## Charge, Spin & Momentum Density III
## New Information on Crystals from Electron Diffraction

**MS09.03.01 QUANTITATIVE CONVERGENT BEAM ELECTRON DIFFRACTION APPLIED TO BONDING STUDIES.** R. Høier, Department of Physics, Norwegian University of Science and Technology, N-7034 Trondheim, Norway.

Methods for quantifying convergent beam electron diffraction patterns have been developed considerably over the last years. By multiparameter least square fitting of observed and calculated patterns we may today determine phases in non-centrosymmetric crystals and magnitudes of individual structure factors with an accuracy down to 0.1 degree and 0.1 %, respectively. The methods used to achieve this high accuracy are demanding both numerically and experimentally. Various strategies are being tested out, based on non-systematic, systematic row or zone axis diffraction, so far all of them on materials with relatively small unit cells.

Methodologically one of the main challenges is related to the numerical computations where the time consuming part is associated with solving a large non-Hermitic eigenvalue problem. This is done repeatedly a large number of times and the standard algorithm in use is very unfavorable for vectorization. We have optimized the diagonalization by determining efficient beam selection criteria. It is also found that the computational efficiency may be strongly increased by using parallel computers. Among the crystal parameters the Debye-Waller factor is still a problem. It is in general anisotropic and atom dependent and difficult to refine in the numerical procedures in use. This fact is in particular clear when experimentally determined bonding distributions are compared with excising computed ones that assume zero thermal vibrations.

Bonding has been investigated in the intermetallic material TiAl, undoped and doped with different other atom types. This material is interesting for high temperature applications, but has an unfortunate brittle-ductile transition at moderate temperatures. It has been found experimentally that the transition temperature is modified by the doping, and e.g. Mn is found to be beneficial in this respect. To understand this effect electron bond distributions of TiAl alloyed with Mn and other atoms have been investigated experimentally by convergent beam diffraction, electron energy loss fine-structure studies and theoretically by LAPW charge density calculations. Influence of dopant type is determined and experimentally consistent differences are seen for Mn, Cr and V.

**MS09.03.02 DEBYE-WALLER FACTORS AND SUB-LATTICE ORDERING IN TiAl.** S. Swaminathan, S. Jayanti, I. P. Jones*, D. M. Maher**, A. W. Johnson***, H. L. Fraser, Dept. of Matls. Sci. and Eng., The Ohio State University, OH, *School of Metallurgy and Materials, University of Birmingham, UK, **Dept. of Matls. Sci. and Eng., North Carolina State University, NC, ***Center for Microscopy, University of Western Australia, Australia.

The Debye-Waller factors of Ti and Al sites of Ti-54Al alloy have been determined by four circle single crystal x-ray diffraction method. The analysis of x-ray diffraction data shows an ordered substitution of excess Al atoms (i.e. those over the stoichiometric composition) on the Ti sites. For the off-stoichiometric alloy studied, the least squares analysis yielded unequal Debye-Waller factors for the two crystallographically equivalent sites on the Ti-sublattice. This result is consistent with the ordering of excess Al atoms on Ti sites. On going research plan involves, data collection and analysis of x-ray diffraction intensities from a series of TiAl single crystals of different compositions. The results of this work and the effect of sublattice ordering on structure factors measured by convergent beam electron diffraction method will be presented.

**MS09.03.03 ACCURATE STRUCTURE FACTOR MEASUREMENTS BY CONVERGENT BEAM ELECTRON DIFFRACTION.** M. Saunders, P. A. Midgley, T. D. Walsh and R. Vincent, H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, UK.

Quantitative Convergent Beam Electron Diffraction (CBED) is now emerging as the most accurate generally applicable method of low-order structure factor measurement for inorganic materials [1,2]. Using an energy-filter attached to a conventional Transmission Electron Microscope (TEM) it is possible to acquire diffraction patterns arising from electrons that have undergone predominantly elastic scattering. The theory of electron diffraction has now developed to the stage where accurate simulations of elastic scattering can be performed. The new techniques of quantitative CBED rely on adjusting the simulation until a best fit is obtained between the theory and experiment. The variable parameters include the low-order structure factors we wish to measure, the sample thickness and various scaling constants. Using silicon as a test case we have demonstrated [1] that quantitative CBED is as accurate as the best X-ray Pendellösung measurements [3]. A description of the zone-axis pattern matching technique developed by Bird and Saunders [4] will be given and the results for the silicon test case will be compared to the best X-ray and theoretical values. More recent results showing the application of the technique to other materials such as Ge, diamond, III-V semiconductors and metals such as Ni and Cu will also be discussed.

