# **Structural Instabilities in Crystalline Solids**

A thesis

submitted to The University of Melbourne for the degree of

Doctor of Science

by

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## Declaration

I declare that all the statements made concerning my responsibility in the joint works contained in this thesis are true to the best of my knowledge.

J.K. Fulagra

T. R. Finlayson 12<sup>th</sup> December, 2014

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## 1. Introduction

#### (a) **Research interests**

Physical properties of crystalline solids are controlled by their structures and often a significant change in a physical property is a consequence of a structural instability. My original interest in this important area of materials physics was stimulated by the research towards my Ph.D. thesis entitled "Superconductivity and Lattice Softening in Vanadium-Silicon Alloys" (Monash University, 1968). While the particular superconducting material of interest to my Ph.D. project, the A15-structure compound,  $V_3$ Si, is also the topic of some of the research papers to be found in this D.Sc. thesis, it is emphasized that none of the papers which resulted from my Ph.D. research project are included in this thesis.

Structural instabilities can be envisaged on various microstructural scales ranging from the "nano" (or atomic) to the "macro" (as one imagines for multi-phase materials). Thus the physical properties measured and techniques employed to research materials of interest for specific projects have been wide ranging. In the research summary section for each chapter, these properties and techniques have been briefly summarized.

#### (b) Arrangement of publications and comments on responsibility

The thesis has been divided into six subsequent chapters. Each chapter contains:

(a) a summary of the research projects undertaken in the particular area;

(b) a list of the publications included in that area;

- (c) a statement of responsibility for each of the publications listed, in tabular form; and
- (d) the papers in order of publication.

Within each list (b), review papers within that topic area have been identified by inserting the words "Review" or "Invited Review" following the particular list entry. In arriving at a statement of responsibility, each publication has been considered from the point of view of:

- (i) intellectual ideas and the <u>direction</u> (D) of the particular project;
- (ii) the <u>collection</u> (C) of the experimental results;
- (iii) the analysis and interpretation (I) of the results; and
- (iv) the <u>writing</u> (W) of the paper and its administration through to final publication, i.e., dealing with reviewers' reports, etc.

A numerical assignment on a scale 0-10, has been given to each of D, C, I and W, to indicate my personal contribution, and the mean (D+C+I+W)/4 is then listed for each paper in the Table (c). Since review papers generally involve somewhat less inputs for items (i) and (ii), in arriving at a numerical figure for my personal input to publications identified as "Reviews" or "Invited Reviews", I have simply assigned my "I" and "W" inputs, with the mean then being (I+W)/2, such that the maximum possible numerical value for a review publication remains at 10.

A percentage of responsibility is recorded at the end of the Table for (c) above, within each chapter. By calculating the weighted average of these percentage figures, it can be seen that my overall responsibility for the papers presented in this thesis is 39.1% per publication.

#### (c) Acknowledgements

I should like to acknowledge the help and encouragement of my Ph.D. supervisor, Professor Bill Rachinger, whose excellent approach to the supervision of his post-graduate students, from which I benefited, I have endeavoured to follow throughout my academic career. I must also acknowledge the suggestion to me during my early days as a Ph.D. student, by the foundation Professor of the Physics Department at Monash University, Professor Bob Street, to look at the material,  $V_3$ Si, which, at the time, had not long been discovered as a type II superconducting material possessing one of the highest transition temperatures achieved at that time, 17K, but, more importantly, which had been observed to exhibit a change of structure from cubic to tetragonal on being cooled below a temperature of around 21K.

Throughout my research I have been pleased to work with some excellent collaborators. I must acknowledge, in particular, Professor Fred Smith, my long-standing collaborator and friend during much of my academic career at Monash University, Dr. Harold Smith, Oak Ridge, who taught me inelastic neutron scattering during a most rewarding period of Outside Studies Programme at Oak Ridge National Laboratories, Professor Dr. Uwe Klemradt, my German collaborator (now at RWTH-Aachen University) whom I met by chance as he read my poster paper at the International Conference on Martensitic Transformations in Lausanne, Switzerland, in 1995, and Dr. John Griffiths whom I first met at the Central Electricity Research Laboratories (CERL), Surrey, England, where I was a Post-doctoral Research Associate, but who subsequently moved to a research career at Monash University and later, CSIRO in Brisbane.

An integral part of research in the university sector is the training of post-graduate students and I have been privileged to supervise the projects of some excellent students whose individual contributions to my overall research output I must acknowledge. Each of these post-graduate students has been named within the appropriate chapter to which his/her project has contributed to my research output. I am pleased to observe that many of my students have gone on to most successful careers in industry, academia or the government sector. In addition, I have been privileged to recruit some post-doctoral fellows as the result of successful grant applications and these are as follows: Dr. Zbigniev Przelozny (GIRD funding), Dr. Cheryl Lim (Monash University Research Fellowship), Drs. Mao Liu, Yoshi Kuroiwa, Georgie Kelly, Tunay Ersez, Xaodong Wu and Xiangyuen Xiong (A.R.C.).

Finally, I must acknowledge the contributions of my wife, Jill, and family, Kate, Graeme and Jane, to my research output. Successful experimental science often involves days and nights spent in the laboratory, weeks at a time away at a National or International Facility or a Conference. For all of these absences, I have enjoyed the total understanding and support from all at home.

#### 3

## 2. Studies of Type II Superconducting Materials

#### (a) **Research summary**

My academic career began at Monash University following a period as a Post-doctoral Research Associate at the Central Electricity Research Laboratories, Leatherhead, Surrey, England. My initial research was concerned with type II superconducting materials, in particular, various niobium-based alloys, (Publications 2.1 and 2.8), A15-structure materials (V<sub>3</sub>Si, V<sub>3</sub>Ge and Nb<sub>3</sub>Sn), (2.8, 2.9 and 2.11), C15-structure materials (HfV<sub>2</sub> and ZrV<sub>2</sub>), (2.4 and 2.7). a eutectic material, In-In<sub>2</sub>Bi in which directional solidification was successfully applied to control the flux pinning properties of the composite material, (2.3) and various layer-structure materials (TaS<sub>2</sub>, TaSe<sub>2</sub> and PdTe<sub>2</sub>) in which, for some examples, an electronically-driven phase transition is observed at a temperature above the superconducting transition (2.2, 2.5 and 2.10). As the result of a successful application to the Australian Research Grants Committee (A.R.G.C.) (and later just A.R.C.), Professor Fred Smith and I were able to design and install capacitance dilatometry facilities with which we subsequently studied the structural behaviour of many materials as revealed by the measurement of thermal expansion coefficient. (Much of this research is presented in Chapter 3.) Such a measurement is extremely sensitive to the appearance of a structural instability in the sample, but in some cases, the data can also be analyzed via thermodynamics, to reveal both the electronic and lattice contributions to the overall structural behaviour of the material (Publication 2.1).

Dr. Paul Currie undertook his Ph.D. project on the  $In-In_2Bi$  system and in addition to studying the variation in flux-pinning behaviour with microstructural changes in a directionally-solidified system, we found it necessary to correct the In-Bi phase diagram available at that time in the literature and to publish a revised diagram which now appears in the current collection of binary alloy diagrams.<sup>1</sup> Publications 2.3, 2.6 and 2.16 resulted from his project.

