Abstract of Address:

More than 20 years of Cr based research: A personal perspective

South Africa is one of the world's main producers of Chromium (Cr). Cr and its alloys has many unique properties that ignite the interest of the scientific community. However, the potential of Cr and Cr related materials as a socio-economic tool in the improvement of lives have not been optimized in the South African context. Presently much of the Cr mined in SA is exported without adding much value to it. Material research into this South African commodity is therefore expected to impact noticeably in many spheres.

We are motivated to study Cr alloys, not only for the potential long term impact thereof on the South African community, but because these alloys exhibit a great variety of antiferromagnetic properties that excite the interest of the scientific community at present. Cr alloys constitute the prototype of a class of model systems that undergo magnetic phase transitions associated with the nesting of the electron and hole Fermi surfaces. The beauty of the variety of properties of Cr based materials originates in the spin-density-wave (SDW) state that is formed when the electron and hole Fermi sheets overlap on cooling through the Néel transition, T_N. In pure Cr the SDW is incommensurate (I) with the lattice, resulting in an ISDW phase. As the Fermi surface is very sensitive to the electron concentration per atom (*e/a*), it is possible to adjust the relative sizes of the electron and hole fermi surfaces through doping. In general, doping with elements to the left of Cr, such as V, decreases the *e/a*, making the electron Fermi sheet smaller relative to the hole Fermi sheet. However, those elements to the right of Cr, such as Mn and 5d elements, increases the e/a, with an increase in the size of the electron Fermi sheet, resulting in a better overlap between the electron and hole Fermi sheets and the SDW can become commensurate (C) with the lattice. The decrease in *e/a* normally results in a destabilization of SDW with a concomitant decrease in T_N, while increase in e/a results in an increase in T_N to a maximum, where a critical *e/a* is reached when optimum overlap of the electron and hole Fermi sheets occur. Following on, T_N decreases as *e/a* is further increased. This is seen in Cr with group 8-elements used as dopants. Another mechanism used in tuning T_N, is that of electron-pair breaking, observed when using elements with an e/a similar to Cr with Mo as dopant. There are, however, exemptions to this simple rule, for example when Cr doping with Al and Ga. This makes probing SDW characteristics interesting and challenging.

The SDW state contributes a large component, of magnetic origin, to nearly all the physical properties of Cr alloys. Thus, once the fundamental role of the SDW contributions to these physical properties is understood, these alloys can be tailored to give specific desired properties, such as particular thermal expansion, elastic constants, electrical resistivity, and so forth. These give endless opportunities for a vast range of promising applications for Cr based materials.

From a purely scientific perspective there has also been renewed interest in the properties of dilute Cr alloys, particularly in their magnetic phase diagrams, quantum critical behaviour and their role as spacer layers in magnetic multilayer thin film structures. The contributions that the Chromium Research Group has made to various

topics of current interest are now discussed in three categories relating to bulk, thin films and nanoparticle research on Cr materials.

Firstly, the richness in the variety of magnetic phases observed in Cr alloy systems make investigations into their magnetic phase diagrams appealing. The theoretical canonical model is useful to explain the main features of the magnetic phase diagrams of these alloys, as well as many of the physical properties observed. However, the addition of detailed aspects is required to explain many unusual and unique features. One such unusual feature in magnetic systems that has come to the foreground are quantum criticalities. These occur where an order parameter is continuously suppressed down to 0 K at an instability point known as quantum criticality. This suppression of the magnetic properties can be obtained through the tuning of various parameters, such as concentration, magnetic field or pressure. This led to the discovery of novel electronic ground states in magnetic materials and new concepts of low lying excitation spectra in condensed matter systems.

Considering this new and interesting research field, the Chromium Research Group's focus has during the last decade moved to extending the physical properties measured under extreme conditions in order to probe the SDW behaviour, study magnetic phase diagrams and quantum critical behaviour in these systems. Results obtained indicate various novel findings in the field of Cr alloys, including a newly proposed magnetic phase diagram for the Cr-Al system. This system was further investigated through doping with Mo that is isoelectronic with Cr. This led to a study on the quantum critical behaviour in the Cr-Al-Mo alloy system and an investigation into SDW phonon coupling effects on the specific heat of Cr alloy systems. In line with these types of investigations Mo doping of the Cr-Si alloy system was also probed as to gain greater insight into this alloy system that showed most interesting characteristics. These include sharp first order ISDW to paramagnetic transitions in certain concentration ranges, while continuous second order CSDW to paramagnetic transitions are observed in other concentration regions. Results suggest the existence of two critical points in a Cr-Si-Mo phase diagram: a suggested critical end point in the magnetic phase diagram of this system and suppression of the antiferromagnetism at a second critical point. This is the first time that this behaviour has been reported in Cr alloy systems.