[1] M. Saunders, et al. (1995) Ultramicroscopy 60, 311.
[2] J.C.H. Spence and J.M. Zuo (1992) Electron Microdiffraction, Plenum, New York.
[3] Z.W. Lu, et al. (1993) Phys. Rev. B47(15), 9385 and references therein.
[4] D.M. Bird and M. Saunders (1992) Ultramicroscopy, 45, 241.

**MS09.03.04 DETERMINATION OF BOND CHARGE DENSITY AND TEMPERATURE FACTORS FOR NiAl BY CONVERGENT BEAM ELECTRON DIFFRACTION.** A. L. Weickenmeier, W. Nüchter, J. Mayer, Max-Planck-Institut für Metallforschung, Seestrasse 92, 70174 Stuttgart, Germany

Quantitative convergent beam electron diffraction (CBED) is increasingly appreciated as a very powerful tool to determine bond charge densities and temperature factors (TF) of very small (spot size 20 nm or less) areas of crystalline specimens. Using the Bloch wave formalism, CBED patterns are computed with extremely high accuracy as a function of the TFs and structure factors (SF, Fourier coefficients of the crystal potential). To derive the TFs and SFs the simulations are fitted to experimental patterns. Once a sufficient number of SFs has been obtained the potential is synthesized and by means of Poisson's equation converted to the total charge density. Using the measured TFs for the given temperature the total charge density of a corresponding crystal made from neutral atoms is constructed and subtracted yielding the bond charge density. Since the bond charge density is only a small fraction of the total charge density (of order 1 percent) maximum accuracy in experiment and data analysis is required.

The material we investigated is the ordered intermetallic phase NiAl, which is of technical interest as a high performance material at elevated temperatures. Since the room temperature brittleness is usually attributed to a partially covalent bonding, an experimental determination of the bond charge density will yield important information on the mechanical behavior.

With our energy filtering Zeis EM912 Omega transmission electron microscope equipped with a cooled YAG scintillator CCD-camera we have examined stochiometric NiAl at liquid nitrogen temperature. Specimens were prepared in different crystallographic orientations and investigated under various incident beam directions and for different thicknesses. Patterns were taken showing

either high or low order Bragg reflections to extract either TFs or SFs. The analysis for the TFs shows that the variance of the results is of order 5 percent for the mean vibration amplitude which is readily explained by experimental errors and uncertainties. The accuracy of SFs obtained so far is in the order of a tenth of a percent. First results on bond charge density clearly reveal a covalent bond between Ni and Al atoms.

## Charge, Spin & Momentum Density IV
## Magnetization & Momentum Densities

### MS09.04.01 AB-INITIO QUANTUM MECHANICAL CALCULATIONS OF POLARISED NEUTRON DIFFRACTION: RESULTS IN TRANSITION METAL COMPLEXES. P.A. Reynolds, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Metal-ligand bonding in metal complexes is poorly understood. Spin density is a fundamental property, it is much modified by bonding effects, and it has important chemical consequences. Consider the instability of triplet $H_2$ and the stability of singlet $H_2$. In certain magnetically simple cases in paramagnetic crystals we can estimate many Fourier components of the spin-density, with an accuracy of ca. 1%, by use of polarised neutron diffraction. *Covalence*, resulting in delocalisation of positive metal-centred spin density onto ligand atoms is particularly marked in our recent results on [As($C_6H_5$)$_4$][TcNCl$_4$] in which 26% of an ionic, technetium centred, $4d_{xy}^1$ spin density has been delocalised onto the chlorines' in-plane $3p_\pi$ orbitals. *Spin-polarisation*, due to electron-electron correlation, is also marked in the TcN bond. The nitrogen spin population is negative, -0.18 e. *Spin-orbit coupling* besides causing canting of the magnetisation, as in Cr(II) Tutton salt, can also cause large changes in the radial distribution of the spin density around the metal site, as in CoCl$_4^{2-}$.

