (see e.g. Fig. 10) shows that these displacement waves exist in discrete regions of the crystal about 100–500 Å (1 Å ≡ 10^{-10} m) in diameter.

3. Precursive Effects and Martensite Formation

There is at present some discussion concerning the relationship between precursive effects and the subsequent structural transformation (Wayman 1983). For materials which exhibit transformation in structure, the precursive effects are inevitably observed so it seems impossible to have the 'chicken' without the 'egg'. On the basis of the precursive phenomena, which have inevitably been experimental findings, a number of theories have been proposed to attempt to account for the transformation mechanisms.

Phenomenological Theories

These theories have followed the traditional approach to the theory of martensite formation (Christian 1965) by a minimization of the free energy with respect to lattice strain to determine a critical size for nucleation. Cook (1975) specifically treated the ω transformation in Zr–Nb alloys in this manner but his theory would

seem to be equally applicable to any example involving premartensite displacement waves.

Electronic Theories

Various attempts have been made to account for the phase transformations as direct results of electronic contributions to the free energy of the crystal. For specific cases where the Fermi surface begins to intersect Brillouin zone boundaries, the free energy of the crystal can be lowered by a distortion of the crystal structure. Such an idea has been applied successfully to In–Tl (Novotny and Smith 1965).

Labbé and Friedel (1966) accounted for the phase transformation in the A15 materials via a splitting of degenerate d bands. Their model was later extended by Barisic and Labbé (1967) to calculate the temperature dependence of the elastic constants.

Lattice Anharmonicity

An alternative approach has been to emphasize the phonon behaviour of the crystal and to estimate the anomalous properties on the basis of a highly anharmonic lattice potential (Testardi 1972). The separation of purely electronic and purely lattice contributions to the behaviour of thermoelastic materials is not readily achieved since the two are intimately associated via electron–phonon coupling for which there is very little direct experimental information (Smith and Finlayson 1980).

Defect Theories

A quite different approach has been to account for the macroscopic properties of the crystal in terms of the behaviour of microscopic defects. The model of Varma *et al.* (1974) requires an array of point defects while the theory of Clapp (1973) combines the strain near lattice defects with the anharmonic lattice vibrations to produce localized 'soft-mode' centres. With their defect model Varma *et al.* have offered a plausible explanation for the anomalous behaviour of lattice strain $\Delta a/a$ versus hydrostatic pressure, at room temperature, exhibited by V_3Si (Blaugher *et al.* 1974). In addition Chui (1975) showed that a kink on the transverse acoustic phonon branch resembling that shown on the TA_1 branch for Nb_3Sn (Axe and Shirane 1973) results from a model consisting of vacancies arranged periodically on a two-dimensional square lattice with lattice softening.

This theory is similar to that presently applied to some of the 'soft-mode' ferroelectric materials which exhibit structural phase transitions (Halperin and Varma 1976) and, with the accumulation of experimental data on lattice defects and lattice displacement waves etc. accompanying the increased sophistication of diffraction experiments (Moine *et al.* 1982), these theories are likely to gain in popularity and, perhaps, applicability.

4. Conclusions

A review of recent work on certain thermoelastic martensite materials has revealed precursive phenomena in a number of different physical properties. Despite the different characters of the materials reviewed—the intermetallic compounds V_3Si and Nb_3Sn, the random alloys In–Tl, and the ordered alloy TiNi—there emerges

commonality in behaviour. There is, in particular, the appearance of pre-transformation defects, which appear to be either static or long-lived lattice displacement waves, accompanying an extreme lattice softening.

From the theoretical point of view, no one theory has been able to account for the various precursive phenomena shown by the different materials. However, in view of the commonality in behaviour, the defect theories would seem to be the most applicable.

