A Tribute to Professor 'Jack' Christian

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Abstract. Jack Christian's contributions to the theory of transformations in metals and alloys are distinguished by their lasting value and standard of scholarship. This paper is a short celebration of his far–reaching influence on the theory of martensitic phase transformations.

1. INTRODUCTION

Professor John (Jack) Wyrill Christian died in Oxford on 27 February 2001, at the age of 74. He was one of the greatest representatives of metallurgy and leaves an awesome legacy of scholarly writings, including the inspiring *Theory of Transformations in Metals and Alloys*, the latest editions of which are in press.

As a person, he was modest and courteous to all who were fortunate to meet him, irrespective of status. He always found the time to listen; every response or comment that he made was concise and pregnant with meaning. His immense depth and breadth of knowledge came from his passion for the subject. His favourite subjects were probably martensitic phase transformations, mechanical twinning and the plastic deformation of body–centred cubic metals.

Jack Christian graduated in physics but he pursued the then ill–defined subject of metallurgy to become a Professor of Physical Metallurgy at Oxford in 1967. He was elected Fellow of the Royal Society of London in 1975. The Society was founded in 1660. Its motto, *Nullius in verba*, is an expression of its enduring commitment to evidence as the basis of knowledge about the natural world. The founders of the Society would have been proud of Professor Christian's contributions in this respect.

I first met Professor Christian in 1979 at a conference on phase transformations, held at York University [1], and shortly afterwards at ICOMAT 79 in Boston [2]. My lasting impression of those meetings is the kindness with which he treated me, a mere student, even though there must have been many demands on his time. This paper is a personal view from one who has benefited from his work and from his friendship. Some moving tributes to Jack's life can be found in Hirsch [3] and Taylor & Bowen [4].

2. THEORY

In a complete discussion of the theory of phase changes, the following two questions must be considered [5]:

(i) Why does a particular phase change occur?

(ii) What is the mechanism of the transformation?

To answer these questions requires a combination of thermodynamics, kinetics, crystallography and interfacial structure.

3. THERMODYNAMICS

There is a substantial change in the free energy when martensite eventually forms at the M_S temperature from supercooled austenite; typically $\Delta G^{\gamma\alpha}_{M_S} \doteq -1000\ \mathrm{J\,mol^{-1}}$. Some of this is dissipated as heat, which at high rates of transformation causes recalescence with a consequent change in microstructure. For example, the local heating causes the mode of lattice–invariant shear to change from twinning at the centre of a plate to slip at the peripheries [6]. The *average* rise in the temperature has been measured for Fe–31Ni wt.% to be about 30 °C from –60 °C.

The free energy dissipated is substantially less than that expected from independent thermodynamic data [6]. A large fraction therefore remains as stored within the steel, frequently in the form of elastic strains due to the shape deformation.

In 1958, Christian [7] rigourously derived the strain energy density for martensite as a function of the transformation strains using Eshelby's theory [8] for a constrained transformation in which the phases remain coherent. The elastic strain energy per unit volume (G^e_V) of a transformed region with the same shear modulus (μ) and Poisson's ratio (ν) as the isotropic constraining matrix is given by [7]:

$$\begin{aligned}\frac{1-\nu}{\mu}G^e_V =& \overbrace{\frac{2}{9}(1+\nu)\Delta^2 + \frac{\pi t}{4l}\delta^2 + \frac{\pi t}{3l}(1+\nu)\Delta\delta}^{\text{contribution from volume change}} \\ &+ \quad \underbrace{\frac{\pi}{8}(2-\nu)\frac{t}{l}s^2}_{\text{contribution due to shear}}\end{aligned} \tag{1}$$

where s is the shear strain (typically 0.2), δ (typically 0.03) the expansion normal to the habit plane and Δ the uniform dilatation strain. t and l are the thickness and diameter respectively of the oblate spheroid shape used to represent the martensite plate. It is sometimes difficult for those not involved with martensite to appreciate that the strain energy remains dependent on the plate aspect ratio even when $s = 0$; this arises because δ is directed normal to the habit plane.