During a period of Outside Studies Programme which I spent at the Institute for Precious Metals and Precious Metal Chemistry, in Schwäbisch Gmünd, Germany, as an Alexander von Humboldt Fellow, I studied the superconductivity and microstructure in the C15 structure materials,  $HfV_2$  and  $ZrV_2$ , (Publications 2.4 and 2.7).

Research on layered structure materials formed the basis for the M.Sc. project of Mr. Gerry Bristow (Publications 2.2 and 2.5). At the same time, a Materials Preparation Officer employed in the Department of Physics, Mr. Andrew Vas, successfully grew a large single crystal of PdTe<sub>2</sub>, unique for the existence of superconductivity within an octahedrally bonded, dichalcogenide, crystal structure. This motivated me to undertake the measurement of the lattice dynamics of this crystal as part of the period of Outside Studies Programme spent at Oak Ridge National Laboratories (Publication 2.10).

Following the discovery of high-temperature superconductivity in 1986<sup>2</sup>, I was one of two Principal Investigators on a project funded under the Generic Industrial Research and Development (GIRD) scheme, the goal of which was to research materials for application in a superconducting magnetic energy storage (SMES) device. The project had the industrial

<sup>&</sup>lt;sup>1</sup> Binary Alloy Phase Diagrams – Second Edition eds. T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak (A.S.M., 1990) Vol. 1, pp. 748-51.

<sup>&</sup>lt;sup>2</sup> J.G. Bednorz and K.A. Müller, <u>Z. Phys. B – Condensed Matter</u> 64, 189-93 (1986).

support of the State Electricity Commission of Victoria (SECV) and Olex Cables. My role in this project was the study of the superconducting properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>-based materials which we prepared using both powder metallurgy and thermal and plasma spraying techniques, followed by various heat-treatment procedures (Publications 2.12 - 2.15, 2.17 and We employed critical temperature and critical current density (based on a.c. 2.19). susceptibility and magnetometry) to measure superconducting properties and various microstructural techniques such as X-ray and electron diffraction as well as Raman spectroscopy since the Raman spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> is sensitive to the oxygen stoichiometry. The Ph.D. projects of Drs. David Garvie, Don Lowe and John Long were in this area (Publications 2.12 - 2.13 and 2.17 - 2.19). David Garvie undertook a systematic study of the influence of rare-earth additions to the flux pinning properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (2.17). Don Lowe, who was initially employed as a Research Assistant on the GIRD project, enrolled as a Ph.D. student following changes to the Federal Government regulations controlling GIRD-funded research. He proceeded to investigate the phenomenon of the time dependence of magnetization for A15 structure superconductors (2.18), which, initially, was reported to be a unique property of high-T<sub>c</sub> materials<sup>3</sup> but which I had observed during my own Ph.D. research on V<sub>3</sub>Si and had then researched systematically in a small project (Publication 2.11). John Long's project was focused on the Raman spectroscopy analysis (2.19).

The GIRD funding also enabled me to employ a Post-doctoral Fellow, Dr. Zbigniev Przelozny, who brought to the research an excellent theoretical background on type II superconductivity (Publications 2.13 and 2.14). I was also invited by the editor of the series "Studies in High Temperature Superconductors", Professor Anant Narlikar, to prepare a review article entitled "Flux Penetration and Critical Currents in High-T<sub>c</sub> Ceramics", during this period (Publication 2.15).

## (b) List of papers in order of publication

- 1. Smith, T.F. and Finlayson, T.R., 'Thermal Expansion of b.c.c. Solid Solution Alloys in the System ZrNbMoRe' J. Phys. F: Metal Phys. 6, 709-23 (1976).
- 2. Bristow, G.K., Finlayson, T.R. and Smith, T.F., 'Hall Coefficient Sign Reversals in 2H Transition Metal Dichalcogenides' <u>phys. stat. sol</u>. (b) **82**, K81-4 (1977).
- 3. Currie, P.D., Finlayson, T.R. and Rachinger, W.A., 'Magnetization of a Two-Phase Superconductor: Directionally Grown In-22 at %Bi' <u>Scripta Met</u>. **11**, 59-63 (1977).
- 4. Finlayson, T.R. and Khan, H.R., 'Superconductivity and Stoichiometry in the C15 Laves Phase HfV<sub>2</sub>' J. Less-Common Met. **57**, 237-9 (1978).
- 5. Bristow, G.K., Cornelius, C.A., Smith, T.F. and Finlayson, T.R., 'Hall Coefficient of TaS<sub>2-x</sub>Se<sub>x</sub> Layer Compounds' J. Phys. F: Metal Phys. 8, 2165-71 (1978).
- 6. Currie, P.D., Finlayson, T.R. and Smith, T.F., 'The Phase Diagram for In-rich In-Bi Alloys' J. Less-Common Met. **62**, 13-24 (1978).
- 7. Finlayson, T.R. and Khan, H.R., 'The Superconductivity and Metallurgy of C15 Materials: Hf-V and Zr-V' <u>Appl. Phys</u>. **17**, 165-72 (1978).

<sup>&</sup>lt;sup>3</sup> K.A. Müller, M. Takahige and J.G. Bednorz, <u>Phys. Rev. Lett.</u> **58**, 1143-6 (1987).

- 8. Smith, T.F. and Finlayson, T.R., 'Superconductivity and Lattice Instability' <u>Contemp.</u> <u>Phys.</u> **21**, 265-75 (1980). (**Review**)
- Finlayson, T.R., 'Nb<sub>3</sub>Sn A Special Purpose Electrical Conductor' <u>Metals Forum</u> 8, 3-13 (1985). (Review)
- 10. Finlayson, T.R., Reichardt, W. and Smith, H.G., 'Lattice Dynamics of Layered-structure Compounds: PdTe<sub>2</sub>' <u>Phys. Rev. B</u> **33**, 2473-80 (1986).
- Fraser, J.R., Finlayson, T.R. and Smith, T.F., 'Time-Dependent Magnetization Behaviour for Type II Superconductors - V<sub>3</sub>Si' <u>Physica C</u> 159, 70-4 (1989).
- 12. Finlayson, T.R., Garvie, D.A., Lowe, D.B., Przelozny, Z. and Smith, T.F., 'Critical Currents in Polycrystalline YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>' <u>Cryogenics</u> **30**, 467-73 (1990).
- Przelozny, Z., Finlayson, T.R., Garvie, D.A., Lowe, D.B. and Smith, T.F., 'A Study of Dissipation Mechanisms in High-T<sub>c</sub> Superconductors' <u>Supercond. Sci. and Technol</u>. 4, S433-5 (1991).
- 14. Przelozny, Z. and Finlayson, T.R., 'Thermally Assisted Flux Flow in High T<sub>c</sub> Superconductors' <u>Physica B</u> 168, 236-8 (1991).
- Przelozny, Z., Finlayson, T.R. and Smith, T.F., 'Flux Penetration and Critical Currents in High-T<sub>c</sub> Ceramics' in <u>Studies of High Temperature Superconductors</u>, ed. A.V. Narlikar (Nova Science Inc. 1992) Vol 10, pp. 125-48. (Invited Review)
- Currie, P.D., Finlayson, T.R. and Smith, T.F., 'Magnetization and Flux Pinning Studies of Superconducting In 21.8 at% Bi Eutectic Alloys' <u>J. Alloys and Compounds</u> 183, 288-302 (1992).
- 17. Garvie, D.A., Finlayson. T.R. and Przelozny, Z., 'Flux Pinning Study of  $Y_x(RE)_{1-x}Ba_2Cu_3O_{7-y}$  Superconductors' in <u>Advances in Superconductivity IV</u> Proceedings 4th Symposium on Superconductivity (ISS '91) eds. H. Hayakawa and N. Koshizuka (Springer-Verlag, 1992) pp. 327-30.
- 18. Lowe, D.B. and Finlayson, T.R., 'Modelling the *U-J* Dependency from Magnetic Relaxation Measurements' <u>Supercond. Sci. and Technol.</u> **11**, 1032-5 (1998).
- 19. Long, J.M., Finlayson, T.R. and Mernagh, T.P., 'Measuring Oxygen Stoichiometry in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> by Micro-Raman Spectroscopy' <u>Supercond. Sci. and Technol.</u> **11**, 1137-42 (1998).