Calculations must be able to duplicate these covalence, spin polarisation, and spin-orbit coupling effects. This requires a correlated relativistic wavefunction (example CoCl$_4^{2-}$). In some cases approximations such as the Unconstrained Hartree-Fock method may be appropriate in description of metal-ligand bonding, but other approximations such as the Restricted Hartree-Fock method never are (example TcNCl$_4^-$).

### MS09.04.02 THE USE OF MAXIMUM ENTROPY IN THE INTERPRETATION OF MAGNETIZATION DENSITIES IN NITROXIDE COMPOUNDS. P. Schleger[1,2], A. Puig-Molina[1], E. Ressouche[1], O. Rutty[1], and J. Schweizer[1]. [1]Commissariat a l'Energie Atomique, Centre d'Etudes Nucleaires de Grenoble, Department de Recherche Fondamentale sur la Matière Condensè,17 rue des Martyrs, 38054 Grenoble Cedex 9, France; and [2]Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex 9, France.

A maximum entropy method for the reconstruction of magnetization densities in both centric and acentric crystal structures will be presented which is not restricted to weak spin systems, and allows for the incorporation of relevant corrections such as extinction. Thus it is now possible for the first time to reconstruct, without the application of a model, the real space magnetization densities in essentially any physical system from polarized neutron diffraction experiments. This, for example, dramatically simplifies the interpretation process of data on non-centrosymmetric nitroxide free radicals.

### MS09.04.03 MAGNETIZATION DENSITY PROFILES IN MAGNETIC MULTILAYERS. J A C Bland, Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, UK

The capabilities of polarized neutron reflection (PNR) for directly determining the magnetic and non-magnetic structure in thin and ultrathin magnetic films and multilayers are reviewed. It is shown that the vector magnetization density profile can be obtained with atomic layer resolution in favourable cases and that the combination of structural and magnetic information provides decisive advantages. Estimates of the interface roughness and layer thicknesses can be accurately made and diffuse scattering measurements can be used to probe spin disorder at interfaces. The magnetisation profile across chemically homogeneous ultrathin films can be accurately measured and examples of recent measurements in both ultrathin Fe films and trilayer structures are given and compared with the results of conventional magnetometry measurements. Vector magnetometry measurements of the layer dependent magnetic moment orientations are shown to provide a powerful approach to the study of coupling behaviour in ferromagnetic (FM)/non-magnetic (NM)/FM trilayer structures. Finally the thickness dependent magnetic moment of epitaxial Cu/fcc Ni/Cu(001) structures with competing perpendicular and shape anisotropies is determined as a function of applied field and compared with the results of magnetometry measurements. A strong variation in moment is found which is reflected in the variation of the ratio of orbital and spin moments with thickness determined from X-ray circular dichroism (XMCD) experiments.

### MS09.04.04 HIGH RESOLUTION COMPTON SCATTERING AS PROBE OF FERMIOLOGY AND ELECTRON CORRELATIONS. A. Bansil, Physics Dept., Northeastern Univ., Boston MA 02115, USA

In 1993, the I. U. Cryst. Commission on Charge, Spin, and Momentum Densities started a new project, "Fermiology of High-Tc Superconductors via High Resolution Synchrotron-based Compton Scattering Spectroscopy". Properly timed to exploit the rapid world-wide development of high resolution spectrometers, this project has generated vigorous activity. A substantial progress has been made in delineating the nature of electron states in simpler systems which serve as the foundation for understanding complex materials. Feasibility of determining Fermi surface radii via high resolution Compton has been demonstrated.[1] Careful comparisons between the measured and computed spectra in Li, Be, and LiMg[1-3] clearly reveal departures from the conventional one-particle local density approximation (LDA) picture of the ground state momentum density of the electron gas; work on a variety of other systems is in progress. Reconstruction of the full 3D density from a series of Compton profiles in Li is beginning to yield direct insight for the first time into the size of the momentum density break at the Fermi momentum in a metal.[3] Much work has been carried out by a number of groups in standardizing data handling procedures for synchrotron-based Compton data using Si as a target material. This talk provides an overview of the relevant work completed to date, and outlines areas of further study likely to prove fruitful in establishing high resolution Compton as a tool for investigating Fermiology related issues in wide range of materials.

[1] Y. Sakurai, et al., Phys. Rev. Letters 74, 2252(1995).
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[3] W. Schulke et al. (preprint).