For typical values of the parameters in equation 1, the strain energy term of an elastically accommodated plate with $t/l = 0.05$ comes to about 600 $\mathrm{J\,mol^{-1}}$, which is less than typical values of $|\Delta G^{\gamma\alpha}_{M_S}|$. Since this energy is stored as elastic strains in the matrix, it does not contribute to the latent heat of transformation. In a later paper [9], Christian suggested that the calculation may be an overestimate since linear elasticity theory has been applied to deal with large strains; furthermore, the energy may be decreased by plastic deformation or by the formation of self–accommodating packets.

Many martensites contain finely spaced transformation twins. The stored energy per unit volume due to this internal microstructure is approximately σ_t/d_t where $\sigma_t \doteq 0.2\,\mathrm{J\,m^2}$ is the coherent twin–boundary energy per unit area and $d_t \doteq 20\,\mathrm{nm}$ the twin spacing. This gives an energy of about 100 $\mathrm{J\,mol^{-1}}$ [9].

Some martensites contain dense tangles of lattice dislocations and Christian made significant comments about these in his 1979 review [9]. The dislocations are not a necessary feature of the transformation but are probably created by the plastic accommodation of the shape deformation. The consequent reduction in G_V^e must therefore be greater than the extra stored energy due to the dislocation debris. The combined contributions of the elastic accommodation–strains and the dislocation debris to the total stored energy must therefore be equal to or less than that given by equation 1. The value calculated using equation 1 is an upper limit.

The total stored energy thus amounts to about 700 $\mathrm{J\,mol^{-1}}$; clearly, $|\Delta G_{M_S}^{\gamma\alpha}| \geq 700\mathrm{J\,mol^{-1}}$ in order for transformation to occur. The fact that the value of $|\Delta G_{M_S}^{\gamma\alpha}|$ is frequently greater than the stored energy suggests that something different happens at the nucleation stage.

4. KINETICS

Martensite can form at temperatures close to the absolute zero and at speeds approaching that of sound in the metal; the mechanism of nucleation must be consistent with these observations. Random phase and composition fluctuations of the type associated with classical nucleation are not reasonable in these circumstances. The probable mechanism involves heterogeneous nucleation with the dissociation of three–dimensional arrays of dislocations. The faulted structure between the partials becomes the nucleus of martensite when the circumstances are right for the rapid growth of the embryo. In most cases this means that the chemical driving force for transformation must be large enough to allow the partials to propagate rapidly. It is interesting that theories like these are able to explain key observations, for example, that the activation energy for nucleation is related directly to the driving force for transformation.

There have in recent decades been proposals to explain the nucleation of martensite in terms of lattice instabilities. Christian [9] and others [10] have pointed out some inconsistencies in this approach; for example, the elastic constants remain finite at the M_S temperature, and the very morphology of martensite strongly suggests that the whole lattice does not become mechanically unstable. It is still feasible that the strains in the vicinity of a defect induce a small region to undergo a strain spinodal; however, a process like this is not essentially different from the earlier model of heterogeneous nucleation by faulting at arrays of dislocations. In any event, there are so many unknowns associated with these theories that convincing validation or useful application has proved impossible.

5. MECHANISM

Christian's 1951 paper [11] on the dislocation pole–mechanism for the martensitic transformation of cobalt emphasised the role of interfacial structure. Indeed, interfacial structure in general continued to be one of his key interests in the decades that followed [12,13,14].

Christian's assessment of the structure of the martensite/austenite interface leads to considerable constraints on the crystallography of martensitic transformations. It is obvious that the interface must be glissile to be able to move at low temperatures and at high speeds; it must therefore be coherent or semi–coherent. A stress–free coherent interface is rare because the lattice deformation must be an invariant–plane strain. This leaves semi–coherent interfaces in which the interfacial dislocations can glide as the interface moves (dislocation climb would necessitate the diffusion of atoms). It follows that the Burgers vectors of the interface dislocations must not lie in the interface plane unless the dislocations are screws.

A further condition for a semi–coherent interface to be glissile is that the line vectors of the interfacial dislocations must be parallel to that which remains invariant to the lattice deformation. It is otherwise necessary to have multiple sets of non–parallel dislocations to accommodate the misfit, interference between which can render the interface sessile.

It follows that an essential requirement for martensitic transformation is that the lattice deformation which changes the parent into the product phase must leave one or more lines invariant (unrotated, undistorted). A deformation which leaves one line invariant is called an *invariant–line strain* which is the minimum requirement for martensitic transformation.

