**DETERMINING THE ELECTRON DENSITY
AND
VOLUME EXPANSION AT GRAIN BOUNDARIES USING
ELECTRON ENERGY-LOSS SPECTROSCOPY**

A Dissertation

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ABSTRACT

Grain boundary (GB) energy is an essential parameter in determining the microstructure of metallic and other materials, and tremendous effort has gone into determining the structure, energy and properties of GB's. Presently, GB energies are most often calculated because it is difficult and/or tedious to determine them experimentally. Grain boundary modelling studies have revealed correlations between GB energy and: i) a change in electron density due an atom deficit at the GB, and ii) a rigid body translation normal to the GB, or the so-called normal volume expansion, which may also be associated with an atom deficit. In this work, valence electron energy loss spectroscopy (VEELS) and extended energy-loss fine structure (EXELFS) analysis in a scanning/transmission (S/TEM) electron microscope were used to examine fundamental GB properties such as the electron density and volume expansion, respectively.

In VEELS, plasmon peaks are generated due to collective oscillations of the valence electrons in the solid due to the interaction with the incident high-energy electron beam. Based on the Drude model, the plasmon energy is proportional to the valence electron density. Four well-characterized GB's with different GB energies were examined in this work. Plasmon energy profiles obtained from line scans across the GB's revealed that the plasmon energy is lower at the GB than the bulk due to a lower valence electron density, and that the energy decreased with increasing GB energy. The decrease in valence electron density was also found to extend further into the matrix on either side of the GB's with increasing GB energy. Moreover, plasmon damping at the GB's increased with increasing GB energy, presumably because additional scattering of the plasmon occurs with increasing disorder at the GB. The intensity of the GB response function, obtained by Fourier deconvolution, showed an increase in intensity with GB energy, revealing the effects of different plasmon frequencies and dielectric constants at the GB. Localization of the VEELS signal was found to depend on the orientation of the sample, while sample thickness was found to have a negligible effect on the plasmon peak energy at the GB.

The volume expansion in a GB can be experimentally determined using EXELFS in a S/TEM, where the electron beam can be focused to form a sub-nanometer probe, allowing one to

determine changes in nearest neighbor (n.n.) distances at a GB with nanometer-scale spatial resolution. In this investigation, EXELFS performed on three GB's showed that the average n.n. distances at the GB's increased with increasing GB energy. Fourier filtering also revealed an increase in static disorder with increasing GB energy. The total volume expansion at the GB calculated according to the plasmon energy profile showed excellent agreement with volume expansions measured using other experimental techniques. Thus, EXELFS provides complementary information to VEELS on the volume expansion at the GB. Taken together, the results of this investigation experimentally and conclusively demonstrate that the GB energy increases proportional to the decrease in electron density and concomitant increase in specific volume expansion at a GB.

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1. Introduction

Grain boundary (GB) energy plays an important role in recrystallization and grain growth behavior and thereby, determining the microstructure and properties of a material. Determining the GB energy has been of great importance to the scientific community for decades [7]–[12]. Both experimental procedures and computer simulations, have been employed to calculate the GB energy and correlate the same with the structure of the GB at the atomic level. The orientation difference between the adjoining crystals gives rise to mismatch between the crystal lattices at the GB, that can be accommodated by translation of the grains parallel to the GB plane (in the x, y direction) and/or volume expansion perpendicular to the GB plane (z direction). These three independent translations associated with the GB are called translational, or microscopic degrees of freedom (DOF), and are denoted by $T = (T_x, T_y, T_z)$. Translations along the x, y directions (T_x, T_y) allow the atoms at the GB to relax, and thereby, lead to the lowest energy GB state with no long-range strain field in the GB plane [13]. On the other hand, due to volume expansion (T_z) in the perpendicular direction, the atomic volume increases and the density decreases locally.

Seeger and Schottky [14] proposed the dependence of the GB energy on volume expansion at the GB for metals. Since the crystals must remain strain-free parallel to the GB, all changes in spacing occur normal to the boundary. Due to this volume expansion the average distance between atoms at GB is larger than that of ideal crystal. This leads to redistribution of the conduction electrons and consequently lowering of electron density at the GB. This redistribution increases the energy in the GB and may be the dominant part of the GB energy. They found good agreement for copper and silver with measured GB energies.

A variety of computational processes were employed by other researchers in order to correlate the electron density with the GB energy. Smith and Ferrante [15] have shown a correlation between GB energy in Al with the relative atomic density at the GB using perturbation theory. Electron density function calculations by Wright and Atlas [1] on Al $\Sigma 11(1\bar{1}3)[110]$ and Al $\Sigma 3(1\bar{1}2)[110]$ twin boundaries, shown in Fig. 1, have shown results consistent with experimental estimates, but lower than the extrapolated GB energy obtained by Smith and Ferrante [15]. In contrast, Uesugi and Higashi [16] examined six $[110]$ symmetric tilt grain boundaries in Al using first principle calculations and concluded that the GB energy results mainly from the

Figure 1: Electron densities at $\Sigma 11$ tilt GB of Al, in a plane perpendicular to the $[110]$ direction [1]. Darker shades of gray correspond to regions with higher electron densities and atoms are designated by unfilled circles.

elastic energy and that the effect from the electron bonding is secondary. Lu and Kioussis [17] have provided reliable GB energy and volume expansion for a $\Sigma 5(210)[001]$ tilt boundary in Al based on density functional theory and the local density approximation. In addition, the GB energy and volume expansion for $\Sigma 9(2\bar{2}1)[110]$ tilt and $\Sigma 5(001)$ twist grain boundaries in Al and Cu were calculated using first-principles calculations based on density-functional theory [18]. In summary, these studies show that there is a correlation between the electron density at the GB and the GB energy, but it is still not clear how much the change in electron density contributes to the energy and how this varies with the atomic structure of different boundaries.

Wolf [2] has also explored in great detail, the interrelation between GB energy and volume expansion for symmetrical and asymmetrical tilt and twist boundaries in Cu and Au using Lennard Jones potential and embedded-atom-method (E.A.M.) potential as shown in Fig. 2. According to Wolf [19], this volume expansion is one-dimensional because on the plane of the GB, the unit cell dimensions are fixed as they are determined by the lattice parameter of the grains (bulk) on the either side of the GB. The three-dimensional volume expansion (ΔV), can be related to the one-dimensional free volume of a GB (δV) by the following equation:

$$\Delta V = \delta V \cdot A \quad (1)$$

where A is unit-cell area of the GB and δV is the volume expansion per unit length, with units of length $[\text{m}^3/\text{m}^2]$.

Figure 2: Correlation between GB energy and volume expansion per unit area normalized by lattice parameter for symmetric and asymmetric tilt and twist grain boundaries in (a) Au and (b) Cu [2].

It should be noted that δV can be as low as 0.1 of the lattice parameter (a_o) or even less. Wolf [19] found an almost linear relationship between GB energy and δV for all types of boundaries using both potentials. However, there is a considerable amount of scatter in the GB energy for any particular value of volume expansion which cannot be explained using Wolf's model. Tschopp and McDowell [20] calculated the GB energy vs. boundary expansion for symmetric and asymmetric GB's in Al and their results show a similar increasing trend with a decreased slope, but also significant scatter.

Due to the normal volume expansion at the GB, the atomic density at the GB is lower than that of the bulk. In other words, the nearest neighbor (n.n.) distance between atoms at the GB increases, giving rise to a decrease in valence electron density at the GB. Therefore, from a theoretical perspective, measuring the variation of these two parameters, i.e.: i) the decrease in

local electron density, and ii) the increase in n.n. distance with GB energy, should enable one to correlate the dependency of the GB energy on these parameters.

There has been a significant effort to determine the quantity δV for grain boundaries experimentally. Merkle [26],[27] has used high-resolution electron microscopy (HREM) to experimentally determine the excess volume for grain boundaries using grain boundaries of known orientation. Values determined using HREM showed significant differences from values calculated using EAM potential [2], [19]. Shvindlerman *et al.* [23] performed thermodynamic GB modeling by correlating the equilibrium angle at the GB with hydrostatic pressure to experimentally determine the GB excess free volume for Al tilt GB's. High-precision difference-dilatometric technique was employed by Steyskal *et al.* [24] to measure the removal of GB volume due to grain growth and thereby measuring volume expansion at GB in metals. These methods are either based on rigorous thermodynamic modelling or applicable to GB's with known orientation relationships or dependent on measuring properties from numerous grain boundaries to produce a statistical average data. The HREM procedure relies on the optimum defocus of the objective lens and small deviations of beam tilt alignments or orientation of the crystal may lead to error in calculations.

Due to the complexity of the experiments, volume expansion data is often calculated using various computation models. First principles calculations on GB's have been employed recently to calculate the normal volume expansion. The volume expansion is determined from the difference in the total volume (V_g) of a super cell containing the GB and the total volume (V_s) of a single crystal supercell with equal number of atoms [16]. The volume expansion is given

by $\Delta V = \frac{V_g - V_s}{2S}$, where S is the cross section of the super cell. These calculations showed an increase in lattice parameter normal to the GB plane along with slight shrinkage in the GB plane. Using a similar method, the difference in the free volume per atom of the supercell, with and without the GB, was determined to calculate the excess free volume at the GB was calculated by Takata *et al.* [22]. The fraction of volume expansion in the GB was given by $F(r) = \frac{\Omega_{gb} - \Omega_B}{\Omega_B}$, where Ω_{gb} is the free volume per atom in the cell with a GB, and Ω_B is the free volume per atom in the cell of perfect crystal. Even though this procedure may overestimate the GB expansion at the core of the GB, it showed a decrease in $F(r)$ with distance from the GB, as one might expect.

In the present research, the electron density in the GB is measured locally using valence electron energy-loss spectroscopy (VEELS) and the change in n.n. distance is determined using extended electron energy loss fine structure (EXELFS) analysis in a scanning/transmission (S/TEM) electron microscope, and these are correlated with the GB energy. The reasons for selecting these specific techniques are discussed in the following sections.

1.1. Valence electron energy-loss spectroscopy (VEELS)

The dielectric response of a medium to an external perturbation, e.g., an impinging electron, is governed by the dielectric function. The dielectric behavior of a medium is described by the dielectric function ε or the relative dielectric permittivity $\varepsilon = \varepsilon_t \varepsilon_0$ [25], which is a function of frequency ω and wave vector $\mathbf{q}$, and where ε_t is the total permittivity and ε_0 is the permittivity of vacuum. Electron energy loss spectroscopy (EELS) allows one to obtain the dielectric function as a function of frequency ω and wave vector $\mathbf{q}$. In the low-loss range of the EELS spectrum (0-50 eV), plasmon peaks are generated due to collective oscillation of the valence electrons in the

solid produced by interaction with the incident high-energy electron beam [26]–[28]. Fermi [29] introduced a model for the valence excitation, which is based on the complex, frequency-dependent dielectric function of the material $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where ε_1 and ε_2 are the real and imaginary part of the dielectric function, respectively. When a charged particle, in this case a high-energy incident electron, passes through a material it introduces an electromagnetic pulse, which is composed of components of different frequency ω . Each component of frequency generates polarization to the medium that induces an electric field, which pulls back the charged particle and thereby slows it down. The energy E and the momentum $\mathbf{p}$ transferred from the incident electron to the medium can be related to the independent variables ω and $\mathbf{q}$ by the following relations: $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{q}$, where $\hbar$ is Planck's constant divided by 2π . Ignoring relativistic effects, the probability $P_b(\omega)$ of energy loss $\Delta E = \hbar\omega$ can be related to the bulk loss function:

$$P_b(\omega) = \text{Im} \left\{ \frac{-1}{\varepsilon(\omega)} \right\} = \frac{\varepsilon_2(\omega)}{(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)} \quad (2)$$

For single electron losses, peaks in energy loss function occurs when $\varepsilon_2(\omega)$ (represents optical absorption at frequency ω) has a maximum, but is still less than $|\varepsilon_1(\omega)|$. When $\varepsilon_1(\omega)$ is 0 and $\varepsilon_2(\omega)$ is small, the maximum in the loss function occurs due to plasmon oscillations. The dielectric formulation is a very straight forward and simple way to relate energy loss function/spectra to the optical absorption of material. The dielectric function $\varepsilon(\omega)$ or its inverse ($1/\varepsilon$) are both linear and being complex functions, they have real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts. The real and imaginary parts are dependent on each other and connected by the Kramers-Kronig

relations [26] so, it is possible to calculate $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ from an experimentally obtained energy loss function $\left\{\frac{-1}{\varepsilon(\omega)}\right\}$. The dielectric function for a free-electron system is given by:

$$\varepsilon = 1 - \frac{\omega_p^2}{\omega(1+i\gamma)} \quad (3)$$

where $\omega_p = \{ne^2/\varepsilon_0 m\}^{1/2}$ is the plasmon frequency for a free-electron gas and γ is a damping constant. The plasmon energy, E_p , is defined by:

$$E_p \cong \hbar \left[ne^2/\varepsilon_0 m \right]^{1/2} \quad (4)$$

where n is the valence electron density, e is the electron charge, and m is the electron mass. As a result of Eqn. (4), the plasmon energy can be correlated with the valence electron density. By measuring the plasmon energy from the GB and matrix it should be possible to directly determine the difference in electron density between the GB and matrix. As proposed by Seeger and Schottky [14], this change in electron density at the GB could be related to the GB energy.

In low-loss VEELS spectra, the most prominent feature is the bulk plasmon, and its position is dependent on the valence electron density n . Therefore, by measuring the peak position of the bulk plasmon, the local variation in valence electron density due to segregation in an alloy, or the presence of defects in pure metals, can be detected. For example Cundy *et al.* [3] have shown a decrease in plasmon energy by 0.05 eV at the GB of quenched Al-7 wt% Mg alloy due to segregation of Mg at the GB as shown in Fig. 3. They have also shown an increase in plasmon energy within 50 nm on either side of the GB due to denudation of Mg. The plasmon energy corresponding to defect free pure Al and Al-Mg alloy (from grain interior) were measured as

calibration and used to correlate plasmon energy to alloy composition at the GB of the Al-Mg alloy. This plasmon loss technique has been employed to detect the local variation of

Figure 3: Plasmon energy profile across a high angle GB in Al + Mg alloy showing Mg segregation at the GB and denude zone on either sides of the GB [3].

alloy composition for simple free electron like systems, e.g., different Al alloy systems as discussed by Williams *et al.* [30], but to fully interpret the localized plasmon interference at the GB or any planar interface, the Fermi theory of dielectric excitation has to be extended to include the effect of two different dielectric media [31].

When an electron beam travels parallel to an interface between two different dielectric media, at a distance b (impact parameter) from the interface, the probability P_I of energy loss per unit distance, or more strictly the ratio of energy loss intensity to zero loss peak (ZLP) intensity is given by:

$$\frac{d^2 P_I(b, \omega, q_y)}{d\hbar\omega dq_y} = \frac{e^2}{4\pi^2 v^2 \varepsilon_0 \hbar^2 v(\omega, q_y)} [Im\{-1/\varepsilon_B\}\{1 - \exp\{-2vb\}\} + Im\{-2/(\varepsilon_A(\omega) + \varepsilon_B(\omega))\} \exp\{-2vb\}] \quad (5)$$

where the interface is modelled as infinitely extended plane parallel to the electron beam [32], the term $\hbar q_y$ appearing in the equation is the momentum transfer in the plane of the interface and normal to the beam direction (along z) and $v^2 = q_y^2 + (\omega/v)^2$. Ignoring the dependence of the dielectric functions on q , and integrating q_y up to q_c (some value of high cut off), one obtains:

$$\frac{dP_I(b, \omega)}{d\hbar\omega} = \frac{e^2}{2\pi^2 v^2 \varepsilon_0 \hbar^2} [Im\{-1/\varepsilon_B(\omega)\} \ln\left(\frac{q_c v}{\omega}\right) + K_0\left(\frac{2\omega b}{v}\right) (Im\{-2/(\varepsilon_A(\omega) + \varepsilon_B(\omega))\} - Im\{-1/\varepsilon_B(\omega)\})] \quad (6)$$

Here, $Im\{-1/\varepsilon_B(\omega)\}$ is the bulk plasmon contribution and the loss function $Im\{-2/(\varepsilon_A(\omega) + \varepsilon_B(\omega))\}$, which appears at smaller values of b , gives the interface loss. Eqn. 6 is a generalized expression for a surface or interface plasmon. These two terms together give the effect of the interface, and decrease exponentially with impact parameter b as $K_0(\theta) \approx \exp(-\theta)\sqrt{\pi/2\theta}$ for large scattering angle (in mrad) $\theta = 2\omega b/v$ [33]. The intensity in the interface loss is compensated for by an increasing subtraction from the bulk loss known as the *begrenzungs* effect [32]. Even though this equation does not account for relativistic effects, calculations by Howie *et al.* [34] have shown that it is reasonably accurate. For example, this equation can predict the position of the interface plasmon quite accurately, but with considerably more intensity [32]. Nevertheless, these equations are used in the Discussion section to explain some of the features of the VEELS spectra acquired from the GB's.

Mecklenburg *et al.* [35] have measured the temperature distribution in operating microelectronic devices at the nanoscale, using VEELS. Thermal expansion changes the number density of the valence electrons locally, which is connected to the plasmon energy E_p by Eqn. (4).