#### (c) Statement of responsibility

Paper No.	D	С	Ι	W	(D+C+I+W)/4
2.1	3	2	2	3	2.5
2.2	4	0	3	6	3.25
2.3	4	0	3	4	2.75
2.4	8	10	8	8	8.5
2.5	4	0	3	3	2.5
2.6	4	2	3	4	3.25
2.7	8	10	8	8	8.5
2.8			2	3	2.5
2.9			10	10	10.0
2.10	4	5	4	8	5.25

2.11	7	5	6	6	6.0
2.12	7	2	3	7	4.75
2.13	5	0	3	4	3.0
2.14	5	0	3	4	3.0
2.15			4	5	4.5
2.16	7	0	4	4	3.75
2.17	7	0	3	5	3.75
2.18	5	0	4	5	3.5
2.19	6	0	4	5	3.75

Personal Average Total Responsibility:

85/190 (i.e., 44.7% per publication)

### 3. Materials Exhibiting Martensitic Transformations

#### (a) **Research summary**

The term martensitic transformation has its origins in the phenomenon which occurs in quenched Fe-C alloys<sup>1</sup> whereby the fcc structure of austenite distorts to a fct structure without diffusion, thereby producing "martensite" which is partly responsible for the strength of some steels. However, the name has since been applied to the diffusionless transformations which occur in many materials, including some ceramics. Consequently, there has been much discussion in the literature regarding the precise definition of "a martensitic transformation" and throughout the publications of the proceedings of the ongoing series of International Conferences on Martensitic Transformations (ICOMAT) which have been held approximately every three years since 1979, at least one plenary paper is concerned with this definition of the topic of the conference. The best accepted definition is now<sup>2</sup> "a cooperative motion of a set of atoms across an interface causing a shape change and sound."

As mentioned in the Introduction,  $V_3Si$  undergoes a cubic to tetragonal transformation at 21K, which appears to satisfy this definition and for which c/a > 1. The related A15 compound, Nb<sub>3</sub>Sn, also distorts from a cubic to a tetragonal structure but with c/a < 1 and can have a transformation temperature as high as 60K, dependent on precise stoichiometry. In both of these compounds, a strong degree of anomalous elastic softening is observed in the parent (cubic) phase as the crystal is cooled towards the martensitic transformation temperature. The origin of this phenomenon and its possible relationship to superconductivity, has been a topic of much debate. My research, in collaboration with Professor Fred Smith, in which we were able to apply thermal expansion measurements to study the structural stability of materials as a function of temperature, provided the Ph.D. project for Dr. Ernest Gibbs (Publications 3.7, 3.8 and 3.10) and has been the source of a number of my publications in this area. (Publications 3.1, 3.3, 3.6, 3.29, 3.34, 3.36, 3.37, 3.39, 3.41 and 3.45).

In-Tl alloys with compositions in the range 15.5-31 at% Tl, which exhibit a cubic to tetragonal martensitic transformation, also display pretransformation elastic softening, as measured by the temperature dependence of the elastic modulus,  $c' = (c_{11} - c_{12})/2$ . While the structural behaviour of In-Tl has often been likened to that of V<sub>3</sub>Si, research which I have undertaken which has included direct measurement of the phonon dispersion relations for such alloys, and the temperature dependence for certain phonons, has shown this not to be so (Publications 3.9, 3.14, 3.18 and 3.20). The microstructural behaviour for In-Tl and some related martensitically transforming materials was the Ph.D. project for Dr. Peter Norman (Publications 3.12, 3.13, 3.15, 3.16 and 3.19). Research on In-Tl also provided the basis for some of my involvement in a Japanese-Australian research collaboration funded by the Japanese Ministry of Education (M.I.T.I.) (Publication 3.32) and a further collaboration with Professor Gerhard Barsch, Pennsylvania State University (Publication 3.35). The thermal expansion behaviour for the martensitically transforming materials, In-Tl and Ni-Al, provided the Ph.D. project for Dr. Mao Liu (Publications 3.22, 3.24, 3.27, 3.28 and 3.34). An extension of Dr. Liu's project examined the influence of applied stress on the transformation

<sup>&</sup>lt;sup>1</sup> "A History of Martensite: Early Ideas on the Structure of Steel," C.S. Smith, Chapter 3 in *Martensite* eds. G.B. Olsen and W.S. Owen (A.S.M., 1992) pp. 21-39.

<sup>&</sup>lt;sup>2</sup> For example see P.C. Clapp, *ICOMAT* 95 – *International Conference on Martensitic Transformations Part I* eds. R. Gotthardt and J. Van Humbeeck, <u>J. de Physique IV</u> (Colloque C8) suppl. <u>J. de Physique III</u> 5, C8-11-9 (1995).

microstructure for Ni-Al (Publication 3.47). Related research in this area included a study of the pressure dependence of the FCT-FCC phase boundary in the In-Tl system, using superconductivity (Publication 3.33) and resulted in various invited reviews of such structural instabilities (Publications 3.11, 3.17, 3.21 and 3.34).

Other martensitic alloys which have been the focus of specific research projects have been the C15-structure materials, (Hf,Zr)V<sub>2</sub>, (Publications 3.2 and 3.4) Au-Cu-Zn (Publication 3.38), Au-Cd (Publications 3.42, 3.46, 3.49, 3.51, 3.54 and 3.59) and Ni<sub>2</sub>MnGa (Publications 3.48, 3.50, 3.55 and 3.56). Ni<sub>2</sub>MnGa and a study of the transformation in the crystal surface using grazing-incidence diffraction techniques, was the Ph.D. project for a German student, Dr. Georg Landmesser (Publications 3.48 and 3.56) and included an invited review of martensitic transformations at surfaces and interfaces (Publication 3.53). The application of X-ray photon correlation spectroscopy (XPCS) to study time-dependent effects for the transformation in Au-Cd was the Ph.D. project for a second German student, Dr. Leonard Müller (Publications 3.54 and 3.59). I interacted with both of these students through my collaboration with Professor Dr. Uwe Klemradt.