6. MULTIPLE LATTICE–INVARIANT DEFORMATIONS

There have been attempts to introduce more than one lattice–invariant deformation in the crystallographic theory [15]. In subsequent work it has sometimes not been realised that the deformations cannot be chosen arbitrarily. As pointed out by Christian and Crocker [13], there are in fact restrictions on the allowed combinations. When the lattice–invariant deformation is slip, the slip is accomplished by a set of intrinsic dislocations which are a part of the interfacial structure. To ensure a glissile character, the glide planes of these dislocations with respect to the product lattice must meet the corresponding glide planes of the parent lattice edge–to–edge in the interface, along the dislocation lines.

Multiple lattice–invariant deformations necessitate more than one set of intrinsic dislocations; the sets must either have the same line vector in the interface, or their respective Burgers vectors must be parallel. This condition ensures that the interface can move as an integral unit. It also follows that the net deformation can be described as a single shear on some plane which makes a finite angle with the interface plane, and intersects the latter along the line vector of the resultant intrinsic dislocation.

7. CRYSTALLOGRAPHY

Jack Christian was renowned for his ability to absorb scientific literature. This is typified by the 1955 paper [16], in which he demonstrated the essential similarity of the Bowles and Mackenzie, and the Wechsler, Lieberman and Read theories of martensite crystallography. Indeed, the later surface dislocation model of Bullough and Bilby in 1956 was also shown to be formally equivalent to its predecessors. This is all described in the 1965 edition of Christian's book [17].

The diagrams that Christian used in many of his publications to explain the theory led to considerable clarity in the subject. His procedure, during lectures, of explaining martensite is roughly as follows:

(a) The formation of martensite (α') leads to a shape deformation which is described as an invariant–plane strain (Fig. 1a). This has a large shear component, but also a dilatational strain normal to the habit plane [18].

(b) The observed shape deformation cannot by itself effect the change in lattice [19]. There must therefore be a missing component whose effect is not observed because it is on a macroscopic scale cancelled by an inhomogeneous lattice–invariant deformation (slip or twinning).

(c) The Bain strain on the other hand, is a homogeneous deformation which can alter the crystal structure of the austenite into that of martensite (Fig. 2b). However, the orientation relationship implied by the Bain deformation is not the one observed experimentally.

(d) Martensitic transformation is diffusionless. This requires the α'/γ interface to be able to move conservatively, *i.e.* it must be glissile.

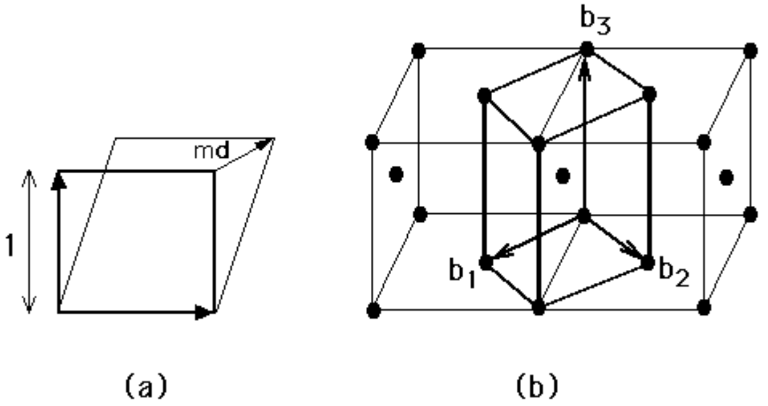

Fig. 2: (a) The shape deformation due to martensitic transformation is an invariant–plane strain. The displacement vector $m\mathrm{d}$ is inclined to the habit plane. (b) It is possible to represent austenite as both a face–centred cubic lattice and one which is body–centred tetragonal. A pure, homogeneous deformation of the latter gives the body–centred cubic or body–centred tetragonal lattice of martensite.

These are the elements of knowledge which led originally to the remarkable mathematical formulations of martensite crystallography. Christian showed that the theories are in essence identical. The basic concepts may be summarised as follows.