By measuring the variation of E_p they were able to map the temperature in 80-nanometer-thick Al wires precisely. Palanisamy *et al.* [36] have proved the existence and studied the damping behavior of the interface plasmon between a semiconducting solid and liquid metal (solid-Si /liquid-Al) interface using VEELS. The experimental results agrees well with calculations based on the dielectric theory, Eqn. (6) and was further corroborated by the energy-filtered TEM (EFTEM) imaging. Plasmon energies were also used to predict and/or determine various physical and mechanical properties of materials e.g., the bulk modulus, cohesive energy per atomic volume, electrical conductivity, etc., at the nanometer level [37]–[39]. The universal binding-energy relationship (UBER) [40] was used to establish the relationship between the plasmon energy and these properties.

Local optical properties and electron densities at $\Sigma 5$ and near $\Sigma 13$ GB's of Fe-doped SrTiO_3 was investigated by Benthem *et al.* [4], [41] using spatially resolved VEELS. Using Kramers-Kronig analysis, the complex dielectric function $\epsilon(E)$ was obtained from each low-loss spectrum in the Spectrum images (SI) and the corresponding refractive index was mapped out across the GB's as shown in Fig. 4. A near $\Sigma 11$ tilt grain boundary in $\alpha\text{-Al}_2\text{O}_3$ was studied by Mülleijans *et al.* [42] using VEELS, to determine the interband transition strength and the electronic structure of the GB quantitatively. From this discussion, it is evident that it is possible to experimentally determine the variation of valence electron density with nanoscale precision at, or near, the interface/GB using VEELS. In the present work, the correlation between this variation of electron density and behavior of GB plasmons with the GB energy is investigated.

Figure 4: Variation in the index of refraction across $\Sigma 5$ and $\Sigma 13$ GB's of Fe-doped SrTiO_3 [4].

1.2. Extended electron energy loss fine structure (EXELFS)

As mentioned earlier in the Introduction, it should be possible to measure changes in the lattice parameter (or atomic volume per atom) using extended electron energy loss fine structure (EXELFS) analysis in TEM by measuring the nearest neighbor (n.n.) distances. EXELFS is a site specific technique, where a sub-nanometer or sub-Ångstrom probe can be accurately placed on specific atomic columns, thereby harnessing information about the n.n. distances, coordination number, static disorder etc., at with nanometer-scale resolution. Due to the advantage of high

spatial resolution, EXELFS has been employed to study crystalline materials [43]–[45], amorphous materials of SiC [46], and metallic glasses [47].

During interaction with high energy incident electrons, the core electron of an atom may receive sufficient energy from the beam electron to get ejected from its shell. This ejected electron can be represented as a spherical wave originating from the ionized atom. Due to the presence of neighboring atoms, the outgoing spherical wave gets back-scattered from the neighboring atoms producing an incoming wave with a slight phase shift. The interference between the outgoing and incoming waves give rise to a sinusoidal variation in intensity (20–50 eV wide) about 50 eV above the ionization-edge energy. The frequency and the amplitude of this sinusoidal modulation is dependent on the type of the neighboring atoms and their distances from the central atom, or the absorber. With an increase in n.n. distance, the oscillations become rapid and also the amplitude in EXELFS oscillations decreases, making the signal weaker. Due to a volume expansion at GB's, the n.n. distance should be greater at the GB than in the bulk. This would modify the frequency of modulation of EXELFS signal at GB (with respect to EXELFS signal from bulk) and by measuring this difference should allow one to calculate the average increase in n.n. distance at the GB. EXELFS analysis was used to study the change in the n.n. distance and thermal vibration behavior of pure Al particles, using $L_{2,3}$ edge, during heating and cooling through the melting temperature [48]. The increase in n.n. distance from this study agrees well with the values calculated from the volumetric coefficient of thermal expansion for solid Al [49]. It's worth mentioning that the EXELFS calculations are based on uniform radial expansion of the atomic shells about the central atom, but the expansion at the GB is not uniform; the local mismatch at the GB is accommodated by expansion normal to the GB and consequent subtle contraction of the

lattice parameters along the GB plane. Specific techniques used for the Extended X-Ray Absorption Fine Structure (EXAFS) analysis of disordered systems, e.g., averaging of EXAFS signal over a pair distribution function, $g(r)$ [50], or the cumulant expansion/ratio method approach [51] could be employed for EXELFS analysis on GB's. Another straight forward technique, the ratio-method, was employed by Diociaiuti *et al.* [52] to determine the increase in structural disorder due to size effects of Pd clusters using $M_{4,5}$ edge of Pd. The ratio-method was also used by Yuan *et al.*[53] for the analysis of O K-edge to determine the change in O-Si bond length in Si-SiO₂ interface. From the above discussion, it can be concluded that using the ratio method, EXELFS analysis can be employed to determine the increase in the nearest neighbor distance at the GB's.

2. Experimental Procedures

2.1 Materials

Four bi-crystals of 99.999% pure Al with well characterized GB's were used in this study obtained from Prof. Molodov [54]. The bi-crystals were cut, using a slow speed cutter, perpendicular to the GB producing 1mm thick slices. These slices were mechanically polished down to 120 μm and punched to obtain 3 mm discs which contained the GB. The discs were then dimpled down to 20-30 μm at the center and electropolished to perforation using 22 V at -40 °C. The electropolishing solution used was 33volume% nitric acid + 67volume % methanol. These electropolished foils were used for all the EELS experiments and EEL spectra were collected from the GB keeping it nearly edge-on as shown in Fig. 5.

2.2. VEELS

Two different microscopes were used for the VEELS experiments: 1) Nion UltraSTEM 100 at Oak Ridge National Laboratory (ORNL) [55] operating at 100 keV with a cold field-emission gun (CFEG) and energy spread of 0.55 eV, and 2) Hitachi HD2700C at Brookhaven National Laboratory (BNL) [56] with a CFEG operating at 200 keV with energy spread of 0.35 eV. Details of other specifications are listed in Table 1.

Table 1: Microscope specifications.

Microscope	Organization	Specifications
Nion UltraSTEM 100	ORNL	100keV, probe size ~0.85Å, probe current 110 pA, collection semi angles as large as 50 mrad, entrance aperture: 2 mm, energy dispersion: 0.05 eV/channel, HAADF: 80-240 mrad, energy spread: 0.55 eV
Hitachi HD2700C	BNL	200keV, probe size ~ 1.2Å, probe current 20 pA, collection semi angles: 14.5 mrad, entrance aperture: 2 mm, energy dispersion: 0.05 eV/channel, HAADF: 45-242 mrad, energy spread: 0.35 eV

For VEELS experiments, line scans of length 15 nm (as shown by the red line in Fig. 5) were acquired across the GB's. A scan length of 15 nm was selected to obtain clear matrix spectra from adjacent grains, and to avoid any probable delocalization effects from the GB. The width of GB 1 ($\Sigma=3$) is very narrow, and can be regarded as the sharpest GB in Al, extending only two atomic planes. To elucidate the plasmon profile across such a narrow boundary, a step size smaller than the distance between two atomic planes was required and so a step increment of 0.1 nm was used. Spectrum images (SI) were obtained using point-by-point EEL spectra acquisition with a predetermined step size (in this case 0.1nm) along the scan line (red line). EELS spectra up to 50 eV were collected using a Gatan Enfina spectrometer. A dwell time of 0.1sec/pixel was used during acquisition of individual spectra. This dwell time was used to increase the signal to noise ratio in the SI. Individual spectra in the SI were aligned with respect to the zero loss

Figure 5: High-resolution STEM image of GB 4 at an edge-on position. EEL spectra collected across GB along the red line of length of 15 nm. EXELFS signal acquired from the GB and grains from the positions as depicted by the blue circles.

peak (ZLP) using a specific inbuilt routine in Digital MicrographTM software. This process aligned the center of the ZLP with an accuracy of less than 0.05 eV (1 pixel).

Plasmon peaks from individual spectra were fitted with a Gaussian function, which gave the plasmon peak position profile and full width half maximum (FWHM) profile along the entire scan length. Plasmons peaks are asymmetric in nature due to a contribution from a range of scattering vectors [57], so fitting a Gaussian function to plasmon peaks gives rise to fitting errors.

This was minimized by fitting each plasmon peak separately with two Gaussian curves, one with respect to the peak position (maximum amplitude) and another with respect to the FWHM. The former gave the profile of the plasmon peak position and the later gave the FWHM profile along the line scan. The resultant profiles are shown in Fig. 10, which clearly depicts a shift toward lower energy and an increase in FWHM of plasmon peaks at and near all the GB's. The length over which the shift in plasmon peak position and increase in FWHM is discernible is referred to as the plasmon valley and FWHM hill, respectively.

2.3. EXELFS

EXELFS experiments were performed using a FEI Titan 80-300 S/TEM operating at 300 kV with a Schottky FEG. EEL spectra of the Al $L_{2,3}$ (73 eV) and L_1 (118 eV) edges were collected using a spectrometer dispersion of 0.2 eV/channel in the image-coupled mode using the diffraction pattern to accurately place a ~ 0.28 nm probe on the GB. Spectra were also collected from the left grain (LG) and right grain (RG) with the same acquisition parameters, as shown by the blue dots in Fig. 5, usually at least 7-8 nm away from the GB to avoid any interference from delocalization effects.

The EELS spectra were acquired using a post-column Gatan imaging filter (GIF, Tridiem Model 863P), attached to the S/TEM. FEI Filter control software was used to align the spectrometer and Gatan Digital MicrographTM software was used to process the acquired spectra. An energy resolution of 1.2 eV (full width half max of ZLP) was achieved, using an extraction voltage of 4400V. A 2 mm GIF entrance aperture was used to decrease the intensity of the spectra

and the scope magnification was of the order of 150-175 kX. A FEI low-background double tilt holder was used during the experiments.

Two spectra were acquired from each position: 1) the first spectrum was recorded with a ZLP up to ~ 370 eV with a cumulative acquisition time of 4s (summation of 4 spectra with 1 s exposure each), and 2) the second one without a ZLP and containing the Al $L_{2,3}$ edge (from 50 eV to 460 eV) with a cumulative acquisition time of 28 s (summation of 7 spectra with 4 s exposure each) using the same energy dispersion of 0.2 eV/channel. These long dwell times were used to improve the signal-to-noise ratio in the high-loss regime. During long acquisition times, the ZLP of the second spectrum might drift with time, so this was calibrated using the first spectrum (with the ZLP) as a reference spectrum, since it was recorded with a shorter acquisition time. A deconvolution procedure was carried out using the reference spectrum, to remove the effects of plural scattering from the second spectrum during EXELFS analysis.

The EXELFS oscillations corresponding to the Al $L_{2,3}$ edge (73 eV) were analyzed in this work. An EEL spectrum showing the Al $L_{2,3}$ edge and L_1 edge (119 eV) acquired from the matrix is given in Fig. 6 (black line). Pre-edge background removal was performed by curve fitting a power law function to the pre-edge region and subtracting it from the raw spectrum. The background-subtracted spectrum is shown in Fig. 6 (red line). Plural scattering contributions were removed by the Fourier-ratio method using a reference spectrum having a ZLP [5], to obtain single scattering distribution (SSD), as shown in Fig. 6 (blue line).

Figure 6: EXELFS analysis of pure Al spectra acquired from the matrix. Raw (black) Al $L_{2,3}$ (73 eV) edge and L_1 edge (119 eV) edges after background subtraction (red) and plural scattering removal (blue).

3. Results

3.1. STEM of GB's

Bright Field (BF) images of four grain boundaries (GB's), with their corresponding diffraction patterns (DP's) are shown in Fig. 7. The diffraction patterns were acquired using a 20 μm selected area diffraction (SAD) aperture and they show the orientation relationship (OR) between the adjacent grains. These four GB's were numbered and this numbering procedure is followed throughout the thesis in referring to a particular GB:

- GB 1: $70.8^\circ\langle 110 \rangle$ tilt (relatively low energy $\sim 60\text{-}80 \text{ mJ/m}^2$, close to a coherent twin $\Sigma=3$ GB)
- GB 4: $52.7^\circ\langle 110 \rangle$ tilt (medium energy GB $\sim 380\text{-}400 \text{ mJ/m}^2$, close to $\Sigma=11$ (113))
- GB 3: $38.7^\circ\langle 111 \rangle$ tilt (medium energy GB $\sim 450\text{-}470 \text{ mJ/m}^2$, close to $\Sigma=7$)
- GB 2: Mixed $20.9^\circ\langle 100 \rangle 21^\circ$ tilt/twist GB (relatively high energy $\sim 560\text{-}580 \text{ mJ/m}^2$).

The BF images in Fig. 7 were acquired by orienting the grains to a particular zone axis (ZA) which is parallel to the tilt axis of the GB under study. This brings the GB's, especially the tilt GB's (first 3 GB's) very close to an edge-on position, i.e., parallel to the electron beam.

To further ensure the edge-on position, the GB's were studied at higher magnification, as shown in Fig. 8. Any inclination of the GB results in superposition of lattice

Figure 7: Bright-field TEM images of four GB's at edge-on positions, with their corresponding DP's. (a) GB1: 71.4° <110> tilt GB. (b) GB4: 52.2° <110> tilt GB. (c) GB3: 38.47° <111> tilt GB. (d) GB2: 20.4° <100> tilt twist GB.

fringes from both the grains parallel to the GB, so one can minimize the width of the superimposing fringes, to bring the GB to the edge-on position.

Figure 8: High-resolution STEM images of all four GB's at edge-on position. (a) GB 1. (b) GB 4. (c) GB 3. (d) GB 2.

The general structures of the GB's are clearly visible in Fig. 8. GB1, GB 3 and GB 4 were symmetrical tilt boundaries with the tilt axis being $\langle 110 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$, respectively. Symmetrical tilt boundaries can be thought of as formed by joining two identical vicinal surfaces from the neighboring grains [58]. It is clearly seen from the high-resolution STEM images of GB 1 and GB4 in Fig. 8, that two vicinal (111) surfaces, each containing steps, meet at the GB's. Bonding occurs across the GB and the steps become dislocations (edge dislocations for tilt GB's) which have their own elastic strain fields. Between these dislocations, the atomic arrangements become similar for both the grains, creating a region of good matching. The GB's thus formed have areas of good matching interrupted by localized strain fields of dislocation. GB2 on the other hand is a tilt-twist boundary, with the tilt axis being $\langle 100 \rangle$ and twist angle 21 degrees, so it was difficult to bring both the grains to zone axis orientation at the same time. Therefore, lattice fringes from only one grain are clearly resolved.

3.2 Plasmon energies of GB's

Spectrum image (SI) acquired across GB 3 is shown in Fig. 9a as an example. The aligned ZLP from the SI can be seen at 0 eV, followed by 1st and 2nd plasmon peaks at 15 eV and 30 eV, respectively. A shift in the 1st plasmon peak positions at and near the GB, toward lower energy, was observed in Fig. 9a. Enlarged image of the 1st plasmon peak profiles, acquired from all four GB's, are shown in Figs. 9b-d to elucidate the plasmon shift at the GB's more clearly. A decrease in intensity accompanied by a shift of the plasmon peak position toward a lower energy was observed at all GB's, as indicated by red arrows.

Figure 9: (a) Spectrum image (SI) from GB 3. (b-e) Plasmon peak profiles across the four GB's. The vertical lines (dotted) are used as a reference to elucidate the shift in plasmon peak positions, toward lower energy at the GB's.

To visualize the shift in plasmon peak position, ΔE_p , for the various GB's, a spectrum acquired from the matrix (grain) was overlaid with one acquired from the GB, as shown in Fig. 10. Spectra from the grain and GB were normalized (scaled) with respect to the ZLP to account for variations in experimental conditions during acquisition of the spectra. The insets show enlarged image of the plasmon peak positions from the matrix and GB with the black vertical line representing the center of the matrix plasmon peak. The GB plasmons can be seen to be shifted toward the left with respect to the matrix plasmons.

To ensure the plasmon peak shifts were not due to a variation in thickness at the GB's (e.g. GB grooving) [59], [60], thickness maps were calculated using the Log-ratio (relative) routine in Digital MicrographTM software, as shown in Fig. 11. The thickness t is computed as a multiple of the inelastic mean free path (MFP) λ using the following equation: $I_0 = I_t \exp\left(-\frac{t}{\lambda}\right)$, and rearranging one gets : $t = \lambda \ln\left(\frac{I_t}{I_0}\right)$ where I_0 is the integrated area under the ZLP , I_t is the total integrated area (counts) under the whole spectrum. As can be seen from Fig. 11, there is no appreciable variation in thickness along the scan lengths, so one can assume that the shift in the plasmon peak is solely due to the presence of the GB and not due to a variation in thickness at the GB.

Figure 10: (a-d) Low loss spectra, normalized (with respect to ZLP) from the GB (filled curve) and grain (line curve) overlaid to elucidate the GB plasmon peak shift.

Figure 11: (a-d) Thickness maps for all four GB's, calculated using the Log-ratio (relative) method along the line scan.

The plasmon profiles obtained after Gaussian fitting of the plasmon peak for all the four GB's are shown in Fig. 12. It can be observed that the amount of shift toward lower energy for the plasmon peaks (ΔE_p) varies with the GB, and so does the width of the plasmon valley, indicated by dashed lines in Figs. 12a-d. It was similarly observed that the increase in FWHM of plasmon peaks ($\Delta FWHM$), and the width of the FWHM hill, also varied with the GB's, as shown in Fig. 13. The profiles in Fig. 12 also display differences in the values of plasmon peak energies acquired from the Al matrix, which is the same for all of the samples. This is due to the fact that two different microscopes operating at different accelerating voltages were used for this study. GB 1 and GB 4 were studied using a S/TEM operating at 200 keV, whereas GB3 and GB 2 were studied with a S/TEM operating at 100 keV. Since the plasmon shift with respect to the matrix is the only concern here, these differences have no effect on the important quantities ΔE_p and $\Delta FWHM$.