References

Axe, J. D., and Shirane, G. (1973). *Phys. Rev.* B **8**, 1965.
Barisic, S., and Labbé, J. (1967). *J. Phys. Chem. Solids* **28**, 2477.
Batterman, B. W., and Barrett, C. S. (1966). *Phys. Rev.* **149**, 296.
Blaugher, R. D., Taylor, A., and Askin, M. (1974). *Phys. Rev. Lett.* **33**, 292.
Bruce, A. D., and Cowley, R. A. (1980). *Adv. Phys.* **29**, 219.
Buehler, W. J., Gilfrich, J. V., and Wiley, R. C. (1963). *J. Appl. Phys.* **34**, 1475.
Christian, J. W. (1965). 'The Theory of Transformations in Metals and Alloys', p. 916 (Pergamon: Oxford).
Chui, S. T. (1975). *Phys. Rev.* B **11**, 3457.
Clapp, P. C. (1973). *Phys. Status Solidi* (b) **57**, 561.
Cook, H. E. (1975). *Acta Metall.* **23**, 1027.
Gibbs, E. E., Finlayson, T. R., and Smith, T. F. (1980). *Solid State Commun.* **37**, 33.
Gunton, D. J., and Saunders, G. A. (1973). *Solid State Commun.* **14**, 865.
Halperin, B. I., and Varma, C. M. (1976). *Phys. Rev.* B **14**, 4030.
Hastings, J. B., Shirane, G., and Williamson, S. J. (1979). *Phys. Rev. Lett.* **43**, 1249.
Kurdyumov, G. V., and Khandros, L. C. (1949). *Dokl. Akad. Nauk SSSR* **66**, 211.
Labbé, J., and Friedel, J. (1966). *J. Phys.* (*Paris*) **27**, 153.
Michal, G. M., Moine, P., and Sinclair, R. (1982). *Acta Metall.* **30**, 125.
Milewits, M., and Williamson, S. J. (1978). *J. Phys.* (*Paris*) C **6**, 408.
Moine, P., Michal, G. M., and Sinclair, R. (1982). *Acta Metall.* **30**, 109.
Nakanishi, N. (1979). *Prog. Mater. Sci.* **24**, 143.
Norman, P. (1982). An electron diffraction study of premartensitic effects in In–Tl alloys. M.Sc. Prelim. Thesis, Monash Univ.
Novotny, D., and Smith, J. F. (1965). *Acta Metall.* **13**, 881.
Osmond, F. (1894). *C.R. Acad. Sci.* (*Paris*) **118**, 532.
Pahlman, J. E., and Smith, J. F. (1968). *J. Less-Common Met.* **16**, 397.
Sandrock, G. D., Perkins, A. J., and Hehemann, R. F. (1971). *Metall. Trans.* **2**, 2769.
Shirane, G., Axe, J. D., and Birgeneau, R. J. (1971). *Solid State Commun.* **9**, 397.
Smith, T. F., and Finlayson, T. R. (1980). *Contemp. Phys.* **21**, 265.
Testardi, L. R. (1972). *Phys. Rev.* B **5**, 4342.
Testardi, L. R. (1973). 'Physical Acoustics', Vol. 10 (Eds W. P. Mason and R. N. Thurston), p. 193 (Academic: London).
Ti, S. S., Finlayson, T. R., Smith, T. F., Cashion, J. D., and Clark, P. E. (1983). *Aust. J. Phys.* **36**, 185.
Varma, C. M., Phillips, J. C., and Chui, S. T. (1974). *Phys. Rev. Lett.* **33**, 1223.
Wayman, C. M. (1983). Proc. Int. Conf. on Solid–Solid Phase Transformations (Eds H. I. Aaronson *et al.*), p. 1119 (A.S.M.: New York).
Wilkins, S. W., Lehmann, M. S., Finlayson, T. R., and Smith, T. F. (1983). Proc. Int. Conf. on Solid–Solid Phase Transformations (Eds H. I. Aaronson *et al.*), p. 1235 (A.S.M.: New York).

Manuscript received 29 April, accepted 4 May 1983