The Bain strain **B** converts the structure of the parent phase into that of the product; although it achieves the correct lattice, the Bain strain does not give the correct orientation relationship nor does it ensure a glissile interface. When combined with an appropriate rigid body rotation **R**, the net homogeneous lattice deformation **RB** is an invariant–line strain (step *a* to *c* in Fig. 3). However, the observed shape deformation is an invariant–plane strain $\mathbf{P_1}$ (step *a* to *b* in Fig. 3), but this gives the wrong crystal structure. If, however, a second homogeneous shear $\mathbf{P_2}$ is combined with $\mathbf{P_1}$ (step *b* to *c*), then the correct structure is obtained but the wrong shape since

$$\mathbf{P_1P_2} = \mathbf{RB}$$

These discrepancies are all resolved if the shape changing effect of $\mathbf{P_2}$ is cancelled macroscopically by an inhomogeneous lattice–invariant deformation, which may be slip or twinning as illustrated in Fig. 3.

This theory explains all the observed features of the martensite crystallography. It becomes easy to predict the orientation relationship, by combining the Bain strain with a rigid body rotation to make a net deformation which is an invariant–line strain. The habit plane does not have rational indices because the amount of lattice–invariant deformation needed to recover the correct the macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant–plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an invariant–line strain.

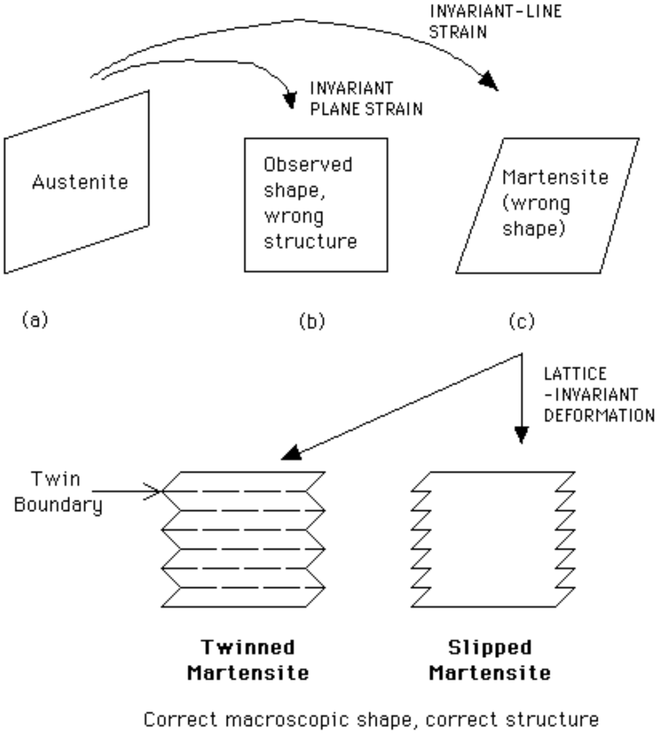

Fig. 3: Schematic illustration of the phenomenological theory of martensite crystallography.

8. PARAMILITARY TRANSFORMATIONS

In attempting to classify transformations, Jack Christian developed original theory which now has wide applicability. He once told me that he borrowed the term ‘military’ transformations from Professor F. C. Frank. A military transformation is one in which the rearrangement of atoms into the new configuration occurs in an orderly and disciplined manner, rather like the case where a queue of soldiers boards a bus without breaking rank (Fig. 4a); martensitic transformations are of this kind. By contrast, in civilian transformations, the atoms move independently from their initial to their final positions (Fig. 4b). The metaphor thus far is useful in visualising the transformation mechanism, but Christian went on to develop it for transformations in which an interstitial solute is much more mobile than the host atoms. The host atoms which define the crystal structure are then transformed by a military mechanism, whereas the interstitial atoms can behave as do civilians. The partial discipline inherent in this process was termed ‘paramilitary’ transformation by Christian [12,20]. In such a process, the movement of interstitial atoms does not affect the macroscopic shape deformation, making diffusion consistent with a displacive mechanism of lattice change. This explains both the mechanism by which Widmanstätten ferrite forms in steels [21] and how some metal hydrides precipitate [22].

9. MORE ABOUT THE SHAPE DEFORMATION

There has been some confusion in the literature about the interpretation of the shape deformation accompanying displacive transformations. Christian has addressed this in a few publications [23,24,25].