An aspect of fundamental interest has been the driving force for the martensitic transformations in certain materials and in particular the contribution of the electronic free energy to the overall thermodynamics (Publications 3.5, 3.12, 3.16, 3.52, 3.57 and 3.58).

Lastly in this area, has been my research, in collaboration with Dr. John Griffiths, on magnesia partially-stabilised zirconia (Mg-PSZ). Our research on this material began as a "curiosity" to answer the question "would Mg-PSZ deform (or 'creep') under load, as a consequence of the stress-induced transformation of the monoclinic phase which comprises its complex microstructure?" The answer to this question was clearly, "yes" (Publication 3.31), but the ongoing research provided a Monash University Post-doctoral Fellowship (Dr. Cheryl Lim) (Publications 3.23 and 3.25), created a M.Eng.Sci. project for Miss Anita Gross (Publications 3.25 and 3.31), the Ph.D. project for Dr. Warren Batchelor (Publications 3.26 and 3.30), followed by an industry-supported (APA(I)) Ph.D. project (with ICI Advanced Ceramics) to study the wear of Mg-PSZ for Dr. Georgie Kelly (Publications 3.40, 3.43 and 3.44).

## (b) List of papers in order of publication

- 1. Smith, T.F., Finlayson, T.R. and Shelton, R.N., 'Superconductivity and Anharmonicity in V<sub>3</sub>Si' <u>J. Less-Common Met</u>. **43**, 21-32 (1975).
- 2. Finlayson, T.R., Thomson, K.W. and Smith, T.F., 'Internal Friction in A15 and C15 Superconductors in the Temperature Range 4-150K' J. Phys. F: Metal Phys. 5, L225-9 (1975).
- 3. Smith, T.F., Finlayson, T.R. and Taft, A., 'Anharmonicity and Superconductivity of Nb<sub>3</sub>Sn' <u>Commun. on Phys</u>. **1**, 167-73 (1976).
- 4. Finlayson, T.R., Lanston, E.J., Simpson, M.A., Gibbs, E.E. and Smith, T.F., 'Elastic Properties of (Hf,Zr)V<sub>2</sub> Superconducting Compounds' <u>J. Phys. F: Metal Phys.</u> 8, 2269-78 (1978).
- 5. Cornelius, C.A., Kosach, M.A., Smith, T.F. and Finlayson, T.R., 'Hall Coefficients for A15 Compounds: Nb-Sn and V-Si' <u>Solid State Commun</u>. **28**, 793-5 (1978).

- Smith, T.F. and Finlayson, T.R., 'Anharmonicity in A15 Superconductors: A Thermal Expansion Approach' <u>High-Pressure and Low-Temperature Physics</u>, eds. C.W. Chu and J.A. Woolam (Plenum, 1978) pp. 315-36.
- 7. Gibbs, E.E., Finlayson, T.R. and Smith, T.F., 'Anisotropic Thermal Expansion of Polycrystalline V25.75at%Si' <u>Solid State Commun</u>. **37**, 33-5 (1981).
- 8. Finlayson, T.R., Gibbs, E.E. and Smith, T.F., 'The Low-temperature Thermal Expansion of Polycrystalline V<sub>3</sub>Ge' <u>Physica</u> **108b**, 1011-2 (1981).
- Wilkins, S.W., Lehmann, M.S., Finlayson, T.R. and Smith, T.F., 'Elastic Neutron Diffraction Studies of Martensitically Transforming and Non-transforming In-Tl Alloys' <u>Solid → Solid Phase Transformations</u> eds. H.I. Aaronson, D.E. Laughlin, R.F. Sekerka and C.M. Wayman (A.I.M.E., 1982) pp. 1235-9.
- Finlayson, T.R., Gibbs, E.E. and Smith, T.F., 'The Cubic to Tetragonal Transformation in Vanadium-Based A15 Compounds - A Thermal Expansion Study' <u>Solid → Solid Phase</u> <u>Transformations</u> eds. H.I. Aaronson, D.E. Laughlin, R.F. Sekerka and C.M. Wayman (A.I.M.E., 1982) pp. 1241-5.
- 11. Finlayson, T.R., 'Structural Transformations and Their Precursors' <u>Aust. J. Phys</u>. **36**, 553-63 (1983). (**Invited Review**)
- 12. Norman, P.D., Wilkins, S.W., Finlayson, T.R., Goodman, P. and Olsen, A., 'Premartensitic Phenomena in In-Tl Alloys and the Role of the Fermi Surface' <u>Scripta</u> <u>Met.</u> **18**, 575-9 (1984).
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Paper No.	D	С	Ι	W	( <b>D</b> + <b>C</b> + <b>I</b> + <b>W</b> )/4
3.1	4	3	4	4	3.75
3.2	7	5	5	7	6.0
3.3	4	3	4	4	3.75
3.4	7	2	4	5	4.5
3.5	5	0	4	5	3.5
3.6	5	2	4	4	3.75
3.7	5	2	4	5	4.0
3.8	5	2	4	5	4.0
3.9	5	0	4	5	3.5
3.10	5	2	4	5	4.0
3.11			10	10	10.0
3.12	5	2	3	4	3.5
3.13	5	2	3	4	3.5
3.14	4	7	4	8	5.75
3.15	5	2	3	4	3.5
3.16	5	2	3	4	3.5
3.17			10	10	10.0
3.18	7	7	7	8	7.25
3.19	5	2	3	6	4.0
3.20	7	6	7	8	7.0

#### (c) Statement of responsibility

3.21			10	10	10.0
3.22	5	2	4	5	4.0
3.23	4	0		3	2.5
3.24	5	0	3 3 3 5	4	3.0
3.25		0	3		2.5
3.26	4 5	0	5	5	3.75
3.20	4	2	4	5	3.75
3.28	4	$\frac{2}{2}$		3 5 5 5 7	3.75
3.29	4	2 2	5	7	4.5
3.30		0	5	7	4.25
3.31	5 5 3 5		3	4	3.5
3.32	3	2 2	2		2.25
3.33	5	5	5	2 5	5.0
3.34	0	U	5	7	6.0
3.35	3	2	3	3	2.75
3.36	3 5 5 5 5 5	2	4 5 3 2 5 5 3 3 3	6	4.0
3.37	5	0	4	5	3.5
3.38	5	2	3	3	3.25
3.39	5	2	4	3 7	4.5
3.40	6	2	4	4	4.0
3.41	Ũ	-	5	5	5.0
3.42	5	2	4	4	3.75
3.43	7	0	5	5	4.25
3.44	7	ů 0	5	5 5	4.25
3.45		Ũ	5	8	6.5
3.46	7	2	5 5 5 5	7	5.25
3.47	7	0	5	7	4.75
3.48	5	2	4		4.0
3.49	7	0	4	5	4.0
3.50	5	0		5 5 3 5 3	2.75
3.51	5	1	3 3 3	5	3.5
3.52	4	0	3	3	2.5
3.53	-	-	7	8	7.5
3.54	5	0	3	3	2.75
3.55	7	ů 0	5	7	4.75
3.56	5	1	3	5	4.5
3.57	3	1	2	2	2.0
3.58	5 7 5 3 3 2	0	3 5 3 2 2	3 7 5 2 2 2	1.75
3.59	2	0	2	2	1.50