Figure 12: (a-d) Plasmon peak positions across GB's, obtained by Gaussian fitting of the plasmon peaks.

Figure 13: (a-d) Plasmon FWHM profiles across all four GB's, obtained by Gaussian fitting of the plasmon peaks.

The plasmon energy profiles (raw data) from all four GB's are shown in Fig. 14a in the same graph for comparison. To depict the difference in ΔE_p and the width of the plasmon valley for the GB's, the plasmon energy of the matrix from GB 3 (15.145 eV) was taken as a reference and the profiles from other GB's were plotted by matching their matrix plasmon energies with this reference energy. Individual profiles for the four GB's were then fitted with a Voigt function, which is a convolution of Gaussian and Lorentzian functions, using OriginTM software. It was found that a Voigt function has a better fit with the plasmon profile than either Gaussian or Lorentzian only. Fig. 14b compares only the Voigt functions to clearly show the trend in plasmon energy profiles from the four GB's. It can be seen that the width and depth (ΔE_p) of the plasmon valley both increase with increasing GB energy.

In order to determine the shift in plasmon energies and plasmon valley widths accurately, the mean and standard deviation (SD) values of plasmon energies of the matrix were calculated for each GB. Examples from GB 1 and GB 3 are shown in Fig. 14c and Fig. 14d, respectively. The blue horizontal line represents the mean value of the matrix plasmons, while the red error bars along the blue line are the SD of the values. The value ΔE_p was calculated by measuring the highest deviation of plasmon energy at the GB from the mean value of the matrix. Any values of plasmon energy that fell below the calculated matrix mean $\pm$ SD values were taken to be part of GB and by measuring the range of such values the width of the plasmon valley was determined.

Figure 14: (a) Comparison of plasmon energy profiles across all the GB's with Voigt function fit. (b) The Voigt fits only, which depict the change in ΔE_p and plasmon valley widths for all four GB's. Measurement of plasmon valley width for (c) GB1 and (d) GB3. The blue lines indicate the mean value and the error bars (red) represents the standard deviation (SD) of the matrix plasmon energies.

Fig. 15a shows a plot of ΔE_p vs. GB energy, and as can be seen from this graph, ΔE_p increases proportionally with the GB energy. A linear fit is possible through the data as shown by the blue line in Fig. 15a. The FWHM of the plasmon valley can be obtained from the Voigt functions used to fit the individual plasmon energy profiles in Figs. 14a-b. In Fig. 15b, the FWHM (calculated from the Voigt functions) and measured (as mentioned in previous paragraph) width of the plasmon valley were plotted as a function of GB energy. Both of these parameters was found to increase with the GB energy, with the FWHM values being slightly more sensitive than the calculated values.

Figure 15: (a) Variation of plasmon peak shifts at the GB's as a function of GB energy. (b) Dependence of measured and FWHM widths of plasmon valley with GB energy.

High resolution STEM images were used to compare the calculated width of the plasmon valley with the apparent width of the GB. The high resolution images in Fig. 16a were processed by masking a FFT of the images followed by inverse FFT for better clarity. For GB 4 and GB 2, planes from the grains on the either sides of the GB's that ended abruptly at the GB were traced, as shown by red lines. The GB width was defined by the region (marked by two parallel blue lines) that contained the end sections of these planes. A slightly different procedure was followed for GB 1 and GB 3. In the cases, straight lines were drawn parallel to the GB plane, and regions which contained the local disregistry of atoms were selected as part of the GB. The measured values of GB width is plotted against GB energy in Fig. 16b, and shows an increasing trend with the GB energy. Comparison of the calculated width of the plasmon valley with the actual width of GB is shown in Fig. 16c, which also shows an increasing trend with an abrupt jump from GB 4 to GB 3.

Figure 16: (a) Measurement of GB widths using high-resolution STEM images. (b) Plot of GB width (measured using the high-resolution STEM images) as a function of GB energy. (c) Plot of measured plasmon valley width as a function of GB width (measured).

The FWHM profiles and variation in the FWHM of the plasmon peaks along a line scan, were obtained by fitting the plasmon peaks with Voigt functions as described earlier. Fig. 17a shows the FWHM profiles obtained by Voigt fitting the raw data from all four GB's. Like the plasmon energy profiles, the Voigt functions gave a reasonably good fit to the FWHM profiles. The Voigt function for all the GB's are shown separately in Fig. 17b for ease of comparison. As can be seen from the plots in Figs. 17c and 17d, the Δ FWHM and width of the FWHM hill increased with the values of GB energy. To quantitatively determine the values of these two parameters the mean values of the FWHM of the plasmon peaks from matrix were first calculated. Δ FWHM was determined by the difference between these mean values and the highest values of the FWHM of plasmon peaks obtained at the GB. Any FWHM value greater than the mean $\pm$ SD value of the matrix plasmon as taken to be the GB contribution, and measuring the range of values that were greater than the matrix value gave the width of the FWHM hill. Figs. 17c and 17d clearly show that Δ FWHM and the FWHM hill both increase with the GB energy, but the Δ FWHM plot also displays an anomalous drop for GB 3. These features will be considered further in the Discussion section.

Figure 17: (a) Comparison of plasmon FWHM profiles across all the GB's with Voigt function fit. (b) The Voigt fits only, that depict the change in Δ FWHM and FWHM hill width for all four GB's. (c) Plot of Δ FWHM as a function of GB energy. (d) Variation in measured FWHM hill width as a function of GB energy.

3.3. Deconvolution of plasmon spectra

An on-axis 2 mm circular entrance aperture was used to acquire the EELS spectra, which therefore records spectra over a range of scattering vector (q), from very low to high values of q . This makes the GB plasmon convoluted with the bulk plasmon, and hence, the spectra recorded require deconvolution to isolate the GB plasmon. For deconvolution, spectra acquired from the GB and matrix were normalized with respect to the ZLP, i.e., scaled so the intensities of the ZLP were identical. Deconvolution of the GB plasmons after normalization of the convoluted spectra was then performed in five different ways. These processes are described below.

1. Gaussian curve fitting to the GB plasmon:

The basic idea behind this process is the GB, having a lower electron density locally, will have its own plasmon peak with a lower energy than the matrix. The intensity going into the GB plasmon should come from the matrix plasmon, thereby reducing the intensity of the later according to the *begrenzungs* effect, but it would be a small fraction of the matrix plasmon. When both these plasmons are convoluted, the whole peak will shift to lower energy with reduced intensity as found in Fig. 10. It is further assumed that the GB spectrum and the matrix spectrum are additive, and as plural scattering was not considered here, it is a reasonable assumption. Gaussian curve fitting was performed by selecting a Region of Interest (ROI) on the left edge of the plasmon peak acquired from the GB. Two criteria were imposed during the curve fitting: i) the FWHM of the GB plasmon should be greater than the FWHM of the matrix plasmon, and ii) the FWHM of the residual matrix plasmon will be equal to the FWHM of the matrix plasmon peak. Based on these criteria, Gaussian fitting is performed for all the GB's, as shown in Fig. 18. The position

of the GB plasmon depends to a large extent on the width of the ROI selected, and it's position on the energy-loss axis; changing either of these results in changes in the position of the GB plasmon. After much trial and error it was found out that the same plasmon peak could be fitted in more than one way giving rise to different values for the GB plasmon. As this process is quite susceptible to error during the ROI selection and curve fitting, this procedure was not adopted for deconvolution.

Figure 18: (a-d) Gaussian curve fit to determine the GB plasmon for all four GB's. The plasmon peak acquired from the GB (solid green curve) is superimposed on the matrix plasmon (red curve), which is used as a reference. The GB plasmon corresponding to the Region of Interest (ROI) is represented by the green Gaussian function and the residual matrix component is represented by the blue curve.

2. Fourier-log deconvolution followed by:

- i) Subtraction (GB spectrum - grain spectrum): This procedure is straight forward. Fourier log deconvolution was used to determine the single scattering distribution (SSD) from the spectra collected from the matrix and GB. In this method, a Gaussian modifier was used during reconvolution. The FWHM of the Gaussian modifier was chosen to be equal to the FWHM of ZLP. This reduces noise without increasing resolution. Decreasing the FWHM of the Gaussian function increases the noise level. A zero loss modifier was also tried but not used because the noise level was higher. The Gaussian modifier effectively reduced the noise level and sharpened the deconvoluted spectra [5]. As mentioned earlier, the assumption is that the spectrum acquired from a GB is a sum (or rather, convolution) of GB and matrix spectra, ignoring plural scattering [61]. The matrix SSD obtained after Fourier log was subtracted from the GB SSD to determine the response of the GB. An example of this procedure is shown in Fig. 19. The SSD from the grain and GB spectra are shown in Figs. 19a-b, respectively, followed by the subtracted (GB - grain) SSD in Fig. 19c.

Figure 19: Single scattering distribution (SSD) obtained by Fourier log deconvolution of the low-loss spectra acquired from the (a) grain and (b) GB. (c) The GB SSD – grain SSD.

This procedure is applied to GB3 as shown in Fig. 20. The plasmon energy profile across GB 3 is shown in Fig. 20a. A total of five spectra were selected for this analysis; one from the matrix and four others from different parts of the GB region as shown in Fig. 20a. Fourier-log deconvolution was carried out on the five spectra after rescaling them with respect to the ZLP. The matrix SSD was subtracted from the GB SSDs to obtain the difference spectra from the four positions on the GB. One more assumption was made, that the thickness of the sample didn't vary along the scan length. The difference spectra for the four positions are shown in Figs. 19b – 19e, and they are superimposed in Fig. 20f. The difference spectra consists of two main features: i) interface/GB response, and ii) *begrenzungs* peak, as shown in Fig.

20d. The GB response is seen to increase with the decrease of impact parameter, i.e., toward the center of the GB in Fig. 20f, as one would expect. At the same time, the point where the difference spectra cuts the X axis was found to be slightly shifted toward the bulk plasmon.

- ii) Division (GB spectrum/grain spectrum): In this process, the GB SSD was divided by the SSD from the matrix and corresponding responses for three positions from GB3 are shown in Figs. 21a-c. In the Fourier-ratio method, the division is carried out in Fourier space, but in the current process the division was carried out in real space. Division by the grain SSD normalized the GB SSD, so the value of the spectra obtained after division had a value of approximately 1 everywhere, except for the GB response function as shown in Figs. 21a-c. Superposition of the three spectra showed the same trend as the difference spectra obtained after subtraction, in Fig. 21d, but the noise level was considerably higher in this process, so sometimes it was difficult to discern the GB response. Hence, this process was not applied to other GB's.

Figure 20: (a) Plasmon energy profile across GB 3. Four positions on the plasmon valley (i.e., near or at the GB) were selected and one position from the matrix (grey color) was chosen as reference. Difference spectra obtained by subtraction of matrix SSD from the GB SSD obtained from (b) right, (c) right towards center, (d) center, and (e) left of the plasmon valley. (f) Superposition of all four difference spectra.

Figure 21: Spectra obtained by dividing the GB SSD obtained from: (a) center, (b) left, (c) right of the plasmon valley, by the matrix SSD. The positions were shown in Fig. 20a. (d) Superposition of these three spectra.

1. Fourier-ratio deconvolution: In this process the normalized spectrum from the grain was used as the instrument response function to deconvolute the GB spectrum. Again a Gaussian modifier was used to reduce the noise, but the FWHM of the modifier was chosen to be that of the FWHM of the ZLP, so this process also didn't change any resolution. The

spectra obtained using the Fourier-ratio method from four different positions of GB3, as shown in Fig. 20a, were plotted in Figs. 22a-d. In Fig. 22e the four spectra were overlaid and a similar trend is seen as in the previous processes. The response from the center of the GB was found to be higher than the left and right positions, along with slight shift of the intersection point on the X axis toward the right.

Figure 22: Spectra obtained by Fourier-ratio deconvolution from: (a) center, (b) left, (c) right toward center, and (d) right of the plasmon valley. The positions were shown in Fig. 20a. (e) Superposition of these four spectra.

2. Direct subtraction of the non-deconvoluted spectra: The idea behind this process is that the spectrum acquired from the GB is the sum, rather than convolution, of the grain spectrum and the GB response spectrum. Therefore, subtraction of the grain spectrum from GB spectrum should give the GB response. As plural scattering was ignored here, this

process is valid at lower energy losses, but not applicable to higher energy losses [61]. The results of the direct subtraction method of non-deconvoluted spectra from the four positions of the GB3 are shown in Figs. 23a-d and compared in Fig. 23e. They showed a similar trend as the spectra obtained after the Fourier-log and Fourier-ratio method.

Figure 23: Difference spectra obtained by direct subtraction of non-deconvoluted matrix spectrum from the spectra acquired from: (a) center, (b) left, (c) right toward center, and (d) right of the plasmon valley. (e) Superposition of all four difference spectra.

The GB responses from the center of GB 3 obtained by the three process (Fourier-log, Fourier-ratio and direct subtraction) are compared in Fig. 24, and they are in good agreement with each other. The noise level in the direct subtraction method was found to be higher because in the Fourier-log and Fourier-ratio methods, a Gaussian modifier was used as a reconvolution function to reduce the noise level. From these five methods the Fourier-log and Fourier-ratio

methods were applied to the other of three GB's due their lower noise level. Fig. 25 and Fig. 26 summarize the results from the four GB's after deconvolution. Only the GB response function from the center of GB 1 is shown, since the plasmon energy profile for GB 1 was very narrow compared to the other three GB's.

Figure 24: Comparison of the GB responses from GB 3 obtained by Fourier-log method (red curve), Fourier-ratio method (green curve) and direct subtraction method (blue curve).

Figure 25: Resultant spectra obtained by Fourier-log method for: (a) GB 1, (b) GB 4, (c) GB 3, and (d) GB 2.

Figure 26: Resultant spectra obtained by Fourier-ratio method for: (a) GB 1, (b) GB 4, (c) GB 3, and (d) GB 2.

3.4. Line scans along GB 4

An EELS line scan 5 nm long was taken along GB 4 in 0.1 nm step increments to elucidate the electron density variation along the GB, as shown in Fig. 27a. A similar line scan was acquired from the grain, shown in Fig. 27b, at a distance of about 8 nm away from the GB for reference, sufficient to avoid any contribution from the GB due to delocalization effects.

Figure 27: (a) EELS line scan (red line) along GB 4 and corresponding HAADF signal. (b) EELS line scan (red line) parallel to GB 4 in matrix and corresponding HAADF signal.

In Fig. 27, the red lines show where the spectra were collected and a corresponding HAADF signal was acquired simultaneously with the EELS line scan. The HAADF signal showed the local atomic registry at the GB as compared to the periodic arrangement of atoms inside the grain. The motivation for the line scan along the GB was to see the effect of registry at the GB on the plasmon energy. The SI acquired from the GB and grain were analyzed using same methodology as mentioned earlier in section 3.2.

Figure 28a shows the HAADF signal (black) from the grain along with the corresponding plasmon energy (E_p) (red). This superposition shows an increase in E_p between the column of atoms and a decrease on the atomic columns, with very little deviation. Calculating the number of rows of atoms in the grain intersected by the line scan and from HAADF signal shows that the number of maxima in the plasmon profile is equal to the number of rows of atoms. Similarly, the FWHM of the plasmons were also overlaid on HAADF signal in Fig. 28b and an increase in the FWHM was observed on the atomic columns. The maximum in FWHM is little bit shifted from the atomic columns in a few places, but an overall correlation was found to exist. In summary, the plasmon energy was found to increase between atomic columns whereas the FWHM was found to be higher on, or near, the atomic columns.

Figure 29a shows the plasmon peak profile for the GB superimposed on the HAADF signal. The maxima of E_p occurs between the atomic columns when the HAADF signal is sharp, but when the signal becomes smeared, the range (difference between max and min E_p) of the plasmon energy profile decreases and a broadening of local maxima is also observed. The FWHM of GB plasmons also showed good correlation with the GB HAADF signal, Fig. 29b, with the maxima appearing on the atomic columns.

Figure 28: (a) Plasmon energy (red) superimposed on corresponding HAADF signal (black) acquired from the grain. (b) FWHM of plasmon peak (blue) superimposed on corresponding HAADF signal (black) acquired from the grain.

Figure 29: (a) Plasmon energy (red) superimposed on corresponding HAADF signal (black) acquired along the GB. (b) FWHM of plasmon peak (blue) superimposed on corresponding HAADF signal (black) acquired along the GB.

3.5. Tilting experiments on GB 3

Tilting experiments were carried out GB 3 near a $\langle 111 \rangle$ ZA, the tilt axis of the GB, to investigate the effect of orientation of the sample with respect to the electron beam on the plasmon peak position. The α (alpha) tilt was kept as constant as possible, but for different orientations the α tilt needed to be adjusted slightly, which gave a total change in α tilt around 3 mrad for the entire experiment. The β (beta) tilt was changed in increment of 12-15 mrad, giving a total change of 48 mrad. Line scans, of length 15 nm with step increments of 0.1 nm, were carried out across the GB for each orientation. The HAADF STEM image of each orientation and their corresponding FFT are shown in Fig. 30. A total of five orientations were studied in this experiment and they were designated as

- a) orientation 1 ($\alpha = 115.69$ mrad, $\beta = -47.24$ mrad),
- b) orientation 2 ($\alpha = 116.39$ mrad, $\beta = -53.55$ mrad),
- c) orientation 3 ($\alpha = 114.29$ mrad, $\beta = -65.62$ mrad),
- d) orientation 4 ($\alpha = 112.89$ mrad, $\beta = -79.08$ mrad), and
- e) orientation 5 ($\alpha = 112.89$ mrad, $\beta = -95.07$ mrad).