Focusing attention on equivalent lattice points which define unit cells of the two structures containing the same number of atoms, a change in shape will accompany transformation if the new set of lattice points can be related to the original set by a homogeneous deformation. Particular vectors, planes and unit cells of one structure are derived from *corresponding* vectors, planes and unit cells of the other structure. There is a lattice correspondence. When interstitial atoms are

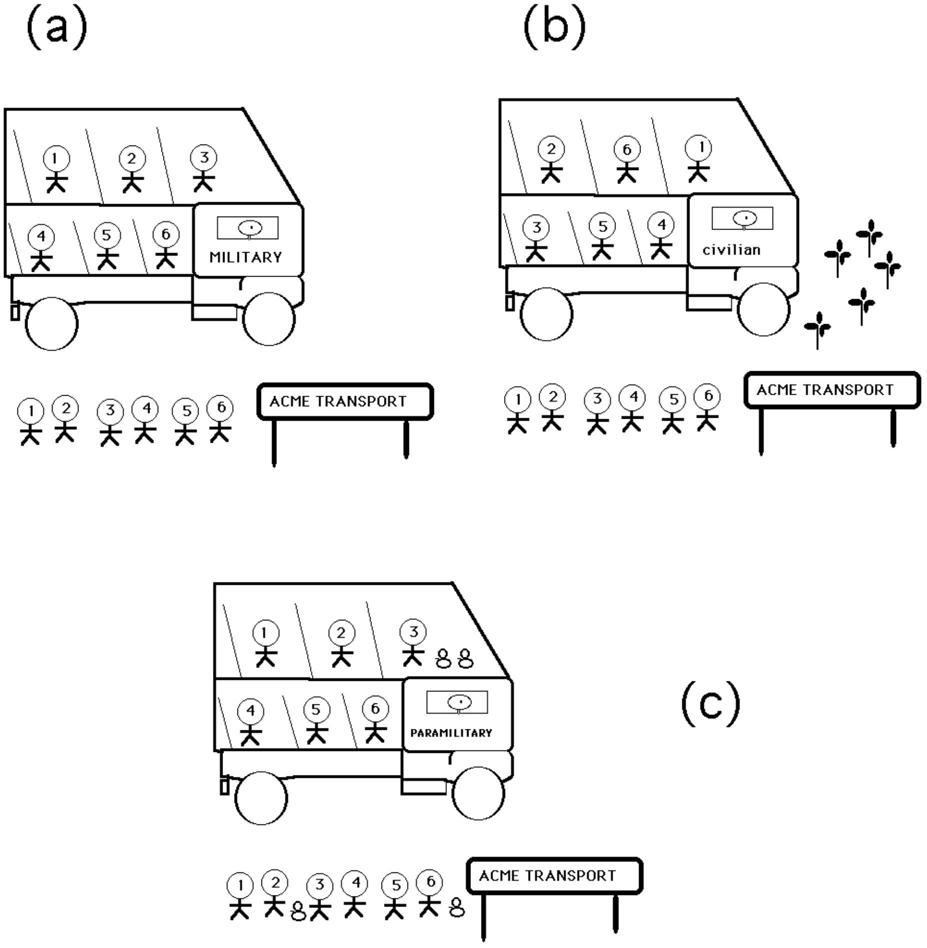

Fig. 4: Metaphors for transformation mechanisms.

present, they may move over large distances without affecting the correspondence.

The implications of the shape change on the mechanism of growth can be illustrated using the virtual operations shown in Fig. 5. A region of the matrix is first removed (leaving behind an equivalent hole) and then allowed to undergo unconstrained transformation with the help of a homogeneous lattice deformation which is not in general an invariant–plane strain (Fig. 5a,b). The particle is then allowed to have any required composition by transferring suitable numbers of solute atoms between interstitial sites in the particle and the matrix, and/or by interchanging atoms of substitutional species in the particle with atoms in the matrix (operation *c*, Fig. 5).

A number of further operations are now possible before the particle is reinserted into the hole in the matrix, in order to reduce the strain energy:

(i) The volume and shape of the particle may be made equal to that of the hole, by transferring atoms over long distances from the particle to sinks within the matrix or at its surface (operation d_1, Fig. 5). The strain energy then vanishes.

(ii) The total number of atoms in the particle may be conserved but its shape may nevertheless be adjusted by the creation and removal of atom sites. The strain energy is effectively that of a hole in the matrix filled with a compressible fluid of different natural volume.