Personal Average Total Responsibility:

254.75/590 (i.e., 43.2% per publication)

## 4. Studies of Stresses in Polycrystalline Materials

#### (a) **Research summary**

The extension of my research into this area evolved quite logically from an experimental development in my research on the A15-structure materials whereby, during the measurement of the thermal expansion coefficient for such materials, they were found to exhibit anisotropy in thermal expansion within their parent (cubic) phase. Clearly this is not possible on thermodynamic grounds, and gave rise to the suggestion initially put forward in Publication 3.7 that such anisotropy could arise via a coupling between a residual stress field and strongly temperature dependent elastic compliance components as are observed in many A15 materials.

At the time, the creation of facilities to measure residual stresses non-destructively by diffraction techniques (using laboratory X-rays and neutrons at the Australian Research Reactor, HiFAR) and the application of these facilities to various materials became the Ph.D. project of Dr. Peter Lambrineas. Scholarship supplementation for this project was awarded by BHP whose interests, quite naturally, were residual stress measurements in steels (Publications 4.1 and 4.2). The original neutron facility involved a modification to the recently commissioned high-resolution neutron powder diffractometer (HRPD)<sup>1</sup> which was found to have sufficiently good resolution for the measurement of residual strains in engineering materials. Consequently, a facility was designed and built, as part of the Ph.D. project of Dr. Lambrineas, for addition to the HRPD at HiFAR. (It was subsequently used for an Honours project for Mr. Andrew Johnston (Publication 4.3).) At the time, neutron strain scanning facilities were being developed at reactors overseas<sup>2</sup> but in our case, we chose to adopt the X-ray "sin<sup>2</sup> technique"<sup>3</sup> as the basis for our neutron residual strain (stress) measurements. The laboratory facility designed and built as part of this Ph.D. project subsequently became the source of a certain amount of contract work to measure residual stresses in engineering materials, under my supervision at Monash University.

My subsequent publications concerned with the measurement of residual stress fields in welds using mainly neutrons but also high-energy X-rays, (Publications 4.4 and 4.5, 4.7 - 4.9) arose through my involvement in the Ph.D. project of Dr. Anna Paradowska. While Anna's main supervisors were Drs. John Price and Raafet Ibrahim, Mechanical Engineering Department, Monash University, from the commencement of her project she relied on my expertise in this field for the advancement of her research. A preliminary version of Publication  $4.9^4$  was credited with the Welding Research Institute of Australia, Sir William Hudson Memorial Medal for the best research paper for 2009, of relevance to the Institute.

Also in this chapter I have included my research in collaboration with Dr. John Griffiths concerned with the partition of stress in a metal-matrix composite (MMC) where we have

<sup>&</sup>lt;sup>1</sup> C.J. Howard, C.J. Ball, R.L. Davis and M.M. Elcombe, <u>Aust. J. Phys.</u> 36, 507-18 (1983).

<sup>&</sup>lt;sup>2</sup> "The Early History of Neutron Stress Measurement", A. Krawitz, <u>Mater. Sci. Forum</u> **571-572**, 3-11 (2008).

<sup>&</sup>lt;sup>3</sup> Elements of X-ray Diffraction (Second Edition), B.D. Cullity (Addison-Wesley, 1978) pp 451-6.

<sup>&</sup>lt;sup>4</sup> 'Measurement of Residual Stress in Repair Welds with Consideration of Stringer and Temper Bead Procedures', J.W.H. Price, A.M. Paradowska and T.R. Finlayson. Presented at the 9<sup>th</sup> International Conference & Exhibition on "Operating Pressure Equipment" (Surface Paradise, Q'ld, Australia) 26 – 28 August, 2009.

used the commercial casting alloy, A356, of composition Al-7Si-0.4Mg as a model MMC. In this research using neutron diffraction at both the ENGIN-X instrument at the ISIS Pulsed Source of the Rutherford Appleton Laboratories, U.K., and the Kowari instrument at the Australian Research Reactor, OPAL, we have studied specific questions concerning the residual stress components in the Si particles and the Al-based matrix, the stress borne by the particles and matrix for a sample under load and the modifications to these stresses upon loading the sample. (Publications 4.6, 4.10, 4.11 and 4.12). During the last three years, my expertise in this area has given rise to my participation in the supervision of the PhD project of Mr. Paul Mignone, Department of Chemical and Biomolecular Engineeering, University of Melbourne, which is concerned with the mechanical properties of the composite, W-Cu which has potential high-temperature applications. Paul is currently preparing his thesis.

#### (b) List of papers in order of publication

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- Lambrineas, P., Finlayson, T.R., Griffiths, J.R., Howard, C.J. and Smith T.F., 'Neutron Diffraction Residual Stress Measurements on a Thin Steel Plate' <u>N.D.T. International</u> 20, 285-90 (1987).
- 3. Johnston, A.I., Finlayson, T.R. and Griffiths, J.R., 'Triaxial Residual Stress Measurements using Neutron Diffraction' <u>Mater. Sci. Forum</u> **27/28**, 465-70 (1988).
- 4. Price, J.W.H., Paradowska, A.M., Joshi, S., Finlayson, T., 'Residual Stress Measurements by Neutron Diffraction and Theoretical Estimation in a Single-Weld-Bead' Int. J. Pressure Vessels and Piping 83, 381-7 (2006).
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- 8. Paradowska, A.M., Price, J.W.H., Finlayson, T.R., Lienert, U., Walls, P. and Ibrahim, R., 'Residual Stress Distribution in Steel Butt Welds Measured Using Neutron and Synchrotron Diffraction', J. Phys.: Condens. Matter **21**, 124213 (8pp) (2009).
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- 10. Luzin, V., Griffiths, J.R., Davidson, C.J., Finlayson, T.R. and Wang, Q.G., 'Neutron Diffraction Measurement in an Al-Si Casting' <u>Materials Australia</u> **45**, (2) 44-6 (2011).
- Davidson, C.J., Finlayson, T.R., Griffiths, J.R., Luzin, V., Wang, Q.G., Rajakesari, J. and Llorca, J., 'Neutron Diffraction Determination of Macro and Microstresses in an Al-Si-Mg Composite and Observed Changes with Plastic Strain' <u>Proceedings of the 36<sup>th</sup></u> <u>Annual A&NZIP Condensed Matter and Materials Meeting</u> ed. G. Stewart (ISBN 978-0-646-57071-6) (Australian Institute of Physics, 2012) (http://www.aip.org.au/wagga2012) (Paper No. WP03).
- Griffiths, J.R., Davidson, C.J., Finlayson, T.R., Oliver, E.C., Wang, Q.G. and Fitzpatrick, M.E., 'The Development of Stress in Inclusions Caused by Plastic Flow in the Matrix of a Two-Phase Composite and its Effect on the Relief of Initial Residual Stress' <u>Proceedings of the 8<sup>th</sup> Australasian Congress on Applied Mechanics (ACAM 8)</u> 23-26 November, 2014, Melbourne, Australia.