At orientation 1, Fig. 30a, the grain on left side was off the ZA with the grain on the right also a little off the ZA position, as can be seen from the HAADF image and corresponding FFT. With subsequent tilting, orientation 2 (Fig. 30b), the grains were brought closer to the ZA and in orientation 3, both the grains are on the ZA (Fig. 30c). Tilting was continued in the same direction, now moving away from the ZA position, orientation 4 (Fig. 30d), until both grains were far off the ZA and the lattice fringes are not clearly visible anymore, orientation 5 (Fig. 30e). The

SI acquired in each orientation were analyzed as before and the plasmon energy profiles from each orientation are plotted in Fig. 30f.

The plasmon energy profiles were fitted with a Voigt function as shown in Fig. 31a, where it can be seen that the function fits the profiles quite precisely. In Fig. 31b, only the Voigt functions are shown for clarity. In this figure, it can be observed that the plasmon profile as a whole, shifted toward lower energies as the sample was tilted in to orientation 3, where both the grains were on the ZA. In this orientation the matrix plasmon energies are the lowest. The plasmon energies of the matrix started increasing as the tilting was continued away from the ZA, orientation 4 and 5, but the plasmon energies from the GB continue to decrease toward lower values. To visualize the difference between ΔE_p at different orientations, the plasmon profiles were plotted keeping their matrix plasmon energies at a same reference energy (chosen arbitrarily), as shown in Fig. 31c. ΔE_p was found to increase with tilt, with the maximum being at the last position, orientation 5. The corresponding FWHM of the plasmon profiles were also fitted with Voigt functions, and are plotted in Fig. 31d. The FWHM profiles decrease as the sample is tilted toward the ZA, attaining the lowest value at orientation 3 where both the grains are on ZA, and increased as tilting continued away from the ZA.

Figure 30: (a)–(e) HAADF STEM images of each orientation and their corresponding FFT. (f) Plasmon profiles across GB 3 for all five orientations.

Figure 31: (a) Plasmon profiles across GB 3 for all five orientations fitted with Voigt function. (b) Only the Voigt functions for all five orientations. (c) The Voigt functions were plotted keeping the matrix plasmon energies at an arbitrarily chosen reference energy. (d) Voigt function fit of the plasmon FWHM profiles across GB 3 for all five orientations.

The results from this tilting experiment are summarized in Fig. 32. Three to four line scans were acquired from each orientation and ΔE_p was calculated for each of the scans and then averaged to obtain a mean and SD value for each orientation. This average ΔE_p is plotted against the β tilt (in mrad) in Fig. 32a, which shows an increase with tilt, except for orientations 2 and 3. The FWHM and calculated width of the plasmon valley vs. β tilt plot, Fig. 31b, shows a

steady decrease with tilt with a slight increase at orientation 3. The increase in FWHM of the plasmon peaks at the GB, ΔFWHM , was also plotted against β tilt, Fig. 32c, which shows an increase from 0.055 eV to 0.075 eV with a slight decrease at orientation 3. The width of the FWHM hill, as calculated from raw data, showed a similar trend as ΔFWHM when plotted against β tilt in Fig. 32d.

Figure 32: A plot of (a) the plasmon peak shift, (b) the plasmon valley width (measured) and the FWHM of the plasmon valley, (c) increase in FWHM of plasmon peak (ΔFWHM) at GB 3, and (d) width of the plasmon FWHM hill profile, as a function β tilts (mrad).

The variation of plasmon energies for the matrix and GB were also plotted separately with the α and β tilts, as shown in Fig. 33. The matrix and GB plasmons follow similar trends with both the tilts, but one thing to be noted is that, between orientations 4 and 5, there was no change in α tilts, only β tilts changed by 15 mrad. The plasmon peak energies of the matrix remained almost constant between these two orientations, but the GB plasmon energy decreased significantly.

Figure 33: Variation of plasmon energy of the matrix (black curve) and the GB (red curve) as a function of β tilts (mrad).

3.6. Thickness effect on plasmon peak shift

To evaluate the effect of sample thickness on the plasmon energy profile at the GB, two different samples of GB 4 with thicknesses of 0.57λ and 2.40λ , λ being the inelastic mean free path for Al, were studied. The low-loss spectra from these two samples are shown in Fig. 34a. The thin sample was studied using a microscope operating at 200 keV and as shown in Fig. 34a it has only a small 1st plasmon peak. The thicker sample was studied using another microscope operating at 100 keV and its low-loss spectrum contained pronounced 2nd and 3rd plasmon peaks, as seen in Fig. 34a. The thickness was measured using the Fourier-log method as described previously. Line scans were acquired across GB 4, at edge-on positions, from these two samples with a scan length of 15 nm and a step increment of 0.1 nm. Details of the data analysis procedure were described in the Experimental Procedures.

The plasmon energy profiles are shown in Fig. 34b, the red one being the profile from the thick sample and the blue one from the thin sample. The profiles were fitted with Voigt functions for clarity. It can be seen that the maximum in ΔE_p , the maximum shift in plasmon energy on the GB with respect to the matrix for these two samples is the same, i.e., ΔE_p (thin) = 0.045 ± 0.006 eV and ΔE_p (thick) = 0.044 ± 0.006 eV. The only difference between the plasmon energy profiles is the width of the plasmon valley, the thick being almost 2 nm wider than the thin sample. A comparison between the plasmon FWHM profiles obtained from the line scans is shown in Fig. 34c. The maximum increase in FWHM of the plasmon peaks, ΔFWHM , for the thin sample was found to be slightly higher than that of the thick sample, but by less than 0.01 eV. The FWHM valley for the thin sample was sharper, i.e., 1.9 nm lower than the thick sample.

Figure 34: (a) Low-loss spectra obtained from the thin (blue) and thick (red) sample. (b) Plasmon energy profile across GB 4 obtained from the thin (blue) and thick (red) sample. (c) Plasmon FWHM profile across GB 4 obtained from the thin (blue) and thick (red) sample. (d) Schematic diagram of the transmitted electron beam within a thin specimen and the entrance aperture of the spectrometer having a collimating effect [5].

3.7. EXELFS data analysis and results

The obtained SSD, Fig. 6 (blue line), is normalized with respect to the energy loss intensity of an isolated atom μ_0 (in the absence of backscattering from neighboring atoms) to obtain $\chi(E)$ using the following equation:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \quad (7)$$

To relate $\chi(E)$ to structural parameters, the E space was converted to wave vector k space using:

$$k = \sqrt{\frac{2m}{\hbar^2} (E - E_0)} \quad (8)$$

where E is the energy transfer and E_0 is the threshold energy. Conversion to k space gives $\chi(k)$, which was then multiplied by k^2 to yield $k^2\chi(k)$, as shown in Fig. 35a. The k^2 term compensate for the attenuation of the EXELFS signal at higher k values. $\chi(k)$ is given by:

$$\chi(k) = \sum_j N_j S_j(k) F_j(k) e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)} \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2} \quad (9)$$

where N_j is the number of neighboring atoms of j th type at a distance r_j from the central atom, $F_j(k)$ is the back-scattering amplitude from the neighboring atoms, σ_j is the Debye –Waller factor to account for the static disorder and thermal vibration, $\phi_{ij}(k)$ is the total phase shift of the electron wave (central atom phase shift twice and once by the back scattering atoms), $e^{-2r_j/\lambda_j(k)}$ accounts for the inelastic losses in the scattering process with λ_j being the electron mean free path. $S_j(k)$ is just an amplitude reduction factor due to many body effects.

Figure 35: (a) The blue curve is the weighted EXELFS spectrum $k^2 \chi(k)$ vs. k , obtained after multiplying $\chi(k)$ by k^2 . EXELFS spectrum $\chi(k)$ vs. k is obtained after background removal, normalization, and E to k conversion. The red curve represents a Hanning window function with a wave vector range of $k_{\min} = 3 \text{\AA}^{-1}$ and $k_{\max} = 7.5 \text{\AA}^{-1}$. (b) Fourier transformation (FT) of the weighted EXELFS spectrum $k^2 \chi(k)$ in momentum (k) space into the radial distribution function (RDF) in distance space.

In short, the EXELFS wave is determined by the back scattering amplitude ($N_j F_j(k)$), which gets modified by reduction factors $S_j(k)$, $e^{-2\sigma_j^2 k^2}$ and $e^{-2r_j/\lambda_j(k)}$, the distance dependent term $1/kr_j^2$, the sinusoidal function which is dependent on interatomic distances ($2kr_j$), and the phase shift term $\phi_{ij}(k)$ [62]. The resultant $k^2\chi(k)$, corresponding to the raw spectrum in Fig. 6a is shown in Fig. 35a. To determine the interatomic distance from the EXELFS data, Fourier transformation of $k^2\chi(k)$ to real space was performed using *ATHENA* [63] software (a data analysis software for X-ray absorption spectroscopy) with a Hanning window function having a wave vector range of $k_{min}= 3\text{\AA}^{-1}$ to $k_{max}=7.5\text{\AA}^{-1}$, as shown in Fig. 35a (red line). The corresponding radial distribution function (RDF) is plotted in Fig. 35b.

Superposition of $k^2\chi(k)$ obtained from the EELS spectra acquired from the grains and GB's for the three GB's analyzed are shown in Fig. 36. In this figure it can be seen that the frequency and amplitude difference in $k^2\chi(k)$ between the GB and grain spectra are more pronounced at higher k values. To emphasize this change at higher k values, wave vectors ranging from $k_{min}= 4.5\text{\AA}^{-1}$ to $k_{max}=7.5\text{\AA}^{-1}$ were selected for Fourier transformation, using Digital MicrographTM ELP software. The change in frequency at GB 1 (Fig. 36c) was very subtle due to the negligible change in interatomic distance for GB 1.

Fig. 37 shows the RDF obtained after Fourier transformation of $k^2\chi(k)$ for the GB's using a wave vector range of $k_{min}= 3\text{\AA}^{-1}$ and $k_{max}=7.5\text{\AA}^{-1}$. The 1st peak in the RDF obtained from the GB was found to be shifted towards the right side with respect to the 1st RDF peak of the grain (LG). Similarly, RDF peaks for GB 4 and GB 1 showed a shift toward higher distances compared to the grain/matrix. RDF peaks obtained using a higher range of k values are shown in

Fig. 38, using the same sequence as Fig. 37. Similar differences between GB and matrix RDF peak positions were observed but the differences (amount of shift) was found to be more compared to the previous case, as shown in Table 2:

Table 2: Increase in nearest neighbor distance corresponding to two different wave-vector ranges.

k range ($\text{\AA}^{-1}$)	GB 3	GB4	GB1
3-7.5	0.05-0.06 $\text{\AA}$	0.04-0.05 $\text{\AA}$	0.00-0.02 $\text{\AA}$
4.5-7.5	0.09-0.11 $\text{\AA}$	0.06-0.08 $\text{\AA}$	0.001-0.003 $\text{\AA}$

Figure 36: The weighted EXELFS spectrum $k^2\chi(k)$ vs. k obtained from the grain and: (a) GB 3, (b) GB 4, and (c) GB 1.

Figure 37: The radial distribution functions (RDF's) obtained after Fourier transformation (FT) of the weighted EXELFS spectrum, $k^2\chi(k)$, of the grain and: (a) GB 3, (b) GB 4, (c) GB 1, using a wave vector range of $k_{min}=3\text{\AA}^{-1}$ and $k_{max}=7.5\text{\AA}^{-1}$ with a Hanning window function.

Figure 38: The radial distribution functions (RDF's) obtained after Fourier transformation (FT) of the weighted EXELFS spectrum, $k^2\chi(k)$, of the grain and: (a) GB 3, (b) GB 4, (c) GB 1, using a wave vector range of $k_{min}=4.5\text{\AA}^{-1}$ and $k_{max}=7.5\text{\AA}^{-1}$.

In order to estimate the variation in the static disorder at the GB's, the 1st peak in the RDF was selected using a Hanning window function, as shown in Fig. 39a by a red line, and a back Fourier transformation was performed to isolate the single-shell contribution. With this Fourier filtering, the frequency associated with the RDF peak is filtered out from r space data and back transformed into k space as shown in Fig. 39b. All the contribution from the higher shells and higher frequency noise have been removed from the Fourier filtered spectrum. This procedure was applied to the RDF data obtained from all these GB's and the Fourier filtered spectrum (first shell only) from the grain and GB are compared in Fig. 40. It can be noted that the amplitudes of the filtered spectra from the GB's are slightly lower than that of the grains, which could be due to an increase in Debye-Waller factor σ at the GB, which imparts increased damping effect [62].

Fourier filtering not only separates the contribution of individual shells, but it also decomposes the EXELFS wave into amplitude and phase functions. The amplitude function $A(k)$ have been depicted as the blue line (magnitude) in Fig. 39b. $A(k)$ is given by:

$$A(k) = \frac{N}{kr^2} F(k) e^{-2k^2\sigma^2} e^{-2r/\lambda(k)} , \quad (10)$$

where $F(k)$ is the scattering amplitude. From this equation, it can be seen that the amplitude function, obtained after Fourier filtering, contains information about the Debye-Waller factor σ which can be used as an input to the ratio method [52] :

$$\ln[A(k)/A_m(k)] = \ln[Nr_m^2/N_m r^2] + 2k^2[\sigma_m^2 - \sigma^2] + 2[r_m - r]/\lambda(k) , \quad (11)$$

where the subscript m denotes the model system, in our case the defect free crystal, or the grain, and the unknown being the GB. The last term can be omitted as $[r_m - r] \ll \lambda(k)$, $\lambda(k)$ being

Figure 39: (a) The red curve is a Hanning window function used to filter out the first-neighbor shell EXELFS from the high frequency noise and outer shells. (b) The Fourier filtered spectrum (first shell) obtained by inverse transform and multiplication by the window function. The blue curve is the amplitude function $A(k)$ derived using the Fourier transform.

Figure 40: The Fourier filtered spectrum (first shell) obtained from the grain and: (a) GB 3, (b) GB 4, and (c) GB 1.

the electron mean free path, on the order of several angstroms. $A(k)$ and $A(k_m)$ were obtained from Fourier filtering, as discussed above, and a plot of $\ln[A(k)/A_m(k)]$ vs k^2 was obtained, which has a slope of $2[\sigma_m^2 - \sigma^2]$. In practice, this plot was found to be non linear in nature and least-square curve fitting was done to measure the slope. The log ratio plots from the three GB's are shown in Fig. 41a. The plot of $\ln[A(k)/A_m(k)]$ vs k^2 from GB 3 was found to have the highest slope and the one from GB 1 is almost horizontal. The values of $[\sigma_m^2 - \sigma^2]$ obtained are plotted against GB energy, in Fig. 41b. In spite of having considerable dispersion in the data, it can be seen that the variation in static disorder increases with increasing GB energy.

Figure 41: Log ratio plot for: (a) GB 4, (b) GB 3, and (c) GB 1. The slope of the curve is given by $2[\sigma_{grain}^2 - \sigma_{GB}^2]$, which gives a measure of change in static disorder at the GB. (d) Increase in static disorder at the GB's, $[\sigma_{grain}^2 - \sigma_{GB}^2]$ is plotted as a function of GB energy.

4. Plasmon Discussion

4.1. Plasmon spectra

4.1.1. Plasmon intensity at the GB

In the results Section 3.2, it was evident that the plasmon peak showed a decrease in intensity accompanied by a shift toward lower energy. This behavior can be explained based on classical dielectric theory, where the theoretical loss spectra for the probability P_I per unit path length for energy loss $\hbar\omega$ is given by:

$$\frac{dP_I(b,\omega)}{d\hbar\omega} = \frac{e^2}{2\pi^2 v^2 \epsilon_0 \hbar^2} [Im\{-1/\epsilon_B(\omega)\} \ln\left(\frac{q_c v}{\omega}\right) + K_0\left(\frac{2\omega b}{v}\right) (Im\{-2/(\epsilon_A(\omega) + \epsilon_B(\omega))\} - Im\{-1/\epsilon_B(\omega)\})] \quad (6)$$

The terms in the Eqn. 6 and their effect on loss spectra were discussed in detail in the Introduction. This equation states that the intensity in the interface originates through increasing subtraction from the bulk loss in a process known as the *begrenzungs* effect. This effect can be clearly observed in the plasmon intensity profile from the line scans across the GB's, as shown in Figs. 9b-e. Due to the *begrenzungs* effect, intensity is being taken out of the bulk plasmon and that is why the SI's appear narrower (due to decreased intensity of the bulk plasmon) and shifted toward lower energy near the GB in Figs. 9b-e. Note that this effect is localized near the GB and as distance from the GB increases, i.e., the impact parameter increases, these effect die off exponentially [33]. It has been shown [32] that at a distance less than about v/ω from the interface (where v is the velocity of the fast electron and ω is the maximum angular frequency), the bulk plasmon is gradually replaced by the interface loss function.

The decrease in plasmon peak intensity described above can be seen clearly in Figs. 10a-c, where the spectrum acquired from the grain and GB are compared after normalization with respect to the ZLP. The plasmon intensity at the GB is lower than the bulk, indicating intensity transfer from the bulk to the interface mode. This decrease in intensity is not discernable for GB 1 due to the negligible contribution of the GB plasmon. At the same time, the plasmon peak is shifted toward lower energy at the GB along with an increase in FWHM. This effect was observed for all four GB's.

