

PS09.02.20 NEW PRECISE X-RAY STRUCTURE AMPLITUDES OF GaAs OBTAINED BY MEANS OF THE PENDELLÖSUNG METHOD. J. Stahn, M. Möhle, U. Pietsch, Institute of Solid State Physics, University of Potsdam, Germany

As reviewed in /1/ the electronic charge density of the semiconductor GaAs (space group F-43m) has been studied by various authors. Although the accuracy of the accumulated X-ray structure amplitudes $|F_H|$ is in the order of 1 % some qualitative and quantitative discrepancies remain among the experimental data and in comparison with the outcome of pseudo-potential and density-functional calculations. In order to obtain highly precise data it is necessary to perform experiments which fulfil either the dynamical or the kinematical theory of X-ray diffraction. We measured some high order strong and medium intensity reflections in the range of $0.5 < \sin\theta/\lambda < 0.8 \text{ \AA}^{-1}$ by means of the Pendellösung method. In order to reduce the absorption the experiment was performed at $\lambda = 0.3 \text{ \AA}$ using the D3 beamline of HASYLAB (Hamburg, Germany). The pendellösung was obtained recording the integral intensity of a $500\mu\text{m}$ thick wafer which was tilted step by step around the normal of the reflecting net plane. The dynamical effect appeared only at dislocation free regions of the wafer. Furthermore the exact knowledge of the wafer thickness, the degree of polarisation and the used wave length were necessary to determine the $|F_H|$ with an accuracy better than 1%. The experimental data are verified using the computer code CRYSTAL92 which is based on the Hartree-Fock approach. The project is supported by the European Community under CHRX-CT93-155 and the BMBF under 05 6471PA.

/ 1/ U. Pietsch & N. K. Hansen, Acta Cryst. B1996 submitted

PS09.02.21 BONDING EFFECTS IN GaAs: MEASUREMENTS OF THE 222/222 BIJVOET RATIO. Andrew W. Stevenson, CSIRO Division of Materials Science & Technology, Private Bag 33, Clayton South MDC, Victoria 3169, Australia

Various X-ray diffraction studies of bonding effects in GaAs have been reported. Early investigations [e.g. De Marco, J. J. & Weiss, R. J. (1964). *Phys. Lett.* 13, 209-210] concentrated on the amount and direction of electron charge transfer. Several attempts at accurately producing electron-density maps have been made.

Stevenson [*Acta Cryst.* (1994). **A50**, 621-632] has recently collected and analysed an accurate and extensive X-ray integrated-intensity data set, for an extended-face-crystal specimen, to yield detailed information on thermal vibrations and bonding effects in GaAs. In particular, the structure-factor magnitudes for the very weak 200, 222 and $\bar{2}\bar{2}\bar{2}$ reflections, for which $h+k+l=4n+2$, clearly showed the presence of bonding effects. A least-squares refinement of the full GaAs data set yielded values for four bonding parameters. These occur in additional atomic-scattering-factor terms which describe the spherical expansion or contraction of the bonded atom relative to an isolated atom, and an antisymmetric component corresponding to nearest-neighbour bonding. The atomic-scattering-factor expressions reflect the atomic-site symmetry for the zinc blende structure and were derived by Moss [PhD thesis (1977). Univ. of Melbourne, Australia]. In the present study, and continuing on from the earlier study, wavelength-dependent measurements of the 222/222 Bijvoet ratio are reported and interpreted in terms of the presence of bonding effects. This Bijvoet ratio is zero in the absence of anharmonic thermal vibrations and bonding effects, and the contribution from the former is relatively small here. Given that extinction effects are also very small for these reflections, such measurements provide a valuable opportunity to study bonding effects directly.