In tandem work on the magnetic phase diagrams of Cr alloys with group-8 diluents resulted in the completion of the phase diagrams of these alloys to much higher concentrations than previously reported. This opened new avenues for research into SDW antiferromagnetism, quantum criticalities and superconductivity in Cr alloys with group-8 diluents, not explored previously. Experimental results obtained for the bulk Cr-Os samples confirmed the existence of a superconductivity dome in the magnetic phase diagram, as well as the coexistence of SDW antiferromagnetism and superconductivity in certain Cr based bulk samples.

Results on Cr-Ru-V give information on the role of SDW effects at 0 K on relationships between various physical properties. Experimental results for the first time provided evidence that in Cr alloys the Seebeck coefficient can be used as a decisive parameter to characterize quantum critical behaviour. These findings were supported by results on Cr-Re-V and Cr-Ir-V. An overview of all the properties of Cr alloys with group-8 diluents should result in a comprehensive overview of quantum critical behaviour in these alloy systems.

Giant magneto resistance in Cr-Fe-Mn alloys were observed together with spin-glass behaviour. For further exploring of MPDs and spin-glass behaviour, a formal collaboration was signed with the Federal University of São Carlos (UFSCar, Brazil) in 2014 and work on new Cr alloy systems with spin-glass behaviour holds promise. These include Cr-Re-Mn, Cr-Si-Mn and Cr-Al-Mn alloys, which shows much promise for future research.

Work on various magnetic phase diagrams have been cited by several researchers, including groups focussing on more applied work. The research contributes novel aspects to the field of magnetism in Cr alloys, emphasizing the need for similar and further studies to explore SDW and spin-glass behaviour, magnetic phase diagrams and quantum criticalities, as well as superconductivity and semiconductor behaviour in certain Cr alloy systems.

Secondly, as thin films and heterostructures form the basis of modern structured materials, it is needed to probe the properties of Cr alloys in confined geometries. These materials can then be tailored for specific applications in devices. Recognizing the importance of this new field, Prof Prinsloo established collaboration with leaders in the field of thin films magnetism. These include Prof Fullerton from the University of California San Diego (UCSD, USA) and Dr Dekadjevi at the Université the Bretagne (UBO, France). A formal agreement with UBO opened up new opportunities for staff and student exchange, as well as joint degrees on postgraduate level.

Understanding of dimensionality effects and proximity magnetism is essential in gaining insight into the behaviour of magnetic structures. Therefore, secondly, work on thin films and heterostructures were started. Initial work on Cr-Mn/Cr and Cr-Ru/Cr together with Prof Fullerton showed innovative results. Evidence of SDW pinning and the effect thereof on the transition temperatures were published. The work on Cr-Al thin film studies drew clear parallels between the physical properties such as grain size, stress and the magnetic behaviours of these thin films. Extending this research therefore gave insight into the SDW behaviour in confined geometries. Our research on thin films and multilayers, has contributed to a more fundamental understanding of the SDW behaviour and has been cited by others working in the field. In addition even our bulk research work were also referred to in thin film studies by other groups. Further work on Cr alloy thin films containing Si, Co, Mo and Re are presently underway in order to gain further insight into the behaviour of the SDW in confined geometries.

Thirdly, ventures into the fields of nano-heterostructures and particles have only started recently. Our paper on the thermal simulation of magnetization reversals for size distributed assemblies of core-shell exchange biased nanoparticles together with our collaborators at UBO have attracted much attention and paved the way for further growth in this regard within our own group. In addition this collaborative work resulted in the graduation of a student with a UJ/UBO co-badged degree.

Following the work on nanomaterials with UBO, research on chomite micro and nanoparticles were initiated within the laboratories of UJ. Currently it is of interest to study the magneto-structural coupling in the geometrically frustrated antiferromagnet, where structural distortion elevates the ground state degeneracy leading to a long-range magnetic order. Cubic ferrimagnetic spinels of the form AB_2O_4, where *A* refers to tetrahedral and *B* to octahedral sites, are presently attracting much attention. For ACr_2O_4, where *A* is a magnetic cation, frustration driven magnetostructural coupling is unexpected as a result of $AOCr^{3+}$ interaction collectively dominating over the frustrated interaction between Cr^{3+} ions. Coupling between the lattice, spin and orbital degrees of freedom in spinel compounds with geometrical frustration have come to the foreground. Our research indicate that doping with a variety of metals in the *A* lattice site has a strong effects on the magnetic properties of chromites. This creates the opportunity for future research on core-shell particles after tailoring these materials for specific required properties, with possible extensions of the work in various applications within the medical and water purification fields. This research is envisaged to be broadened in the next few years with more work on Cr based nanoparticles and films, as well as including a deeper theoretical understanding of the various factors at play in these materials.

It is evident that the completed research on Cr based bulk samples, thin films and nanoparticles have resulted in significant contributions to this field. Furthermore, the scope for future research incorporating Cr based materials is constantly increasing, with opportunities to not only broaden fundamental knowledge in the arena of magnetism, but also to develop new materials that can find applications in modern technologies.