4.1.2. Plasmon peak shift at the GB

As mentioned earlier, GB 1 has the lowest energy among the four GB's, being about 60-80 mJ/m², or close to a coherent twin $\Sigma 3$ GB. GB 4 (close to $\Sigma 11$) has an energy of approximately 380-400 mJ/m², followed by GB 3 (close to $\Sigma 7$), and GB 2, which have energies of 450-480 mJ/m² and 560-580 mJ/m², respectively. The line scans in Figs. 14a-b display systematic differences in the plasmon energy across the four GB's. It is apparent that the plasmon valley gets deeper and wider with increasing GB energy. In addition, the change in volume plasmon energy at the GB (ΔE_p) shows an almost linear dependence on GB energy, as evident in Fig. 15a. The reasons for these behaviors are discussed below.

The plasmon energy loss is given by $E_p = \hbar\omega_p$, ω_p being the free electron plasmon frequency, which depends on the local valence electron density n , $\omega_p = \left\{\frac{ne^2}{\epsilon_0 m}\right\}^{1/2}$. As E_p is proportional to $\sqrt{n}$, the shift in the plasmon peak energy (ΔE_p) provides information about the decrease in local electron density at the GB. As shown in Fig. 15a, ΔE_p increases with increasing GB energy, suggesting that the local electron density decreases proportionally. Wright and Atlas

[1] used density-function-theory (DFT) to calculate the electron density distributions at $\Sigma 11$ and $\Sigma 3$ twin boundaries in Al. According to their calculations there are areas of lower electron density at the GB that extend into regions between the atomic planes oriented normal to the GB. For a $\Sigma 11$ boundary, their model predicts a 10% reduction in the average electron density at the GB compared to the bulk, and this low density extends three atomic layers to either side of the GB. Figs. 14a-b demonstrate that this lowering of the electron density at the GB was revealed by the incident STEM probe through a local change in ω_p , and that the width of the electron deficit region extends out into the matrix on either side of the GB's. However, the results from GB 4, which is close to $\Sigma 11$ with an energy of 380-400 mJ/m², only shows a plasmon peak shift of $\Delta E_p \approx 0.045$ eV, which corresponds to only 0.53% in electron density calculated from Eqn. 4. The reason the difference is so large; i.e., 10% vs. 0.53%, is due to delocalization effects that convolute the GB signal with the matrix signal, as discussed further below.

4.1.3. Determination of delocalization diameter

An experimental estimate of the effective delocalization diameter can be made from the line scan across the $\Sigma 3$ GB (GB 1), which can be considered the sharpest GB in Al, extending for only about two atomic planes, as shown in the high resolution STEM image in Fig. 16a. The width of the GB in Fig. 16a is about 0.23 nm, and this corresponds to a plasmon valley width of 1.69 nm in Fig. 14b, which for a 0.012 nm diameter probe gives an effective delocalization diameter of approximately $1.46 \approx 1.5$ nm. The delocalization diameter associated with inelastic scattering has been investigated by various researchers using experimental methods and theoretical calculations. A brief comparison between the present experimental value of the delocalization diameter (~ 1.5 nm) and values available in the literature is presented in the following paragraph.

Egerton's formula [64] based on the Rayleigh criteria for resolution,

$$L_{50} = 0.52\lambda/\langle\theta\rangle, \quad (7)$$

estimates the delocalization distance L_{50} to be 3-4 nm at 15 eV energy loss, which is about twice the present experimental value of 1.5 nm. In Eqn. 7, $\langle\theta\rangle$ is defined as the median scattering angle containing 50% of the inelastically scattered intensity. Our experimental result for the delocalization diameter was found to be in better agreement with Erni and Browning's [65] calculations, which are based on a treatment by Muller and Silcox [66] for a 200 keV electron probe with a FWHM of ~ 0.14 nm. Muller and Silcox [66] used a quantum mechanical approach to calculate the probability $P(b,E)$ of losing a discrete amount of energy E at different b (impact parameter) from an atom. The summation of the contributions of perpendicular and parallel excitations give the total scattering probability $P(b,E)$. The delocalization diameter, d_{50} , at 15 eV energy loss from this treatment was estimated to be around 1-1.2 nm, which is in good agreement with our experimentally obtained value of 1.5 nm. The difference between these two calculated and experimental values may be due to slightly different experimental conditions used during spectra acquisition. Similarly, L_{80} , the area containing 80% of the electrons contributing to the signal, was estimated to be ~ 5 nm which is more than three times the present experimental value. In summary, our experimental measurement on GB 1 makes it possible to conclude that: 1) Egerton's formula overestimates the delocalization diameter at low energy losses (less than 70 eV) while the calculations by Erni and Browning [65] give a reasonable estimate, and 2) contributions from the delocalization diameter, L_{80} , appear almost negligible compared to L_{50} , even in the low energy-loss regime. The experimentally determined delocalization diameter can be used to deduce

the actual width of the plasmon valley (in the absence of any delocalization effect) across a GB, and its correlation with the GB width is discussed in the following paragraphs.

The measured width of the plasmon valley for GB 4 in Figs. 14b and 15b is 2.5 ± 0.3 nm. Taking the effective delocalization diameter to be 1.5 nm, the actual width of the plasmon valley is 1.0 ± 0.3 nm, which is almost twice that of the measured width of 0.48 nm for GB 4 from the STEM image in Fig. 16a. This leads to the important conclusion that the lowering of electron density extends over a distance about twice the physical thickness of the GB and into the perfect lattice of the surrounding grains. This means that the decrease in electron density spreads smoothly over 2-3{111} atomic planes on either side of the GB, which is in good agreement with Wright and Atlas's calculations [1]. Extending this picture to the other GB's, it is found that the lowering of density extends even further with increasing GB energy. For GB 2 with the highest energy, the lowering of electron density extends up to 1.53 ± 0.15 nm on either side of the GB, while the width of the physical GB is only about 0.76 nm.

4.1.4. Plasmon energy profile and electron density across the GB

The GB width measured from the STEM images gives a rough estimate of the thickness of the boundary and shows an increase with GB energy in Fig. 16b. GB 4 and GB 3 have a difference in energy of only ~ 50 - 70 mJ/m² (i.e., 380-400 mJ/m² vs. 450-480 mJ/m²), and their widths are comparable, while the measured width of the plasmon valley in Fig. 16c shows a sharp increase from GB 4 to GB 3. This means that even if their physical widths are comparable (Fig. 16b), GB 3 has a wider area on either side of the GB with a lower electron density compared to GB 4. Moreover, the plasmon peak shift at the GB, ΔE_p , for GB 3 is higher than GB 4 by 0.005 -

0.01 eV, as shown in Fig. 14b, indicating greater deficiency in valence electron density at GB 3 compared to GB 4. That means that with increasing GB energy, the plasmon valley and thus, the valence electron density profile across the GB gets wider and deeper.

Similarly, the plasmon valley width across the GB 2, (having the highest energy of approximately 560-580 mJ/m²) was found to be 4.63 ± 0.3 nm, which is higher than GB 3. The ΔE_p for GB 2 was also observed to be higher than GB 3 by 0.006 - 0.01 eV, as shown in Fig. 14b. The increase in width of GB 2 is less than expected based on the widths obtained for GB 4 and GB 3, but this unexpected result may be related to the particular GB structure, since the other two GB's are pure tilt boundaries while GB 2 is a tilt-twist boundary. More investigation on similar tilt-twist GB's is required to confirm this hypothesis. In summary, it can be concluded that the drop in valence electron density at the GB increases, and it extends further inside the grains with increasing GB energy.

Similar results were obtained by Benthem *et al.* [4], where they reported an index of refraction across $\Sigma 5$ and $\Sigma 13$ GB's of SrTiO₃ using spatially resolved EELS. The widths of the refractive index plots, which are similar to plasmon valley widths, show an increase with increasing GB energy. The plot widths for $\Sigma 5$ and $\Sigma 13$ GB's were ~ 5 nm and ~13 nm, respectively, which are considerably higher than the present $\Sigma 3$ and $\Sigma 11$ GB's. With increasing GB energy, the refractive index plots got wider and deeper, similar to the present experimental results, and a similar drop in valence electron density at the GB's was also observed.

4.1.4.1. Effect of probe broadening

The variation of the plasmon valley width could also be related to probe broadening associated with different sample thicknesses. As an example, the case of GB 3 and GB 4 is considered here. The thickness of the thin foils for GB's 3 and 4 were found to be ~ 80 nm. Using Goldstein's equation [67], a probe broadening of 3.5 nm was calculated for GB 4 which was examined using a 200 keV microscope, while a probe broadening of 6.7 nm was calculated for GB 3, examined in a 100 kV microscope. Later it will be shown that beam broadening of nearly 10 times (due to thicker samples) increases the plasmon valley width by only about 2 nm. The plasmon valley widths for GB 3 and GB 4 were 4.27 ± 0.4 nm and 2.5 ± 0.3 nm, respectively, almost an increase of 2 nm. However, the EEL spectra were acquired when both the grains were at ZA orientation. This favors for channeling conditions, which can restrict beam broadening for great depths inside a crystal [68]. Allen *et al.* [69] showed no significant reduction in spatial resolution of EEL spectra due to probe broadening. Therefore, it seems reasonable to conclude that any effects from probe broadening can be ignored when considering the four GB's in this study.

4.1.5. Increase in FWHM of plasmon across the GB

The increase in FWHM of the plasmon peaks across the GB's were also measured, as shown in Fig. 17. The FWHM of the plasmon peak at the GB increases because of increased damping of the plasmon excitation. The GB contributes to additional scattering due to its less ordered structure, so electrons at and near a GB are expected to have a shorter lifetime compared to the bulk. Damping of plasmons by the GB, and hence, the increase in FWHM (Δ FWHM) was found to increase with GB energy, as shown in Fig. 17c. An exception to this trend was observed

for GB 3, where the ΔFWHM was found to be less than expected based on the GB energy and electron density deficit. The FWHM of the bulk plasmon from the matrix (away from the GB) for GB 2 and GB 4 was found to be 1.06 ± 0.02 eV, while for GB 3 it was 0.98 ± 0.02 eV. GB 2 and GB 4 were both analyzed after bringing them near to a [110] ZA, whereas GB 3 was analyzed on a [111] ZA. This indicates a potential anisotropy in the dampening behavior of the plasmon FWHM, which may be causing the anomalous decrease for GB 3 in Fig. 17c. Anisotropy of the FWHM in Al or other cubic systems has not been previously mentioned in the literature, but anisotropy in the dispersion of the FWHM of plasmons has been reported for Mg single crystals [70] and in Be monocrystals [71]. In Mg, the plasmon width was found to be broader along the c axis than along the a axis, which is opposite to what was observed in Be. Using an empirical pseudopotential method, Bross [72] calculated the dispersion in plasmon energy and linewidth for Al taking into account band structure effects. The linewidth dispersion was found to be anisotropic in single crystal Al for q along the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions as a function of q^2 . However, damping of the plasmons at the other three GB's was found to increase with increasing GB energy. Hence, it can be concluded that the FWHM of the plasmon increases as the electron density at the GB decreases, or as the local disorder and energy of the GB increases.

Figure 42a shows the plasmon energy and corresponding FWHM profile of the plasmons along a line scan acquired from GB 3, when both grains were on a ZA. In this figure, the width of the FWHM hill is seen to be greater than the corresponding plasmon valley width, and the width of the hill increases with increasing GB energy. The FWHM of the plasmon also starts increasing before the plasmon energy shift towards lower energy. This is also true for the other ZA orientations as shown in Figs. 42b-d. The damping effect could be due to diffuse scattering at

the GB [73], or a change in momentum due to elastic scattering of the plasmons from a static inhomogeneity of electrons [74], but in any case, the plasmon is found to be more sensitive to the damping effects than the effects of change in local electron density.

Figure 42: Comparison between the plasmon energy profile (red) and FWHM profile (yellow) across GB 3 at: (a) orientation 3, (b) orientation 2, (c) orientation 4, and (d) orientation 5.

4.2. Deconvolution

An on-axis 2 mm circular entrance aperture was used to acquire all of the EEL spectra, which recorded a range of scattering vector q from very low to high values [57]. This makes the GB plasmon convoluted with the bulk plasmon, and hence, the spectra require deconvolution. GB 3 is selected as an example to discuss the effects of the GB on the plasmon energy, the FWHM, and later, to compare with the results obtained from other GB's.

The deconvolution procedure was thoroughly discussed in the Results Section 3.3. Deconvolution of GB 3 spectra using Fourier-log and Fourier-ratio techniques yielded essentially similar results. The GB response and corresponding *begrenzungs* effect from four distinct positions on the plasmon line profile across GB 3 are shown in Figs. 20b-e. It is evident that as the probe proceeds toward the GB from the right, the intensity of the GB response starts increasing and almost simultaneously the *begrenzungs* peak, which represents the intensity drop of the bulk plasmon due to presence of interface/GB, also deepens. One interesting point worth noting in Fig. 20b is that when the probe is positioned near the edge of the plasmon valley, only the *begrenzungs* peak is present and the GB response is negligible. That means that the amplitude of the bulk plasmon starts decreasing before the appearance of the GB plasmon. As the probe moves further toward the GB, i.e., the impact parameter b decreases, the GB response first appears prominently in Fig. 20c. Both the GB response and the *begrenzungs* peak keep increasing and attain a maximum value when the probe is on the GB in Fig. 20d. Comparison of GB response from four different positions is shown in Fig. 20f. The GB response is not found to be shifted toward lower energies,

similar to theoretical calculations using relativistic effects predicted for the case of an interface plasmon peak (IPP) for a Si/SiO₂ interface [57].

The GB response from all four GB's obtained using Fourier-ratio analysis are compared in Fig. 43. The reason for using Fourier-ratio deconvolution is that the resulting spectra retained the original ZLP, which could then be used to normalize the responses from the four GB's. It is observed that as the GB energy increases, the GB response and correspondingly *begrenzungs* peak also increase except that the GB 2 response is found to be smaller than the GB 3, whereas it should be greater, since GB 2 has a higher energy than GB 3. This anomaly can be explained in terms of the sample thickness difference between GB 2 and GB 3. The sample used for studying GB 2 was actually very thin. The thickness of the sample was determined using Digital MicrographTM software, by calculating the ratio of the total intensity and ZLP intensity (I_T/I_0). The spectra acquired from GB 2 contains a low-loss peak from an Al₂O₃ layer formed during sample preparation, which has a maximum at 22.5 eV. This peak added intensity to I_T and thereby, results in an over estimate of the thickness of GB 2 sample. A quick comparison of EELS spectra acquired from GB 2 and GB 3 (both from matrix) in Fig. 10 reveals that GB 2 has a much smaller 1st plasmon peak than GB 3 (after normalizing with respect to the ZLP). The effect of the Al₂O₃ plasmon peak is removed by subtracting it from the low loss spectrum. This subtraction should not affect the position or the form of the Al plasmon [75]. After subtraction, it was found that the GB 3 sample is almost three times thicker than the GB 2 sample. After normalizing the spectra from GB 2 and GB 3 with respect to the ZLP, the response from GB 2 is multiplied by three to yield the response of a sample equivalent to a thickness of GB 3. After the thickness correction, the GB responses are shown in Fig. 44, where GB 2 has a higher response than GB 3.

Howie *et al.* [76] calculated the GB response for diffuse interfaces between Al and Mg. Fig. 2 in [77] shows the diffuse interface response with respect to a dimensionless parameter qa (0.01-5), where q is the momentum transfer and $2a$ is the thickness of the interface. According to their calculations with increasing thickness of the interface, i.e., as qa increases, the interface gets more diffuse and consequently the intensity of the response function decreases. In VEELS experiments, the value of q is fixed by the entrance aperture of the spectrometer. Hence, the value of $2a$ increases with increasing GB energy, as shown previously, and the electron density at the GB decreases accordingly, which is opposite to the diffuse interface, indicating that these GB's are structurally sharp. The gradient of the dielectric function $\varepsilon(x, \omega)$ of a diffuse interface also decreases with increasing thickness of the boundary, but as the GB energy increases in the present investigation, the electron density at the GB decreases more and consequently the change in local

Figure 43: Comparison of the GB response functions from four GB's after normalization with respect to the ZLP.

Figure 44: Comparison of the GB response functions from four GB's after normalization with respect to the ZLP and sample thickness corrections.

dielectric function at the GB should be more. Hence, the experimentally observed trend of GB response function herein is found to be opposite to that obtained in the case for the diffuse interfaces. This indicates that the increase in the GB response with GB energy is due to the increasing electron deficiency at the GB. As the GB energy increases, the width of the plasmon valley and simultaneously the variation of dielectric function $\varepsilon(x, \omega)$, which is a function of valence electron density across the GB increases, and that is reflected as the increase in the intensity of the response function.

4.3. Characteristics of GB response and *begrenzungs* peak

As discussed in the previous section, it was observed that as the probe proceeds toward the GB from the matrix, the intensity of the GB response starts increasing almost simultaneously with the *begrenzungs* peak, as shown in Figs. 20b-e. It was also shown previously that the FWHM in Figs. 17a-b increases, and the amplitude of the plasmon in Fig. 9 decreases, as the probe crosses the GB. The amplitude profile of the bulk plasmon across the GB is shown in Fig. 45a, where the amplitude is plotted with the FWHM of the plasmon loss for comparison. In this section, the connection between the intensity profile of the GB response and the *begrenzungs* peak with the amplitude and FWHM profile of the plasmon peak is discussed.