PS09.02.22 RARE-EARTH PEROVSKITES, SYNCHROTRON ELECTRON DENSITIES AND MAGNETIC PROPERTIES Victor A. Streltsov, Crystallography Centre, University of Western Australia, Nedlands 6907, Australia

The relationship of the electron density to the magnetic properties of some rare earth (RE) perovskite-orthoferrites, REFeO_3 , was studied by imaging the deformation electron density ($\Delta\rho$) with synchrotron radiation.

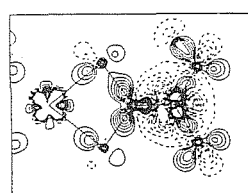
Strong magnetic effects are due primarily to electron spin density. Exceptional precision is required to measure small spin-dependent cross-sections directly. Spin density and charge density are related by the effect of un-compensated spins on the electron probability density. Exchange correlation between electrons occurs when atoms overlap. Their "fermion" character prevents two electrons from occupying the same quantum state. If a two-electron spin wave function component is symmetric, the corresponding anti-symmetric space component reduces electron density in the region of maximum overlap.

Exchange Hamiltonians are invariant to arbitrary simultaneous rotation of all spins, causing degeneracy additional to that for spatial symmetry. Ordering of magnetic states with the same exchange energy for a crystal generates an exchange multiplet. The effects of the higher symmetry of the exchange Hamiltonian may influence a deformation density image strongly.

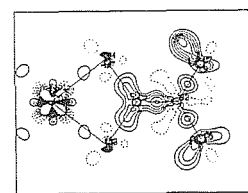
High precision synchrotron X-ray imaging can be applied to such systems, sometimes with unexpected consequences. Metal-metal interactions, though subordinate to nearest-neighbour cation-anion interactions in terms of energy, can affect electron density strongly. Results for $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ and the C-type RE oxides suggest that cation-anion effects on the electron density could become larger if the RE atom site symmetry were lowered. The REFeO_3 compounds, have distorted perovskite structures with low (C_3) symmetry of the RE atom sites, suitable for testing this hypothesis. The conclusions, based on high precision diffraction imaging for YFeO_3 , SmFeO_3 , GdFeO_3 and DyFeO_3 with synchrotron radiation, will be described.

PS09.02.23 ELECTRON DENSITY STUDIES ON METAL TRIS-DITHIOCARBAMATE AND METAL BIS-DITHIOCARBAMATE COMPLEXES. By Li-Ya Tan, Chi-Rung Lee, Chih-Chieh Wang, & Yu Wang, Department of Chemistry, National Taiwan University, Taipei Taiwan, R.O.C.

Electron density distributions on three metal dithiocarbamate complexes, $\text{M}(\text{S}_2\text{CNR}_2)_3$, $\text{M}=\text{Fe}(\text{III})$, $\text{Co}(\text{III})$, and $\text{Ni}(\text{S}_2\text{CNR}_2)_2$, are studied by accurate single X-ray diffraction data measured at 140K using $\text{MoK}\alpha$ radiation. The metal ions of the former two compounds are 6-coordinated with a geometry between trigonal prism and octahedron. The twist angles of MS_6 polyhedron viewed from C_3 -axis are *ca* 33° for $\text{Fe}(\text{S}_2\text{CN}(\text{C}_4\text{H}_8))_3$, and *ca.* 46° for $\text{Co}(\text{S}_2\text{CNMe}_2)_3$ (60° for ideal octahedron and 0° for ideal trigonal prism). The Nickel(II) in the complex $\text{Ni}(\text{S}_2\text{CNEt}_2)_2$ is in a 4-coordinated planar geometry with Ni at 1 position. Detail electron density distributions will be presented for bonding characterization. The interesting *d*-orbital populations on these high spin d^5 Fe(III), low spin d^6 Co(III), and d^8 Ni(II) will be compared. A comparison between experiment and molecular orbital calculation is also going to be discussed. The agreement between experimental results and MO calculations is good in the case of Co(III) complex (see figures below), but not so good in the other two cases.



$\Delta\rho_{\text{multipole}}$



$\Delta\rho_{\text{DFT}}$