Paper No.	D	С	Ι	W	(D+C+I+W)/4
4.1	7	2	5	5	4.75
4.2	6	2	3	4	3.75
4.3	7	3	4	6	5.0
4.4	3	0	2	2	1.75
4.5	5	2	3	4	3.5
4.6	4	3	2	4	3.25
4.7	3	0	2	3	2.0
4.8	4	3	2	5	3.5
4.9	3	3	2	3	2.75
4.10	2	0	2	2	1.5
4.11	2	1	2	6	2.75
4.12	2	2	3	3	2.5

#### (c) Statement of responsibility

Personal Average Total Responsibility:

37.0/120 (i.e., 30.8% per publication)

## 5. Structural Studies in Various Dielectric Materials

### (a) **Research summary**

My initial research in this area was concerned with structural behaviour of the alkali-metal thiocyanates which involved interesting lattice dynamical behaviour arising from their structure comprising spherical anions and rod-shaped, thiocyanate cations. The research involved both ultrasonic velocity and phonon dispersion measurements and provided the Ph.D. projects for Dr. Mark Irving who studied CsSCN (Publication 5.1) and Dr. David Cookson, KSCN (Publications 5.3 - 5.5). At the same time, Dr. Steven Prawer undertook structural studies of the hydrogen-bonded material, CsH<sub>2</sub>PO<sub>4</sub> which exhibits ferroelectricity, in a Ph.D. project which involved the first ever measurements of the elastic constants for a crystal of monoclinic symmetry (Publication 5.2).

In later research supported by an A.R.C. grant, the phase transitions in  $SrTiO_3$  and  $K_2Mn_2(SO_4)_2$  were studied using high-resolution, capacitance dilatometry (Publications 5.6 and 5.7).

Research undertaken in collaboration with my German colleague, Prof. Dr. Uwe Klemradt, was concerned with the stability of passivation layers on GaAs and involved the final-year, honours (Miss Kylie Crompton) and M.Sc. (Prelim.) (Mr. Jason Smith) projects, in which grazing-incidence X-ray measurements were used to study the structure of the passivation layer (Publications 5.8 and 5.9).

A further honours project undertaken by Mr. John Daniels, in collaboration with Dr. Lou Vance, ANSTO, was concerned with the phase transitions in the perovskite materials,  $Ca_{1-x}Sr_xTiO_3$ , of some significance for the artificial mineral, Synroc (Publications 5.12 and 5.14). John Daniels then undertook a Ph.D. project which firstly involved the design and construction of facilities at the Australian Research Reactor, HiFAR, to study the structural behaviour of ferroelectric and piezoelectric materials by stroboscopic diffraction methods. This initial technique development was the subject of an ANSTO Scientific Highlight<sup>1</sup> (Publication 5.10) and gave rise to a number of successful applications of stroboscopic diffraction, studying both the ferroelectric transition in TGS (Publications 5.11 and 5.13) and the dynamical behaviour of domains in a series of ferroelastic ceramics (Publications 5.15, 5.16, 5.18 and 5.19). In his final year of Ph.D. candidature (2006), Dr. Daniels was awarded the AINSE Gold Medal for Post-graduate Research.

A small project to observe the influence of both magnetic and electric fields on the phase transition in TGS was completed in collaboration with Dr. Jason Lashley, Los Alamos National Laboraties (Publication 5.17).

## (b) List of papers in order of publication

1. Irving, M.A., Prawer, S., Smith, T.F. and Finlayson, T.R., 'The Room Temperature Elastic Constants of Caesium Thiocyanate' <u>Aust. J. Phys</u>. **36**, 85-92 (1983).

<sup>&</sup>lt;sup>1</sup>www.ansto.gov.au/research/bragg\_institute/current\_research/scientific\_highlights/past\_highlights/2005\_jan

- 2. Prawer, S., Smith, T.F. and Finlayson, T.R., 'The Room Temperature Elastic Behaviour of CsH<sub>2</sub>PO<sub>4</sub>' <u>Aust. J. Phys</u>. **38**, 63-83 (1985).
- 3. Cookson, D.J., Finlayson, T.R. and Elcombe, M.M., 'Phonon Dispersion Relations for Potassium Thiocyanate' <u>Solid State Commun</u>. **64**, 357-9 (1987).
- 4. Cookson, D.J., Elcombe, M.M. and Finlayson, T.R., 'Neutron Diffraction Studies of Potassium Thiocyanate' <u>Mater. Sci. Forum</u> **27/28**, 113-6 (1988).
- Cookson, D.J., Elcombe, M.M. and Finlayson, T.R., 'Phonon Dispersion Relations for Potassium Thiocyanate at above Room Temperature' <u>J. Phys: Condensed Matter</u> 4, 7851-64 (1992).
- 6. Liu, M., Finlayson, T.R., and Smith, T.F., 'High-resolution Dilatometry Measurements of SrTiO<sub>3</sub> along Cubic Tetragonal Axes' <u>Phys. Rev. B</u> **55**, 3480-4 (1997).
- Kuroiwa, Y., Liu, M., Finlayson, T.R., Smith, T.F. and Itoh, K., 'Thermal Expansion and the Phase Transition in a Langbeinite-Type K<sub>2</sub>Mn<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> Single Crystal' <u>J. Phys. Soc.</u> <u>Jpn. 66</u>, 1840-1 (1997).
- 8. Crompton, K.E., Finlayson, T.R., Kirchner, C., Seitz, M. and Klemradt, U., 'Microstructural Study of a Passivation Layer on GaAs: An Application of X-ray Reflectivity under Grazing Angles using a Synchrotron Source' <u>Surface Review and</u> <u>Letters</u> **10**, 373-9 (2003).
- 9. Smith, J.D., Finlayson, T.R., Kirchner, C., Klemradt, U., Seitz, M. and Sutter, J.P., 'An Application of Synchrotron Radiation to Study the Microstructure of Passivation Layers on GaAs' <u>Mater. Forum</u> **27**, 21-7 (2004).
- Daniels, J.E., Studer, A.J., Finlayson, T.R. and Hagen, M.E., 'Development of a New Instrument to Observe Time-resolved Neutron Diffraction Intensities in Association with Phase Transitions' in <u>Physics for the Nation</u> (Proceedings of 16<sup>th</sup> National Congress of the Australian Institute of Physics) (Canberra, A.C.T. Australia) 31 January – 4 February, 2005. ed. M. Colla, ISBN 0-9598064-8-2 (Australian Institute of Physics, 2005) Paper No. MOC 34.
- 11. Daniels, J.E., Finlayson, T.R., Studer, A.J. and Hagen, M.E., 'Time Resolved Studies near the Ferroeloectric Transition in Triglycine Sulphate during the Application of High-Voltage Fields' <u>Ferroelectrics</u> **339**, 175-82 (2006).
- 12. Daniels, J.E., Elcombe, M.M., Finlayson, T.R. and Vance, E.R., 'Neutron Diffraction Study of Polycrystalline Ca<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> Mixed Perovskite Materials' <u>Physica B</u> **385-386**, 88-90 (2006).
- 13. Daniels, J.E., Finlayson, T.R., Studer, A.J. and Hagen, M.E., 'Time Resolved Neutron Diffraction Studies of Triglycine Sulphate near the Ferroeloectric Transition during the Application of High-Voltage Electric Fields' <u>Physica B</u> **385-386**, 97-9 (2006).
- Daniels, J.E. and Finlayson, T.R., 'Automated Apparatus for Dynamical Mechanical Analysis using the Piezoelectric Ultrasonic Composite Oscillator Technique' <u>J. Phys. D:</u> <u>Appl. Phys.</u> **39**, 5290-3 (2006).
- Daniels, J.E., Jones, J.L. and Finlayson, T.R., 'Characterisation of Domain Structure from Diffraction Profiles in Tetragonal Ferroelastic Ceramics' <u>J. Phys. D: Appl. Phys.</u> 39, 5294-9 (2006).
- 16. Daniels, J.E., Finlayson, T.R., Studer, A.J. and Jones, J.L., 'Time-resolved Studies of Ferroelectric Materials using Neutron Stroboscopic Techniques during the Application of