The FWHM attains a maximum value where the amplitude reaches its minimum value, with a small shift observed in the plot being due to fitting errors associated with noise in the data. When the GB is on, or in a near edge-on position, both of these profiles should look symmetrical across the GB. The profile of the *begrenzungs* peak obtained after deconvolution is compared with the FWHM in Fig. 45b, and the *begrenzungs* peak profile across the GB is compared with the amplitude of the bulk plasmon in Fig. 45c. The GB plasmon and *begrenzungs* peak profiles were obtained using a software routine written by Mr. Eric Hoglund. The valley width of the *begrenzungs* peak profile is similar to the width of the FWHM hill, as can be seen in Fig. 45b. It can be inferred from this that the intensity coming out of the bulk plasmon peak is contributing to the increase in the FWHM of the GB plasmon. Again, as shown in Fig. 45c, the plasmon amplitude profile across the GB is similar to the *begrenzungs* peak profile. Ideally this should be the case as the intensity transferred from the volume plasmon as a *begrenzungs* peak

results in the decrease in amplitude of the volume plasmon neglecting diffraction effects. Comparison of the plasmon amplitude profile with the profile of GB response, in Fig. 45d, shows that the width of the GB response profile is much narrower than that of the amplitude. This suggests an important point; i.e., only part of the intensity loss from the volume plasmon goes to the creation of the GB plasmon.

The loss of intensity becomes more evident when profiles of the *begrenzungs* peak and the GB response are compared in Fig. 46a. The width of the *begrenzungs* peak profile is wider than the GB response profile, making the later more localized to the GB. This conclusively proves that the intensity loss as a *begrenzungs* peak partly goes to activate the GB plasmon. This feature is observed in other GB's as well, as shown in Figs. 46b-c. The GB1 profile is not shown here, as a slight change in the GB response could not be separated from the noise in the data. The blue curves in Fig. 46 were obtained by adding the GB response profile to the *begrenzungs* peak profile, and represent the total intensity loss at the GB. This loss in intensity of the plasmon across the GB can be explained in terms of decreased inelastic scattering due to the lower electron density at the GB. The blue curves in Fig. 46 appear to be non-symmetrical about the GB with greater lowering on the side of the non-ZA grain, compared to the grain on the ZA. At a non-ZA position, due to the momentum dependence of the plasmon FWHM [27], the plasmon linewidth increases. Therefore, more intensity is lost as a *begrenzungs* peak in increasing the FWHM of the plasmon peak of the non-ZA grain as compared to the ZA grain. Hence, the blue curve is asymmetric across the GB.

Figure 45: Comparison of: (a) the amplitude profile and the FWHM profile of the plasmon, (b) the *begrenzungs* peak profile and the FWHM profile of the plasmon, (c) the *begrenzungs* peak profile and the amplitude profile of the bulk plasmon, and (d) the plasmon amplitude profile and the GB response profile, across GB 3.

In summary, three phenomena are taking place simultaneously at the GB:

- 1) A decrease in plasmon intensity due to lowering of the inelastic scattering.
- 2) A loss in intensity as a *begrenzungs* peak.
- 3) Partial recovery of the lost intensity as a GB response.

The combined effect of these three processes makes the bulk plasmon narrower and shifted toward lower energy near the GB, as apparent in Fig. 9.

Figure 46: Comparison of the Voigt function fits to the *begrenzungs* peak profile (BP), the GB response profile (GB), and summation of the *begrenzungs* peak profile and the GB response profile (GB + BP) across: (a) GB 3, (b) GB 4, and (c) GB 2.

The intensity, or the total excitation probability, of the plasmon across an interface of GaAs and vacuum was calculated by Wang [78]. The total excitation probability (dP / dz) is given by the sum of the volume plasmon (dP_v / dz) and the interface plasmon (dP_i / dz), excitation probabilities per unit distance. Wang [78] showed a drastic change in the (dP_v / dz) *vs* x and (dP_i / dz) *vs* x curves, x being the impact parameter, occurs when the electron is very near the interface, or about $x \approx 0.3$ nm. In contrast, the total excitation probability, i.e., the

summation of (dP_v / dz) and (dP_i / dz) , remains almost constant, which is not in agreement with the present experimental results. The present VEELS results show that the GB response function appears when the probe is about 2.5 nm away from the GB and the *begrenzungs* peak appears when the probe is even further away. This variation near the GB is found to be not as localized as predicted by Wang's calculations [78]. Again, the summation of these two effects is found to decrease near the GB (Fig. 46), while according to the calculations, (dP / dz) is almost constant inside GaAs. One possible reason for this disagreement could be that Wang [78] assumed no dispersion at the interface, i.e., the dielectric function $\varepsilon(\omega)$ is independent of the scattering vector q . This assumption might hold well if the electron density didn't change at the GB, but this brings up an important question: Can a change in electron density at the GB change the local response of the material to an external electric field, i.e., the electron probe?

4.4. Plasmon frequency and dielectric constant of a GB

Hunderi [73] developed a model to explain the anomalous absorptivity in alkali-metal films evaporated on a cold substrate. In this model the GB's are represented by flat ellipsoidal disks having a different dielectric constant from the bulk medium. The electrons at and near the GB have a short lifetime compared to the bulk as the GB contributes to additional scattering due to its disordered structure. This model assumes defects along the GB make the electron density at the GB different (lower) than the bulk material, and as a consequence make the plasma frequency at the GB different than the bulk. An effective dielectric constant, ε_g , was calculated for the material to account for the volume fraction of ellipsoidal disks. This model can successfully explain the absorptivity of alkali-metal films by incorporating contributions from the plasma resonance at the GB. Building on this concept Nagel *et al.* [79][80] put forward a two-

carrier model to explain the frequency dependence of relaxation time in Drude's model. In this model the material is divided in two regions, areas with perfect lattice and areas which are highly disordered, e.g., GB's. According to their argument, electrons in these two regions respond differently to an applied electromagnetic field. However, in this model the difference between relaxation times τ is considered, leaving the electron densities the same; τ at the GB being smaller than the perfect crystal. The value $\varepsilon_2(\omega_p)$, the imaginary part of the dielectric function, is increased to incorporate the effect of relaxation time, where ε_2 is given by:

$$\varepsilon_2 = \frac{\omega_p^2}{\left(\omega^2 + \frac{1}{\tau^2}\right)\omega\tau} \quad (8)$$

From these assumptions the apparent collision frequency is calculated and good agreement is found with the infrared dielectric response of Au films. Contrary to the assumption of variation in relaxation time at the GB's, Krishan *et al.* [74] proposed a model based on the idea of variation of the electron density at the GB. The basic idea is that in a weakly inhomogeneous system plasmons can elastically scatter from the inhomogeneities changing the initial momentum and this scattering broadens the plasmon line width. This idea is based on the experimental evidence by Brambring *et al.*[81] where elastic scattering of surface plasmons was reported for static electron density fluctuations in a thin metal film. Krishan *et al.* [74] used perturbation theory to sum over all possible final states of wave vectors after scattering, to formulate an expression for the damping rate. Though the model predicts an auto correlation length, which is three times the actual crystal size, this model agrees well with the dampening behavior of plasmons obtained by Festenberg [82]. It is further observed that during theoretical calculations of the interface plasmon for a Si/SiO₂ interface using Eqn. 6, better agreement with experiment is achieved by inserting an extra layer

of a third material (SiO) at the interface [83]. This experimental observation further strengthens the argument of a different dielectric response of GB's.

The GB plasmons, obtained after deconvolution in Section 3.2, showed an increase with the increasing GB energy. Formation of the GB plasmon is due to the fact that the GB has a different plasmon frequency ω_{GB} , than the bulk. As the electron density varies at the GB with a change in GB energy, the plasmon frequency at the GB ω_{GB} , changes and so does the dielectric function at the GB, as it is dependent on the plasmon frequency. This is why three distinct GB plasmons were obtained from the four GB's having different energies, as shown in Fig. 46. In summary, it can be inferred that GB's have a substantial effect on the position and width of the plasmon peak owing to the different dielectric response due to their lower electron density. This change in dielectric response can be connected to either a change in plasmon frequency at the GB, relaxation time, or scattering vector, or some combination of the three.

4.5. Line scans along GB

The line scans from the matrix parallel to the GB in Figs. 28a-b, show good correlation between E_p and the FWHM of the plasmons with the positions of the atoms, indicating that lattice imaging is possible using plasmon-loss electrons. But the delocalization diameter, L_{50} , was found to be ~ 1.5 nm for a 0.012 nm diameter probe, which suggests that atomic resolution in EELS mapping is not possible with plasmon losses. Plasmon scattering is mostly small in angle and so being delocalized in real space cannot produce atomic resolution by itself. In contrast, experimental works have reported [84] atomic-scale image features can be recorded using plasmon losses. This anomaly can be explained in terms of double scattering events [85]. The low-angle inelastic scattering can be followed (or preceded) by high-angle elastic scattering, and the effect of both give rise to atomic resolution. These two scattering processes are independent, so their effects are additive. Krivanek *et al.* [86] have computed the effect of inelastic scattering for a Si $\Sigma 9$ GB for a sample thickness of 40 nm, viewed along a [011] direction. Interestingly, at optimum defocus for elastic scattering the contribution from inelastic scattering is found to be negligible, which is quite different from our results where the plasmon energy is well-correlated with the atomic positions in HAADF. This could be due to thickness effects, as the Si sample used in [86] has a thickness of only 0.27λ ($\lambda = 150$ nm for Si). In comparison, the Al sample used for the VEELS experiments in Fig. 28, is around 2.5λ ($\lambda = 100$ nm for Al). Inelastic scattering increases monotonically with thickness, but also reduces resolution due to the angular spread of the beam [87]. This reduction in resolution is not obvious in the scans obtained from the matrix in Fig. 28a as the E_p profile correlates well with the HAADF signal. Due to local disorder at the GB in Figs. 29a-b, the perfect correlation of the E_p and FWHM profiles with the HAADF signal is lost. This

might cause artifacts in low-loss imaging of defects [86], so careful simulations are required while imaging defects because of the significant contribution from inelastic scattering.

Sine functions were fitted with the E_p profile from the grain and GB in Figs. 28a and 29a to find out the periodicity of the plasmon energy, and these are shown in Figs. 47a-b. From comparison of the sine fits in Fig. 47c, it is observed that the amplitude of the sine curve for the GB has decreased and its period has also increased compared to the sine curve corresponding to the grain (as shown by the vertical lines). The plasmon profile from the grain has 12 local maxima in the 5 nm scan length, whereas the profile from the GB has 11 local maxima. This implies that the electron density and its variation is lower at the GB and it is smeared out to accommodate the local atomic disregistry at the GB. The ratio of the GB periodicity to the equivalent matrix, or $11/12 = 0.91$, also gives an approximate measure of the decrease in atomic density at the GB, of approximately 9%, which compares favorably with earlier calculations by Seeger and others [9]-[11].

The FWHM of the plasmons from the grain and GB are compared in Fig. 47d. The FWHM of the GB is higher than the grain, as one expects, and also has a longer periodicity, i.e., slower variation than that of the grain. This also suggests a smearing out effect of the electron density at the GB. The FWHM profile and the plasmon profile are also found to vary differently, the plasmon variation being more sensitive to the atomic positions than the FWHM profile.

The average plasmon peak energy at the GB is lower than the grain by 0.02 eV, which is smaller than the ΔE_p value of 0.04 eV reported for GB 4 earlier in this thesis. This may be due to the effect of sample drift during acquisition, causing the scan along the GB to be slightly shifted from the center of the GB.

Figure 47: (a) Sine function fit (blue) of the plasmon energy profile (black) from grain. (b) Sine function fit (red) of the plasmon energy profile (black) along GB. (c) Comparison of the sine function fits from grain (blue) and along GB (red). (d) Comparison of the plasmon FWHM profile from grain (blue) and GB (red).

4.6. Tilting of GB 3

4.6.1. HAADF imaging

HAADF images of GB 3 at different tilts with corresponding FFT's are shown in Fig. 30. The tilt axis is in the plane of the GB and perpendicular to the viewing direction, almost parallel to a $\langle 112 \rangle$ direction. This direction was chosen for a reason. If the tilt axis was chosen perpendicular to the interface, even with very small tilts of $< 1^\circ$, the HAADF lattice image would have disappeared quickly from both the grains making it almost impossible to locate the GB, and thereby severely restricting the tilting range. The left grain in Fig. 30a is very near to a $\langle 111 \rangle$ ZA and the lattice fringes can be resolved in this orientation. The left grain is in a channeling condition, which makes it appear brighter than the right grain. Keeping the left grain on the same ZA, the other grain was slowly tilted towards a $\langle 111 \rangle$ ZA, as shown in Fig. 30b, where one set of lattice fringes appear in the right grain. At the third orientation (Fig. 30c) the right grain is perfectly on the $\langle 111 \rangle$ ZA, though the left grain appears to be a little off. Further tilting throws the left grain away from the ZA and a contrast reversal can be observed in the HAADF image in Fig. 30d. With further titling both the grains lose their periodic intensity variation and appear to be amorphous like. The effect of tilting on the HAADF image contrast is discussed further in the following paragraph.

When a grain is on a ZA orientation the atomic columns are parallel to the incident beam. The attractive interaction between the incident electrons and atomic nuclei causes the electron flux to concentrate along narrow regions of the atomic column [68]. This gives rise to strong electron channeling peaks. As these channeling peaks are concentrated on individual

columns of atoms, scattering at high angles towards the HAADF detector will increase and consequently a grain on a ZA will appear brighter [88]. When the grain is tilted away from the ZA orientation, the channeling component decreases and the contrast in the exit wavefront is significantly reduced, as seen in Figs. 30d and e for example. The probe also broadens significantly inside the sample as observed in amorphous material and consequently the HAADF intensity decreases significantly.

4.6.2. Line scan asymmetry across the GB

Plasmon energy profiles from the line scans across GB 3 are shown in Fig. 48 for four different orientations. It can be readily seen that the profiles at orientations 1 and 4 are not symmetric about the lowest point (energy) of the profile. The profile from orientation 3 is slightly asymmetric, but the one from orientation 5 is fairly symmetric. This inherent asymmetric nature of the plasmon profiles can be explained in terms of the dependency of localization of the EELS signal on crystal orientation, and also on the orientation of the GB plane, as discussed in the following paragraphs.

A grain on, or near to, a ZA position shows a slower decrease/increase in E_p compared to the other side where the grain is not on the ZA, as seen in Figs. 48a and 48c. This slower variation in E_p on the ZA side makes the plasmon valley wider compared to the other side (where the variation is comparatively steeper) making the profile asymmetric. For example, consider the profiles between orientations 1 and 4. The valley is wider on the left side in orientation 1 where the left grain was very close to the ZA position, but the shape of the valley is flipped in orientation 4, i.e., the right side of the plasmon valley is wider when the right grain is near to the

ZA position and the left grain is not on the ZA. On the other hand at orientation 3, the left grain is near to a ZA and the right grain is perfectly on a ZA position, and this is reflected in their plasmon profile, which is significantly more symmetric than orientations 1 and 4. The valley is slightly wider on the right side though.

Similar asymmetric behavior was reported by Fitting *et al.* [89] where the Ti-L_{2,3} edge was recorded to measure the spatial distribution of Ti with respect to a dislocation core. Figs. 11a-b in their paper [89] show the asymmetry in the concentration profile of Ti^{core}, the profile being wider on the side of the grain that was on a ZA orientation. This lead the authors to suggest that the nonlocality of inelastic scattering is more prominent for ZA crystals. When the crystal is rotated off the ZA position, the EELS signal becomes more local.

This nonlocality of the EELS signal for a ZA crystal can be explained by considering double or multiple-scattering processes. When a grain is in ZA orientation, many planes are diffracting and generating Bragg beams, which acts as a ‘primary beam’ for inelastic scattering. Owing to this double-scattering process, the effective volume from where the inelastic signal is generated, is wider (larger) compared to when the crystal is off the ZA. In an off-ZA position, fewer planes are in a diffracting condition, limiting the number of ‘primary beams’ in certain directions and thereby reducing the ‘interaction volume’. Each Bragg beam generates inelastic scattering within the specimen. Reducing the number of Bragg beams reduces the volume from where the EELS signal is generated. This is reason for the EELS signal to be more localized at the off ZA orientation.

Figure 48: Plasmon energy profiles across GB 3 at: (a) orientation 1, (b) orientation 3, (c) orientation 4, and (d) orientation 5.

Figure 49 shows a schematic diagram to illustrate the idea presented in the preceding paragraph. In Fig. 49, a tilt GB is shown with the grain on the left orientated in an ideal two-beam condition. The crystal thickness along the direction of the incident beam is considered to be one extinction distance, ξ_g , which is typically of the order of 25-100 nm for 100 keV electrons and low order reflections [5]. At a thickness of $t = \xi_g/2$ and deviation vector $s = 0$, 100% of the intensity from the incident beam ends up in the diffracted beam. At thickness $t > \xi_g/2$ the intensity of the diffracted beam decreases and at $t = \xi_g$ would go to zero [28]. For 100 keV incident electrons, the elastic scattering angle θ for simple metals exceeds 10 mrad, so to calculate a rough minimum estimate we take $\theta \sim 10$ mrad. As shown in the schematic diagram in Fig. 49, the distance between the incident beam and the diffracted beam at a plane at thickness $t = \xi_g$ is found from simple geometry to be $x = 2\xi_g\theta = 0.5\text{-}2.0$ nm. Given that all Bragg beams generate inelastic scattering inside the specimen and assuming that the delocalization distance associated with each beam is of the same order, the presence of Bragg diffracted beams (which act as primary beams) increase the delocalization length L_{50} by the order of 0.5-2.0 nm in a two beam condition. In Fig. 49, it can be seen from simple geometry that the distance x depends on sample thickness. If $t < \xi_g$, the effective delocalization length is shorter. Again at different crystal orientations, θ is different depending on the planes that are at diffracting conditions, and accordingly, the effective delocalization diameter is altered.

Two points can be concluded from the above discussion:

- 1) The effective delocalization diameter (EDD) is thickness dependent, and
- 2) EDD depends on the orientation of the crystal.

