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STRUCTURE FACTOR MEASUREMENT IN TIAI AND SILICON*

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The accurate measurement of low order structure factors is required for the determination of the electron charge density distribution in crystals. In this work the energy-filtered convergent beam electron diffraction (CBED) rocking curve method has been used for accurate structure factor measurements. This CBED method for structure factor refinement involves matching of the experimental CBED intensities to those calculated using dynamical electron diffraction theory. The CBED experiments were conducted with a Philips EM420 Transmission Electron Microscope coupled with a custom built energy-filtering attachment enabling single electron counting. The theoretical pattern matching was performed using FORTRAN programs which were developed by Swaminathan.¹ Initially the experimental plan involved an attempt to refine structure factors of TiAl by two dimensional Bloch wave calculations. The results of this project have been reported elsewhere.² Subsequently it proved impossible to obtain results with sufficient precision for TiAl reproducibly, i.e. less than 0.1%, from samples of different thicknesses. It is imperative that such consistency of results be obtained. Thus, in order to ascertain the origin of this inconsistency the present study concentrates on the development of the experimental and theoretical tools required for such refinement and measurements for Si, which has been well characterized by other techniques, have been performed.

Experimental rocking curves for $g=220$ obtained from three different sample thicknesses were matched to the theoretically calculated curves. An IMSL library routine incorporating the quasi-Newton method with a finite difference gradient has been used for structure factor refinement.³ Five variables including the coefficient of the crystal potential (V_g), the absorption coefficient (V'_g), the sample thickness (t) and the constant background intensity under the bright field and the dark field rocking curves were fitted by minimizing the quantity χ^2 defined by

$$\chi^2 = \frac{1}{n} \sum_{i=1}^n \frac{[c_i I_{\text{calc}} - I_{\text{expt}}]^2}{I_{\text{expt}}} \quad (1)$$

where n is the total number of points in the rocking curves. The fitted values of the V_g and structure factors (F_g) are given in table 1. These values were tested for local minima by repeating the calculations using different starting points and arriving consistently at the same minimum for the χ^2 . Recently Deininger et al.⁴ have suggested that the above definition of the χ^2 overestimates the significance of the low intensity values and have proposed the use of a χ^2 defined as

$$\chi^2 = \frac{1}{n} \sum_{i=1}^n [c_i I_{\text{calc}} - I_{\text{expt}}]^2 \quad (2)$$

The results of calculations using the χ^2 defined in (2) are also shown in table 1 and the fitted values of

V_g agree within the estimated error irrespective of the definition of χ^2 .

Treatment of anomalous absorption : Without considering anomalous absorption the structure matrix of a centrosymmetric crystal is real symmetric because the imaginary part of V_g is zero. In the Bloch wave treatment anomalous absorption can be treated either by perturbation theory⁵ or by adding a constant to the imaginary part of V_g . The former does not change the structure matrix. However, the latter treatment produces a complex symmetric structure matrix. Consequently matrix diagonalization requires longer computer time in the latter case. The complex matrix formulation has been recommended for high precision structure factor measurements.⁵ However, the present calculations show no marked differences between the complex matrix formulation and the perturbation theory treatment (table 1). Hence, the computationally more efficient perturbation treatment may be utilized to treat anomalous absorption for centrosymmetric crystals.

Table 1: Fitted values of the V_g and F_g . The fitted F_g values strongly agree with the x-ray *Pendellösung* measurements⁶ ($F_g = 67.11$) and CBED rocking curve measurement⁴ ($F_g = 66.53$).

Thickness (t) nm	Best fit : χ^2 by (1)		χ^2 by (2)		Complex Struct. Matrix	
	V_g (volts)	F_g	V_g (volts)	F_g	V_g (volts)	F_g
136.9	4.387	66.951	4.383	66.988	4.390	66.920
144.6	4.385	66.975	4.387	66.929	4.387	66.987
193.4	4.375	67.065	4.378	67.018	4.378	67.035
Average	4.382±.004	67.00±.04	4.384±.003	66.96±.02	4.385±.004	66.97±.03

Structure Factor Measurements in TiAl : A recent study⁷ of the site occupancy in single phase TiAl suggests that the accuracy of structure factor measurements by electron diffraction methods would critically depend on the composition of the material volume sampled by the electron beam and on the accuracy of the Debye-Waller factors used to determine the structure factors. Thus, the validity of recently reported structure factor measurements in TiAl appears to be affected.^{2, 8} Work is in progress to study the compositional and Debye-Waller factor dependency of structure factors in TiAl. The results of these studies will be presented at the meeting.

References

1. S. Swaminathan, Ph. D thesis, The Ohio State University (1994), Columbus, OH.
2. S. Swaminathan et al., *Materials Science and Engineering*, (1993), **A170**, 227.
3. J.E. Dennis and R.B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*, Prentice-Hall, (1983) Englewood Cliffs, NJ.
4. G. Deininger et al., *Ultramicroscopy*, (1994), **54**, 15.
5. C. J. Humphreys and E. G. Bithell, *Electron Diffraction Techniques*, Ed. J. M. Cowley, Oxford Univ. Press, NY.
6. S. Cummings and M. Hart, *Australian Journal of Physics*, (1988), **41**, 423.
7. S. Swaminathan et al., *MRS Proceedings : Fall meeting*, (1994), in press.
8. Z. W. Lu et al., *Acta Metallurgica*, (1994), **42**, 3929.
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