Electric Fields' in <u>RiverPhys</u> (Proceedings of 17<sup>th</sup> National Congress of the Australian Institute of Physics) (Brisbane, Q'ld., Australia) 3 – 8 December, 2006. eds. R. Sang and J. Dobson, ISBN 0-9598064-7-4 (Australian Institute of Physics, 2006) Paper No. WC0325.

- Lashley, J.C., Hundley, M.F., Mihaila, B., Smith, J.L., Opeil, C., Finlayson, T.R., Fisher, R.A. and Hur, N., 'Heat Capacity in Magnetic and Electric Fields near the Ferroelectric Transition in Triglycine Sulfate' <u>Appl. Phys. Lett.</u> 90, 052910-1-3 (2007).
- Daniels, J.E., Finlayson, T.R., Studer, A.J., Hoffman, M. and Jones, J.L., 'Time-resolved Diffraction Measurements of Electric–Field-Induced Strain in Tetragonal Lead Zirconium Titanate' J. Appl. Phys. 101, 094104-1-6 (2007).
- Daniels, J.E., Finlayson, T.R., Davis, M., Damjanovic, D., Studer, A.J., Hoffman, M. and Jones, J.L., 'Neutron Diffraction Study of the Polarisation Reversal Mechanism in [111]<sub>c</sub>oriented PZN-4.5PT' J. Appl. Phys. 101, 104108-1-7 (2007).

#### (c) Statement of responsibility

Paper No.	D	С	Ι	W	( <b>D</b> + <b>C</b> + <b>I</b> + <b>W</b> )/4
5.1	4	0	2	3	2.25
5.2	3	2	3	3	2.75
5.3	6	2	3	3	3.5
5.4	6	2	3	3	3.5
5.5	6	2	3	3	3.5
5.6	5	0	3	4	3.0
5.7	5	0	3	4	3.0
5.8	4	2	2	4	3.0
5.9	4	0	2	4	2.5
5.10	3	0	2	3	2.0
5.11	3	1	2	2	2.0
5.12	3	0	2	3	2.0
5.13	3	1	3	4	2.75
5.14	5	2	2	6	3.75
5.15	3	0	2	3	2.0
5.16	3	0	3	5	2.75
5.17	4	2	2	3	2.75
5.18	2	0	2	3	1.75
5.19	2	0	2	2	1.5

Personal Average Total Responsibility:

50.25/190 (i.e., 26.4% per publication)

## 6. Magnetic Materials

#### (a) Research summary

My research on magnetic materials initially involved the study of the thermophysical properties (thermal expansion, specific heat and magnetic susceptibility) of a series of Heusler alloys,  $Fe_{3-x}Mn_xSi$ , some of which not only undergo a ferromagnetic transition but also exhibit a magnetic re-ordering in their ferromagnetic state. This formed the Ph.D. project for Dr. John Miles who was an employee of the CSIRO, and led to Publications 6.1 – 6.3.

Two small projects which were set initially as student honours projects gave rise to Publication 6.4 concerned with the susceptibilities of various forms of carbon and Publication 6.15 concerned with the study of magnetite in the vicinity of its Verway transition. Another small project in collaboration with Dr. Tunay Ersez, supported by A.R.C. funding, was concerned with the magnetic microstructure of the manganite materials,  $La_{1-x}Sr_xMnO_3$  (Publications 6.7 and 6.10).

The largest project in this area was concerned with the magnetic properties and their variation with microstructural changes of materials produced by melt-spinning, a technology which had been invented for the creation of nanocrystallinity in ribbon-like materials of interest for magnetic applications. The research concerned with Fe-Zr-B alloys was the Ph.D. project of Dr. Xiangyuen Xiong (Publications 6.5, 6.6, 6.8 and 6.9) while the subsequent studies of melt-spun Sm-Co-based materials arose from a collaborative project with Dr. Xiong, funded by the A.R.C. and involving an Australian Postdoctoral Fellowship for Dr. Xiong. Of particular interest in these studies was the phase transitions of the melt-spun microstructures and the accompanying variation in magnetic properties (Publications 6.11 - 6.14).

#### (b) List of papers in order of publication

- 1. Miles, J.R., Smith, T.F. and Finlayson, T.R., 'Thermal Expansion of Fe<sub>2</sub>MnSi' <u>Aust. J.</u> <u>Phys.</u> **41**, 781-90 (1988).
- 2. Miles, J.R., Smith, T.F. and Finlayson, T.R., 'Thermodynamic Study of the Magnetic Ordering of Fe<sub>3-x</sub>Mn<sub>x</sub>Si Alloys' Int. J. Thermophys. **12**, 617-26 (1991).
- 3. Miles, J.R., Smith, T.F. and Finlayson, T.R., 'Low Temperature Thermophysical Properties of Fe<sub>3</sub>Si' <u>Phil. Mag. B</u> 65, 1215-22 (1992).
- 4. Ling, M.F., Finlayson, T.R. and Raston, C.L., `Nonlinear Field-Dependent Susceptibilities C<sub>60</sub> and Carbon Nanotubes'' <u>Aust. J. Phys.</u> **52**, 913-8 (1999).
- 5. Xiong, X.Y., Finlayson, T.R. and Muddle, B.C., 'The Approach to Saturation Magnetisation of Nanocrystalline Fe<sub>90</sub>Zr<sub>7</sub>B<sub>3</sub> Alloy' J. Phys. D: Applied Physics **34**, 2845-53 (2001).
- Xiong, X.Y., Finlayson, T.R. and Muddle, B.C., 'The Effect of Boron Content on the Crystallisation Behaviour and Microstructure for Nanocrystalline Fe<sub>93-x</sub>Zr<sub>7</sub>B<sub>x</sub> Alloys' <u>Mater. Phys. Mech.</u> 4, 34-8 (2001).