The validation of the second point can be observed directly from the experimental data. As the sample is tilted off from the ZA position (orientations 4 and 5 in Figs. 48c-d), the plasmon peak shift ΔE_p , i.e., the difference between the plasmon energies of the matrix and GB, increases with a simultaneous decrease in the plasmon valley width, as shown in Figs. 31a and b. In light of the above discussion it can be inferred that, as the sample was tilted away from the ZA

Figure 49: Schematic diagram of a tilt GB with the left grain in an ideal two-beam condition. The blue arrow represents the incident beam and the red arrow represents the Bragg diffracted beam. The crystal thickness along the direction of the incident beam is considered to be one extinction distance, ξ_g .

orientation, the EDD decreased and consequently the plasmon valley width also decreased. Again with the decrease in EDD, the contribution from the matrix plasmon lessened and the GB plasmon became less convoluted. This is the reason for the increase in plasmon peak shift at orientations 4 and 5.

One may argue that the GB was tilted on the left side (with respect to the beam) at orientation 1, came close to the edge-on position at orientation 3, and again became tilted on the right side at orientation 4. However, if that is the only reason, the plasmon valley width would have been the least at orientation 3, but Fig. 32b shows that the plasmon valley width is maximum at orientation 3. As the sample was tilted away (on both sides) from orientation 3, the plasmon valley width decreased. The sample was rotated in the β direction keeping the α tilts almost fixed. Upon further tilting to orientation 5, where both the grains were off the ZA, the plasmon valley got symmetric, deeper (sharper) and the width also decreased (Fig. 32b), which readily confirms that GB tilt is not the sole reason for this behavior.

Another reason for the asymmetry could be due to the difference in the angular divergence of the beam inside the sample owing to the orientation difference between the grains. In other words, the effects of probe broadening inside the sample, which depends on crystal orientation and thickness of the sample, could lead to the asymmetry of the EELS signal. If that was the case, the HAADF images acquired from the GB would have also shown similar asymmetric character, but the HAADF images did not show such asymmetry. So, in essence probe broadening does not seem to have any effect on the asymmetry of the EELS signal. In conclusion, it can be stated that the primary reason for the asymmetry in the plasmon energy

profiles arises from the variation in localization of the EELS signal with crystal orientation due to double-scattering effects.

4.6.3. Momentum effect

In the results Section 3.5., a decrease in the plasmon energy (E_p) along with decrease in FWHM was observed as the sample was tilted toward the ZA orientation. As the sample was tilted toward a $\langle 111 \rangle$ ZA position, the plasmon energy E_p for matrix and GB both decreased and reached a minimum at orientation 3, when both the grains were in a ZA position, as shown in Figs. 31b. The matrix and GB E_p started increasing again when the sample was tilted off the ZA position. At orientation 5, when both the grains were off diffracting conditions, the E_p at the GB showed a sharp decrease with reference to the matrix. The variation in E_p with the tilting angles are summarized in Fig. 33, where average E_p values from 3-4 line scans at each orientation are plotted. In Fig. 31b, single line scan data were used to give a representative idea of the trend, so the absolute value of E_p might deviate slightly from the average values in Fig. 33. This variation in E_p with sample tilt can be explained by considering the momentum dependent plasmon dispersion of Al. It is apparent that the orientation of the Kikuchi bands with respect to the optical axis (or the entrance aperture) plays a vital role in determining the scattering angle θ and scattering vector $\mathbf{q}$ and thereby the momentum dependency of the plasmon dispersion. In the following paragraphs, the effect of sample tilt on the position of the Kikuchi bands will be described first, followed by the connection of Kikuchi bands with inelastic scattering and finally, the correlation between the position of the Kikuchi bands, scattering vector $\mathbf{q}$, and plasmon dispersion, is considered.

4.6.3.1. Position of the Kikuchi bands during tilting

The Kikuchi pattern was used to orient the sample during the tilting experiment and its position corresponding to orientations 2, 4 and 5 are shown in Fig. 50. It is observed that in these three orientations, the $\langle 111 \rangle$ ZA has gradually moved toward the right (of the optical axis) and at the final position it was shifted just outside the entrance aperture. In all three Kikuchi patterns, one set of near horizontal lines (marked by black arrows) can be seen, which corresponds to the plane that stayed nearly edge-on throughout the tilting experiment. Given the tilting axis and direction, this plane lies perpendicular to the GB plane and was parallel to the viewing direction. This is schematically shown in Fig. 51, with reference to a diffraction pattern acquired from the same GB. The blue lines in Fig. 51b represent the nearly horizontal Kikuchi bands that appear in all three orientations. The black and green lines intersecting the blue lines at the 000 spot in the diffraction pattern represent the Kikuchi lines from the crystal planes in both grains that were nearly parallel to the GB plane. This arrangement of Kikuchi lines represents orientation 3, when both grains are on the $\langle 111 \rangle$ ZA position. When the crystal was further rotated to orientation 5, the black lines shifted to the position of the red lines in Fig. 51b. The angular distance between the black lines (initial position) and red lines (final position) is equal to angle of the tilt through which the plane (in the grains) parallel to the GB plane was rotated.

4.6.3.2. Formation of the Kikuchi bands and its connection with inelastic scattering

When convergent beam in STEM is used, there is a range of angular distribution of the incident electrons. Some of the incident electrons may be in a perfect Bragg condition, which will get elastically scattered to form the Kikuchi lines. Each elastically scattered beam generates

Figure 50: Position of the Kikuchi lines at: (a) orientation 2, (b) orientation 4, and (c) orientation 5 with respect to the optical axis.

Figure 51: (a) Position of Kikuchi lines at orientation 5. (b) Comparison of positions of Kikuchi lines at orientation 3 (black) and orientation 5 (red) with reference to a $[111]$ diffraction pattern obtained from GB 3.

inelastic scattering inside the sample, as shown by the red arrows in Fig. 52. Therefore, the Kikuchi lines are associated with inelastic scattering just like the Bragg beams. This is a double-scattering process where the elastically scattered beams act as ‘primary beam’ for the inelastic scattering [85].

Figure 52: Formation of Kikuchi lines by elastic scattering of electrons in a convergent beam when the convergence angle, α is greater than the Bragg angle, θ_B [6]. This elastically scattered electrons acts as a ‘primary beam’ for the inelastic scattering.

4.6.3.3. Correlation between the position of the Kikuchi bands and the scattering vector q

When the crystal is rotated, the elastically scattered beams ('primary beams') also 'rotate' with the crystal resulting in movement of the Kikuchi lines either to, or off, the optical axis according to the tilting direction. The 'rotation' of the 'primary beam' allows one to access the θ space or the q space associated with the beam/Kikuchi line, by bringing inelastically scattered electrons, scattered over a range of angles, on the optical axis.

To illustrate this concept pictorially, Fig. 51b is redrawn in Fig. 53a with an entrance aperture (collection aperture of spectrometer) which cuts off all the scattering beyond 50 mrad. The schematic in Fig. 53b depicts the Kikuchi pattern for two orientations, as shown previously, without the diffraction pattern. The Kikuchi lines represent the line where the elastically scattered beam, the primary beam, intersects the viewing screen. As this beam generates inelastic scattering on both sides of the Kikuchi lines, as one moves further from the Kikuchi line the scattering angle, and hence the scattering vector q , increases. At orientation 3, the Kikuchi bands representing the planes parallel to the GB plane is at the center of the entrance aperture. The q space corresponding to those set of planes, accessible on either side of the Kikuchi lines, are depicted by black arrows. When the sample is at orientation 5, the Kikuchi lines (red) lie just outside the aperture and at this position, the q space of the inelastic scattering is represented by the red arrows. The inelastically scattered electrons that have been scattered at higher angles are now accessible at this orientation. In other words, electrons that have lost higher momenta can be used to acquire EELS spectra.

Figure 53: (a) Fig. 51b is redrawn with an entrance aperture. (b) The accessible scattering vector through the entrance aperture at orientation 3 (black arrows) and accessible scattering vector at orientation 5 (red arrows).

4.6.3.4. Momentum dependence of plasmon dispersion

The momentum dependency of the plasmon peak position, has been reported theoretically by incorporating a q dependent $\varepsilon(q, E)$, in the expression of the energy loss function $\text{Im}(-1/\varepsilon)$ [27]. For $q < q_F$, q_F being the Fermi wave vector and for free electron gas where damping constant $\Gamma = 0$, one obtains:

$$E_p(q) = E_p + \frac{\hbar^2}{m} \alpha q^2 \quad (10)$$

where α is the dispersion coefficient, given by $\alpha = \frac{3 E_F}{5 E_p}$, E_F is the Fermi energy, and E_p is the plasmon energy. This is the Lindhard model [5], which states that with increase of scattering angle θ , or scattering vector $\mathbf{q}$, the plasmon energy increases.

From simple geometry it can be understood that when the sample was rotated off the ZA to either side, the magnitude of the allowed $\mathbf{q}$ vectors (black arrows in Fig. 53b) associated with the Kikuchi (black) lines, increases through the entrance aperture as the Kikuchi lines are moved off the optic axis. Following this argument and using the dispersion relation in Eqn. 10, the increase in E_p with increasing tilt from the ZA position of the sample can be explained. That is, E_p increases with increasing $\mathbf{q}$. Similarly the FWHM of the plasmon loss ($\Delta E_{1/2}$) is also dependent on the sample tilt, as shown in Fig. 31d. From experimental results, to a first approximation, the dependence of $\Delta E_{1/2}$ on θ , or $\mathbf{q}$, is given by [27]:

$$\Delta E_{1/2}(\theta) = E_{1/2}(0) + B\theta^2 \quad (11)$$

where the constant $B = 1.4 \times 10^4$ eV/radian for Al. As result of this dispersion relation, the FWHM of the plasmons was found to increase when the sample was tilted away from the ZA orientation. From the above discussion, it can be concluded that by tilting the sample and following a specific set of Kikuchi bands, it is possible to access higher momentum space $\mathbf{q}$.

4.6.4. Modification of experimental technique

In this experimental setup it can be seen that there may be contributions from Kikuchi bands associated with other sets of planes. This can be avoided by tilting the sample further away from the ZA position, in the current scenario along the α direction, so that only one set of Kikuchi bands is present. To access just one set of Kikuchi bands the sample should be tilted

in such a way that it falls between two ZA positions common to that particular Kikuchi bands. This situation is shown schematically in Fig. 54, where the red circles represents the entrance aperture of the spectrometer. The red circles are placed off-centered with respect to the Kikuchi lines to emphasis the fact that when the Kikuchi bands are further off the optical axis higher momentum space can be accessible. This procedure should enable one to explore momentum space associated with different sets of planes although the (000) beam and inelastic scattering associated with it will be always present. The inelastic scattering associated with the central beam and the Kikuchi bands are independent of each other, so their effects are additive. The presence of the central beam will impart sufficient intensity to the EELS spectrum to improve the signal to noise ratio. The effect of central beam can be avoided by using a circular beam stopper in addition to a carefully selected camera length, or using an annular entrance aperture. In this experiment, an entrance aperture with a collection semi-angle of 50 mrad was used. To improve momentum resolution an aperture with smaller collection semi-angle, e.g. 12-14 mrad, can be used.

Figure 54: Schematic diagram of Kikuchi map for fcc crystal and Kikuchi lines (indexed). The red circles represents the circular entrance aperture of the spectrometer.

4.6. Thickness effect and choice of accelerating voltage

4.6.1. Probe broadening and resolution

In the results Section 3.6, it was shown that the maximum ΔE_p at the GB for both thick and thin samples is the same. But the plasmon energy profiles and plasmon FWHM profiles was found to be wider in the thick sample. This increase in the width can be explained based on beam spreading inside the sample. Due to the elastic scattering, the electron beam spreads laterally inside the specimen, limiting the spatial resolution. The beam broadening (b) due to elastic scattering in amorphous specimen was derived by Goldstein [67] and is given by the following expression:

$$b = 6.25 \times 10^5 \frac{Z}{E_0} \sqrt{\frac{\rho t^3}{A}} \quad (12)$$

where A is the atomic weight of the element (g/mole), ρ is the density (g/cc), t is the thickness of the foil (cm) and E_0 is the incident energy (eV). Using Eqn. 12 the probe broadening for the thick (245 nm) and thin (76.5 nm) samples as found to be 3.13 nm and 36 nm, respectively, for a 0.13 Å probe. The inelastic mean free path, λ_i , for Al is taken as 134 nm for $E_0 = 200$ keV and 100 nm for $E_0 = 100$ keV [5]. Even if according to the calculations, the beam broadens by almost 10 times inside the thick sample, the values of ΔE_p and ΔFWHM were found to be almost the same for these two samples, apart from the increase in the width of the plasmon valley and FWHM hill, as shown in Fig. 34.

Monte Carlo simulations were also performed on these samples, as shown in Fig. 55, which showed considerable probe broadening for the thick sample. Even though Monte Carlo

simulation results and beam broadening calculated using Eqn. 12 are not in good agreement with each other, but both of these theoretical calculations show the beam broadening in the thick sample is considerably more (~ 10 times) than in the thin sample. In contrast, the plasmon valley width was found to increase by only ≈ 2 nm and FWHM hill by ≈ 1.9 nm for the thick sample. From the Monte Carlo simulation it was observed that for the thick sample $\sim 90\%$ of electron trajectories are confined in the main transmitted beam (between -0.2 nm to 0.2 nm, Fig. 55c), which is similar to the transmitted beam from 200 keV (Fig. 55d), and thereby making the effect of probe broadening negligible. Moreover, the EELS spectra were acquired from the sample when the grains were on or near a ZA orientation. This orientation of the grains promoted channeling effects [68], which reduced the beam broadening inside the sample. Electron beam can broaden inside specimen by $2\alpha t$ even without elastic scattering, where α is the convergence semi-angle of the focused probe and t is the sample thickness. To a first approximation, the probe broadening effect can be added to the beam divergence effect ($2\alpha t$) in quadrature [64]. Therefore, it can be inferred that the increase in the width of the plasmon valley and FWHM hill is attributed to the beam divergence along with the slight probe broadening that occurred in the presence of strong channeling effects.

Moreover, the angle limiting entrance aperture of the spectrometer cuts out all the electrons that get scattered more than the collection semi-angle, β , of the spectrometer. Thus unlike EDXS (energy-dispersive X-ray spectroscopy), beam broadening has lesser effect on the spatial resolution of EELS. For the thick sample, an entrance aperture with a collection semi-angle of 50 mrad was used, which collects most of the elastically scattered energy loss electrons [90].

Therefore the angle limiting entrance aperture is not the primary reason for the increase in plasmon valley or FWHM hill width.

Figure 55: Monte Carlo simulations of 10,000 electron trajectories through: (a) 245 nm Al foil with accelerating voltage of 100 keV; x-axis 50 nm, (b) 76.5 nm Al foil with accelerating voltage of 200 keV; x-axis 50 nm, (c) 245 nm Al foil with accelerating voltage of 100 keV; x-axis 1 nm, and (d) 76.5 nm Al foil with accelerating voltage of 200 keV; x-axis 1 nm.

However, the plasmon energy shift (ΔE_p) was found to be the same for both samples, Fig. 34b, which suggests that the thickness of the sample has no effect on the ΔE_p ,

provided in both cases the sample orientations are the same (on same ZA position) and the GB is at the edge-on position. The reason behind this is the collection semi-angle of the spectrometer for both the cases as much higher than the characteristic angle θ_E , which is the angular half width of the scattered intensity per unit solid angle. θ_E is given by $\theta_E = E_P/2E_0$, ignoring the relativistic effect, where E_P is the plasmon energy and E_0 is the incident energy. For $E_0 \sim 100$ keV, θ_E is of the order of 0.1 mrad [5]. It can be readily inferred that entrance apertures with collection semi-angle of 14 mrad (for the thin sample) and 50 mrad (for the thick sample) will allow most of the inelastically scattered electrons to reach the spectrometer.

4.6.2. Choice of accelerating voltage

In a typical electron microscope using high energy electrons the minimum momentum transfer $q_{min}=\omega/v$ is of the order of 0.1 nm^{-1} [77], where ω is the angular frequency. Howie *et al.* [34] based on the dielectric sandwich structure, estimated that when the interface region consists of one or two atomic layers, the high energy electrons are sensitive to the difference in the dielectric function of the bulk and interface only when $qa > 1 \text{ nm}^{-1}$, a being the thickness of interface. In conventional spectroscopy, the incident electrons are almost insensitive to the interfaces or surfaces as they have typical values of $\omega/v \approx 0.1 \text{ nm}^{-1}$ (for 100keV electrons). Now q_{min} is given by:

$$q_{min} = \frac{\Delta E}{\hbar v} = \omega/v, \quad (15)$$

Therefore, using higher accelerating voltage will make it practically impossible to detect the interface plasmons. For surface modes, with $a=0.5$ nm, it was shown [91] that the required incident energy is $E \leq 200$ eV. So, lower voltages are better and deconvolution is required for spectra if higher voltages are used.

A simple time-of-flight argument can be put forward for a fast electron travelling at a velocity v and at a distance b from an atom. An electromagnetic pulse from the passing electron is felt by the atom for a characteristics time $\Delta t = b/v$ [32]. The velocity of the electron decreases with the decrease in accelerating voltage, giving the atom electrons sufficient time to respond to the electric field. The minimum possible momentum transfer at zero scattering angle, q_{min} , can be correlated with energy loss ΔE , b and v by the following equation:

$$\frac{\Delta E}{v} = \hbar q_{min}. \quad (14)$$

For a given energy loss ΔE , slowing down the electrons will increase q_{min} and thereby, increase the momentum resolution.