(iii) The shape of the particle may be changed by conservative plastic deformation. The lowest strain energy for a plate–shaped particle then occurs if the plastic deformation converts the lattice deformation into a shape deformation which is an invariant–plane strain (IPS) on

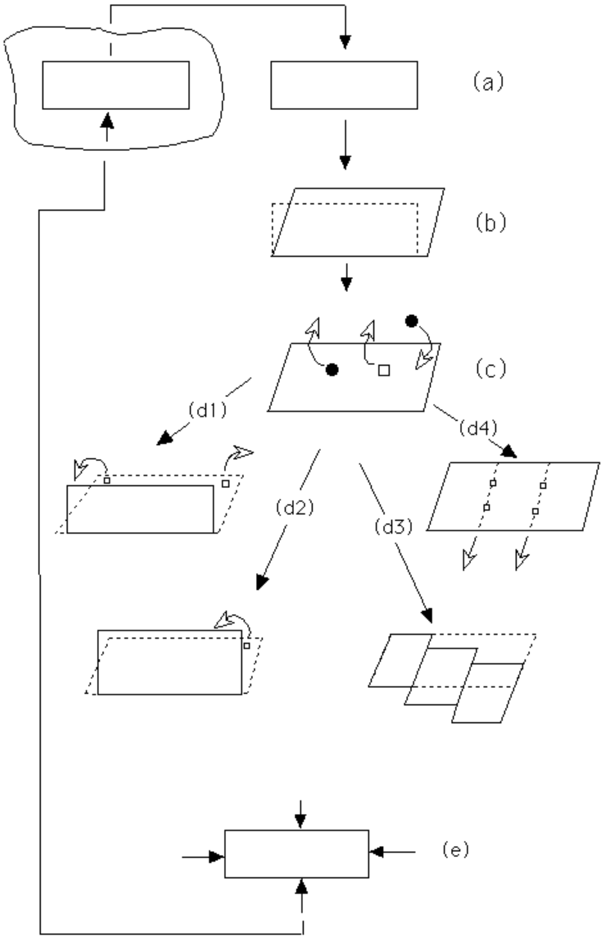

Fig. 5: The virtual operations required to form a particle in a constraining matrix.

the habit plane (operation d_3, Fig. 5).

(iv) The shape of an epitaxially coherent particle may be changed by the removal or addition of particular planes of atoms. If there is no reconstruction of the atom sites, the shape change may retain an appreciable shear component (operation d_4, Fig. 5).

Particles of type d_1 and d_2 require long range diffusion or mass transport. Large scale redistributions of solute atoms can occur during these processes. Transformations of this type are reconstructive. Case (iv) requires the atoms to be mobile for the interfacial dislocations to climb; other diffusion processes may therefore also occur to eliminate the shape deformation [20].

This leaves only the martensitic type change (iii) as a likely candidate for an IPS shape change, but step c (Fig. 5) ensures that the shape change cannot be taken to imply diffusionless transformation. It is easy to see how interstitial atoms can partition between the phases during growth without affecting the IPS shape change. There may also be an interchange of substitutional atoms, but it is likely that the migration of these atoms can only occur over a few interatomic distances – otherwise, any longer range diffusion would destroy the shape change and its associated strain energy at the same time. One implication of the observation of an invariant–plane strain shape change with a significant shear component is that any diffusion of solvent or substitutional atoms during transformation must be absent or minimal.

Suppose that there is an IPS deformation with a large shear and at the same time there is a composition change implying diffusion in the substitutional lattice. Such a transformation has been called diffusional–displacive transformation [23,24]. This does not negate the consequences of the shape deformation, for example the strain energy, the plate shape, the requirement for a glissile interface *etc.* The existence of the shape deformation means that the diffusion flux is not adequate to eliminate the displacive character of the transformation, and furthermore, that most of the atoms must move in a coordinated manner to produce the displacements in the first place. It is a mistake to imagine that the association of diffusion with a phase transformation means that it can be treated as a reconstructive reaction which is close to equilibrium.

10. SUMMARY

This paper is too small to describe the richness of Jack Christian's achievements in the field of martensite. I have, for example, neglected the discussion of his work on the relationship between the O–lattice theory and the crystallographic theory of martensite. But his work is of lasting value; anyone who comes across just one of his papers will inevitably seek out the others, so I need not feel guilty about the selective coverage. It goes without saying that Jack's passing away is a tragic loss to his family and many friends. Nevertheless, I cannot help but feel happy at having known him and to celebrate his work with affection.

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