- Ersez, T., Kennedy, S.J. and Finlayson, T.R., 'Polarised Neutron Scattering Study of Magnetic Correlations and Spin Dynamics in La<sub>0.875</sub>Sr<sub>0.125</sub>MnO<sub>3+δ</sub>' <u>Appl. Phys. A</u> 74 [Suppl.], S725-7 (2002).
- Xiong, X.Y., Muddle, B.C. and Finlayson, T.R., 'The Effect of Cu Addition on the Microstructure and Low-Temperature Magnetization of Nanocrystalline Fe<sub>87-x</sub>Zr<sub>7</sub>B<sub>6</sub>Cu<sub>x</sub> and Fe<sub>81-x</sub>Zr<sub>7</sub>B<sub>12</sub>Cu<sub>x</sub> Alloys' J. Phys. D: Applied Physics 36, 223-8 (2003).
- 9. Xiong, X.Y., Finlayson, T.R. and Muddle, B.C., 'Nanocrystalline Microstructures in Fe<sub>93-x</sub>Zr<sub>7</sub>B<sub>x</sub> Alloys' J. Mater. Sci. **38**, 1161-9 (2003).
- 10. Ersez, T., Schulz, J.C. and Finlayson, T.R., 'Neutron Scattering Studies of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> Colossal Magnetoresistive Perovskites' <u>Mater. Forum</u> **27**, 80-7 (2004).
- Xiong, X.Y. and Finlayson, T.R., 'A Quantitative Study of the Comparison of Sm(Co<sub>0.68</sub>Fe<sub>0.20</sub>Cu<sub>0.10</sub>Zr<sub>0.02</sub>)<sub>7.5</sub> Alloy by 3D-Atom Probe Analysis' <u>Proceedings of the</u> <u>30<sup>th</sup> Annual A&NZIP Condensed Matter and Materials Meeting</u> ed. M. Avdeev (ISBN 1-92079-09-4) (Australian Institute of Physics, 2006) (http://www.aip.org.au/wagga2006/) (Paper TP41).
- Xiong, X.Y. and Finlayson, T.R., 'Influence of Fe Content on the Microstructure and Magnetic Properties of Melt-Spun SmCo-based Alloy Ribbons' <u>J. Iron & Steel Inst.</u> 13, 154-9 Suppl. 1 (2006).
- Xiong, X.Y. and Finlayson, T.R., 'A Study of the Anomalous Field Evaporation of Sm(Co<sub>0.68</sub>Fe<sub>0.20</sub>Cu<sub>0.10</sub>Zr<sub>0.02</sub>)<sub>7.5</sub> Alloy by 3D-atom Probe' <u>Ultramicroscopy</u>, **107**, 781-5 (2007).
- 14. Xiong, X.Y. and Finlayson, T.R., 'Phase Transformation Sequence and Magnetic Properties of Melt-Spun SmCo-Based Alloy after Isochronal Heat Treatment', J. Appl. Phys. **104**, 103910-1-7 (2008).
- 15. Hancock, Y. and Finlayson, T.R., 'Thermal Expansion of Magnetite (4.2 300 K)' <u>Phil.</u> <u>Mag.</u> **89**, 1913-21 (2009).

Paper No.	D	С	Ι	W	(D+C+I+W)/4
6.1	6	1	3	3	3.25
6.2	6	1	3	3	3.25
6.3	6	1	3	4	3.5
6.4	5	2	3	3	3.25
6.5	5	2	4	5	4.0
6.6	5	2	4	6	4.25
6.7	4	0	3	3	2.5
6.8	5	2	4	4	3.75
6.9	5	2	4	5	4.0
6.10	6	4	4	8	5.5
6.11	5	0	5	5	3.75
6.12	5	2	5	3	3.75
6.13	5	1	4	3	3.25
6.14	5	2	5	5	4.25
6.15	5	2	5	6	4.5

#### (c) Statement of responsibility

Personal Average Total Responsibility: 56.75/150 (i.e., 37.8% per publication)

## 7. Novel Alloys for Application in Atomic Absorption Spectrometry

### (a) **Research summary**

The application of atomic absorption spectra for chemical analysis, or Atomic Absorption Spectrometry (AAS), was a discovery by Dr. Alan Walsh of the CSIRO<sup>1</sup> in the early 1950s. The technology was subsequently commercialized through an Australian company, Techtron, which later became Varian Australia Pty Ltd. More recently (2010) Varian Australia was taken over by Agilent Technologies, but until that time, Varian Australia had continued to manufacture and service Atomic Absorption Spectrometers from its Melbourne-based plant and controlled approximately 35% of the market for AAS world-wide.

During the 1990s a problem had developed for certain AAS industrial applications and I was approached by a representative of Varian Australia to undertake a research consultancy to address this problem. The outcome of this most successful consultancy was a particular Ag-Zn alloy which was very quickly applied by Varian Australia to manufacture hollow cathodes for AAS lamps used for the analysis of Zn. So successful was this application that, in collaboration with Varian Australia, I successfully applied for an ongoing research project which involved an Australian Postgraduate Award (Industry) to which I attracted Mr. Derek Oliver (Publication 7.1). His Ph.D. project involved not only solving some ongoing troublesome cathode lamps which were quickly put into industrial practice by Varian Australia, but created research which shed considerable light on the physics of the hollow-cathode lamp (Publications 7.2 - 7.4).

Underlying the operation of a lamp is the sputtering of atoms from the hollow cathode under the action of the applied electric field, or the instability of the atoms in the surface of the material.

## (b) List of papers in order of publication

- 1. Oliver, D.R., Finlayson, T.R. and Sullivan, J.V., 'Varian Benefits from Monash Input' <u>The</u> <u>Industrial Physicist</u> **3**, (2) 34-5 (1997).
- 2. Oliver, D.R. and Finlayson, T.R., 'Reconstruction of Sputtered Copper Atom Densities in a Hollow-Cathode Glow Discharge Lamp' J. Phys. D: Applied Physics **30**, 2097-102 (1997).
- 3. Oliver, D.R. and Finlayson, T.R., 'Effect of Cathode Bore Geometry and Filler-Gas Pressure on the Observed Distribution of Sputtered Copper Atom Densities in a Hollow-Cathode Lamp' J. Analytical Atomic Spectrometry **13**, 443-6 (1998).
- 4. Oliver, D.R. and Finlayson, T.R., 'Modelling the Observed Distribution of Sputtered Atom Densities in a Hollow-Cathode Lamp Discharge' J. Phys. D: Applied Physics **31**, 1857-64 (1998).

## (c) Statement of responsibility

<sup>&</sup>lt;sup>1</sup> A. Walsh, <u>Spectrochemica Acta</u> **7**, 106-17 (1955).

Paper No.	D	С	Ι	W	(D+C+I+W)/4
7.1	6	4	3	4	4.25
7.2	6	2	5	5	4.5
7.3	5	2	5	4	4.0
7.4	5	2	4	4	3.75

Personal Average Total Responsibility:

16.5/40 (i.e., 41.2% per publication)

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