The delocalization distance, L_{50} , also depends on the velocity of the incident electron, v [64] as:

$$L_{50} \propto v^{1/2} \left(1 - \frac{v^2}{c^2}\right)^{1/8}, \quad (13)$$

where c is the velocity of light. L_{50} varies weakly on the velocity of the electrons for E_0 greater than 100 keV. L_{50} was found to increase just by 10% with E_0 increasing from 100 keV to 300 keV, but lowering E_0 below 100 keV significantly reduces the delocalization diameter [64]. From the above discussion, it can be concluded that a lower accelerating voltage, E_0 , is more favorable to

explore GB/interface properties, as it increases the value of ω/v and thereby increases the momentum resolution and at the same time reduces the delocalization diameter.

5. EXELFS Discussion

5.1. Determining the increase in nearest neighbor (n.n.) distance

As observed in Fig. 36, the amplitude of $k^2\chi(k)$ for the GB's was slightly less than for the grains. This can be explained in terms of the Debye-Waller factor, σ_j , which accounts for static disorder and thermal vibration. The term $e^{-2\sigma_j^2 k^2}$ in Eqn. 9 introduces an exponential damping effect, which reduces the amplitude of $\chi(k)$ more at high k values. The inclusion of interatomic distance r through the interference term $\sin(2kr)$ can also modify the amplitude of $\chi(k)$. As the interatomic distance increases the frequency of oscillation increases and the amplitude decreases. As can be also observed in Figs. 36a-b, the frequency of oscillation of $k^2\chi(k)$ for GB 3 and GB 4 is slightly less than for the grains, which may be due to larger nearest neighbor (n.n.) distances at the GB's.

The interatomic distance was determined from a radial distribution function (RDF) obtained by Fourier transformation of $k^2\chi(k)$ to real space as shown in Fig. 35b. The 1st peak of the RDF represents the radius of the first coordination shell of Al atoms, or in other words, the 1st nearest neighbor (n.n.) distance from the central atom. Calculating the increase in the n.n. distance at the GB, $\Delta n.n.$ using the 1st peak of the RDF, allows one to determine the volume expansion at the GB. However, the volume expansion at the GB is not uniform. The expansion perpendicular to the GB is much larger compared to slight contraction within the GB plane. Therefore, the expansion represented by the increase in the 1st shell radius is convoluted by the net expansion-contraction at the GB, thereby giving an average volume expansion. The average volume expansion of the 1st coordination shell at a GB can be calculated from simple geometry as: $\delta_{avg} =$

$\frac{n.n.^3_{gb}-n.n.^3_g}{n.n.^3_g}$, where $n.n._{gb}$ and $n.n._g$ are the n.n. distances at the GB and in the grain, respectively.

The values of δ_{avg} along with the percentage increase in n.n. distance, $\Delta n.n.$ from the EXELFS analysis, are given in Table 3.

Table 3: Percentage increase in the nearest neighbor distance and average volume expansion of 1st coordinate shell corresponding to two different wave-vector ranges.

k range	GB 3		GB4		GB1	
($\text{\AA}^{-1}$)	$\Delta n.n.(%)$	δ_{avg}	$\Delta n.n.(%)$	δ_{avg}	$\Delta n.n.(%)$	δ_{avg}
3-7.5	1.89-2.27	0.058-0.07	1.54-1.92	0.047-0.059	0.0-0.76	0.0-0.023
4.5-7.5	3.4-4.15	0.105- 0.13	2.4-3.22	0.074- 0.10	0.036-0.107	0.001-0.003

From Table 3 it can be seen that $\Delta n.n.$ increases with increasing GB energy. The selection of two different $k_{min} - k_{max}$ intervals to perform the Fourier transformation further confirms the increase in the n.n. distances at the GB's. For GB 3 and GB 4, the $\Delta n.n.$ values are higher for the wave-vector range $k_{min}=4.5\text{\AA}^{-1}$ to $k_{max}=7.5\text{\AA}^{-1}$. The term $e^{-2\sigma_j^2 k^2}$ affects $\chi(k)$ oscillations more in the higher k region, and therefore a higher k range is more sensitive to change in n.n. distance. Furthermore, a higher k range means higher values in E range in energy space, in this case ~ 150 - 290 eV, which ensures negligible effect from the L_1 edge (119eV). Selecting a k_{max} value greater than $7.5\text{\AA}^{-1}$ introduces noise in the data and artifact peaks start appearing in the RDF. For GB 4, an increase of 0.06 - $0.08\text{\AA}$ was observed, which is an approximately 2.4 - 3.2% increase in the 1st n.n. distance.

Similarly, an increase of 0.09-0.11 Å (3.4-4.2 %) in the n.n. distance for GB 3 and a negligible increase of 0.001-0.003 Å (0.04-0.11%) for GB 1 was observed.

The increase in the n.n. distance with increasing GB energy showed a linear dependence, as evident in Fig. 56a. A decrease in plasmon energy (ΔE_p) at the GB also increased with GB energy, as previously discussed in Section 3.1.2. An increase in the n.n. distance also varied proportionally with ΔE_p as well as the measured GB width, as shown in Figs. 56b-c. Taken together, these results mean that as the GB energy increases, the average interatomic distance at the GB, the electron density deficit, and the width of the electron density deficit, all increase proportionally.

Figure 56: (a) Plot of increase in nearest neighbor distance ($\Delta n.n.$) as a function of GB energy. (b) Variation in $\Delta n.n.$ at the GB as a function of plasmon peak shift. (c) Plot of $\Delta n.n.$ as a function of measured GB width.

5.2. Comparison with literature

A comprehensive list of volume expansions from the literature for these three, or similar, GB's either calculated or experimentally determined, is tabulated in Table 4. The table lists the values of δV , which is the volume expansion per unit area normal to the GB. As a GB has a finite width, which contains one or more planes, the total volume expansion can be thought of as the summation of expansions on the individual planes. EXELFS analysis doesn't measure the expansion between planes, it measures the distances between nearest neighbors around a central atom. In order to compare $\Delta n.n.$ from EXELFS data with δV , it seems reasonable to start with the sharpest GB in Al, i.e., the $\Sigma 3$ GB, which extends about two atomic planes. The data for GB 1 ($\Sigma 3$ (111)) obtained by TEM diffraction contrast techniques (different fringe displacement techniques) seem to overestimate the volume expansion value. Because $\Sigma 3$ is a coherent boundary, only the stacking order of the atomic planes changes across the twin interface and there are no missing bonds [58]. The increase in the n.n. distance obtained by EXELFS analysis for the $\Sigma 3$ GB (GB 1) is much lower (almost negligible) compared to other experimental techniques in Table 4, but it is close to values obtained by simulations using EAM and LJ potentials [21] and first principle calculations [92].

The volume expansion for a $\Sigma 9$ (221) GB in Cu (having similar GB energy of $\Sigma 11$ (GB 4)) calculated using first principles predict very high expansions at the GB core [92]. But the values calculated for the fraction of volume expansion just outside the core of $\Sigma 9$ (about 3-6 Å from the GB plane) lies in the range of 0.06-0.08, which agrees well with the average volume expansion at GB 4, δ_{avg} in Table 3, calculated from EXELFS analysis.

Merkle [22] and Buckett *et al.*[21] showed that the volume expansion measured by HRTEM methods can vary widely depending on the image defocus, beam tilt and crystal orientation. A variation in the volume expansion from 0.08Å-0.15 Å was observed for a $\Sigma 11$ [110](113) STGB due to changes in astigmatism [93]. The accuracy of the measurement also depends on the pixel size/width of the acquired digitized image. Stobbs [94] reported an expansion of 0.09 Å using a pixel width of 0.24 Å for volume expansion measurement of a Au $\Sigma 3$ (111) GB. It is almost impossible to measure the volume change accurately when the pixel width is almost 3 times greater. Calculations [21] showed that a pixel width of 0.05 Å is required, for which a minimum magnification of the microscope is approximately 700,000X, or higher. A pixel width

Table 4: A compilation of experimental and theoretical results on the measurement of GB volume expansion in $\Sigma 3$, $\Sigma 11$ and $\Sigma 7$ GB's in various metals.

GB type	Measurement technique	Measurement/std. error (Å)	Ref
Al $\Sigma 3(121)$	α -fringe displacement	0.2	[95]
Au $\Sigma 3(112)$	Moiré fringe displacement	0.56	[96]
Cu $\Sigma 3(111)$	Fresnel fringe displacement	0.12 (± 0.02)	[97]
Cu $\Sigma 3(111)$	Lattice fringe displacement	0.01 (± 0.04)	[98]
Au $\Sigma 3(111)$	Lattice fringe displacement	0.09 (± 0.03)	[94]
Au $\Sigma 3(111)$	Lattice fringe displacement	-0.035 (± 0.04)	[99]
Cu $\Sigma 3(111)$	Simulation	0.036	[100]
Au $\Sigma 3(111)$	Simulation	-0.0016 (EAM)	[21]

		0.008 (LJ)	
Al $\Sigma 3(1\bar{1}1)$	First principle calculation	0.06	[16]
Au $\Sigma 11(113)$	HRTEM	0.118	[21]
Al $\Sigma 11(1\bar{1}3)$	First principle calculation	0.51	[16]
Cu $\Sigma 11$	Simulation	0.61(LJ) 0.25(EAM)	[101]
$\Sigma 11$	HRTEM	0.11-0.13	[93]
Cu $\Sigma 7$	Simulation	0.18(LJ) 0.11(EAM)	[19]
Al $40^\circ\langle 111 \rangle$ tilt	Thermodynamic approach	0.64	[23]

of 0.16 Å is achievable using modern microscopes at 860,000 X magnification. This is not an issue in EXELFS analysis unless there are overlapping edges present [102], which will decrease the width of the Hanning function window used to obtain the RDF, degrading the resolution.

5.3. Determining the volume expansion using EXELFS data

In this section, the volume expansions at GB 3 and GB 4 are calculated by including an increase in the nearest neighbor distance of the atoms in the planes on either side of the GB's. According to Wright *et al.* [1] the decrease in the electron density at GB $\Sigma 11$ extends about 3 atomic planes from the GB. We start by assuming that the electron density decrease at these planes is the result of the increase in average n.n. distance ($\Delta n.n.$) of the atoms in each plane and that

$\Delta n.n.$ decreases linearly from the GB plane. This situation is illustrated in Fig. 57a, where the maximum $\Delta n.n.$ corresponds to an atom in the GB plane. Adding the $\Delta n.n.$ of the planes on either side of the GB plane gives a total expansion of 0.24 Å for the approx. $\Sigma 11$ GB 4 in Fig. 57a, which is in good agreement with values calculated for Cu by Wolf using EAM [101]. Similarly, for the near $\Sigma 7$ GB in Fig. 57b, the volume expansion was found to be 0.8-0.97 Å, which is slightly higher than the experimentally determined volume expansion for an Al $40^\circ \langle 111 \rangle$ tilt boundary of 0.64 Å in Table 4 by Shvindlerman *et al.* [23].

Figure 57: Calculation of the total volume expansion at the GB, considering a linear profile of $\Delta n.n.$ on either side of the GB plane, for (a) GB 4 and (b) GB 3.

A more sophisticated approach of the volume expansion can be made using a Voigt-shaped plasmon profile across the GB. Even if the plasmon signal is delocalized, the plasmon profile gives an estimate about the spatial variation of electron density at and near the GB plane. It was previously shown that the delocalization diameter L_{50} for energy loss of 15 eV and a 0.012

nm diameter probe is ~ 1.5 nm. The plasmon profile acquired from GB 3 shown in Fig. 58a (black line) had a plasmon valley width of 4.2 nm. Neglecting probe broadening, in the absence of delocalization, the plasmon valley should be much narrower as depicted by the red profile in Fig. 58a. Subtracting delocalization effects from the experimentally obtained plasmon profile, a plasmon valley width of 2.7 nm was obtained. This is the total distance over which the variation in electron density extends due to the presence of the GB. The GB portion is fitted with a Voigt function (blue line) which accurately traces the plasmon profile. The number of atomic planes over which this decrease of electron density extends are estimated from the STEM image of the GB in Fig. 16. A portion of the line scan on the GB with a length of 2.7 nm (red line) is selected, as shown in Fig. 58b. The number of atomic planes and their points of intersection with the red line were determined, and it is assumed that the electron density decrease is proportional to $\Delta n.n.$ of atoms in individual planes. From EXELFS analysis, the measured average $\Delta n.n.$ corresponds to the lowest point in the plasmon profile as it was acquired from the GB plane. The $\Delta n.n.$ for successive planes on the either side of the GB plane was determined with reference to the plasmon profile across the GB. This is shown in Fig. 58c, where the Voigt fit of the plasmon profile is used as the reference curve and the intersecting points between the red line (scan line on GB) and the atomic planes are plotted in the abscissa. The corresponding $\Delta n.n.$ for different planes were determined using the Voigt function, as shown by the red symbols in Fig. 58c, and $\Delta n.n.$ approaches zero at the either end of the plasmon valley. The summation of $\Delta n.n.$ from all the planes give the total volume expansion at the GB. The total volume expansion calculated by this method is 0.65Å, which is in excellent agreement to Shvindlerman's measurements [23] of 0.64Å for Al $40^\circ\langle 111 \rangle$ tilt boundary.

Similarly, the total volume expansion for GB 4 is found to be 0.14 Å in Fig. 58d, which is less than the EAM or LJ potential calculations, but is in good agreement with Merkle's calculations using HRTEM technique [93]. With knowledge of the plasmon profile across a GB, an accuracy of 0.01 Å can be achieved in determining the volume expansion using EXELFS analysis. It is important to note that these values are not calculated based on a normal expansion with respect to GB plane, but rather, they are the average volume expansion summed over the GB planes within the primary volume of the electron probe. This calculation shows that EXELFS could be a powerful technique to determine the volume expansion for any unknown GB.

Between the two different profiles: 1) linear, and 2) plasmon loss, used to calculate $\Delta n.n.$ of the successive planes, it is found that the linear profile over-estimates the total volume expansion compared to the experimental values obtained by other techniques. On the other hand, the total volume expansion calculated using the plasmon profile is in good agreement with values reported by Merkle [93] and Shvindlerman [23]. In other words, to accommodate the disregistry at the GB, the n.n. distance of successive planes (which extend inside the grains on either side of the GB) decreases out from GB in a Voigt-like profile, and due to the consequent expansion of atomic volume the electron density across the GB decreases proportionally. Seeger and Schottky [14] suggested that the GB energy depends on the decrease in electron density and concomitant specific volume expansion at the GB, which is in good agreement with our experimental results.

Figure 58: (a) Plasmon energy profile (black) across GB 3; (b) HAADF image of GB 3; (c) plasmon energy profile (red) after subtraction of delocalization diameter, L_{50} ; (d) IFFT of HAADF image of GB 3; the red line represents a length of 2.7 nm across the GB along which the lowering of valence electron density was observed. Calculation of the total volume expansion considering plasmon profile across: (c) GB 3, and (d) GB 4.

5.4. Channeling effects on EXELFS analysis

The $\Delta n.n.$ values obtained by EXELFS analysis may not be localized on the central atom on which the probe is placed. During collection of the EEL spectra from the GB, both grains were on a ZA position, which is favorable for channeling conditions [68]. The column of atoms focuses the electron beam into a narrow peak, which reduce beam broadening inside the sample. Calculations [68] on a Si crystal oriented along a [111] ZA showed narrow channeling peaks occur on atomic columns. In Fig. 58b, the STEM probe with a diameter of $0.28\text{\AA}$, is positioned on a row of atoms shown by the blue square. Due to channeling, most of the beam intensity is focused into narrow channeling peaks on the atomic column on which the probe is positioned (the central atom) as well as on the atomic columns that are located around the central atom [103][104]. This scenario can be thought of as similar to placing a sub- $\text{\AA}$ probe on the central atom as well as the atoms around the central atom simultaneously. Consequently, EXELFS information contains information from all the atoms inside the blue hexagon in Fig. 58b. If we consider the equation for $\chi(k)$, Eqn. 9, it is the summation of intensities of outgoing electron waves from the central atom. In this case, due to channeling, there is more than one central atom, so effectively, an average increase in 1st nearest neighbor distance from all the atoms around the central atom (and not just the central atom) will be obtained from the 1st RDF peak. At the GB, the atomic arrangement is disrupted due to local disregistry, which reduces the cooperative focusing of the atoms and therefore reduces the channeling effect. Hence the average $\Delta n.n.$ obtained from the GB is less localized compared to the matrix. Tilting the sample slightly (less than 1 degree) from the ZA position so that atoms in the columns spread out perpendicular to the optical axis reduces channeling.

6. Conclusions

6.1. VEELS

1. These studies demonstrate that it is possible to directly measure the change in electron density at a GB with sub-nanometer spatial resolution and at the lowest possible GB energies.
2. Low-loss spectra acquired from the four GB's showed an increase in plasmon peak shift toward lower energy with increasing GB energy. Therefore, it can be concluded that lowering of valence electron density at the GB's is clearly correlated with increasing GB energy.
3. A concurrent increase in the ΔFWHM of the plasmon peaks was also observed at the GB with increasing GB energy. This is due to the fact that the electrons at and near the GB have a shorter lifetime compared to the bulk, presumably because the GB contributes to additional scattering of the plasmon due to its less ordered structure. Therefore, it can be inferred that the GB energy increases as the atomic structure of the GB becomes less ordered.
4. The widths of the plasmon valley and FWHM hill were also found to increase with increasing GB energy. That means that the lowering of electron density extends

increasingly further to either side of the GB with increasing GB energy. The lower electron density appears to be about twice as wide as the region of visible atomic displacements in images of the GB's.

5. Plasmon line scans taken along and parallel to the GB, show a decrease in E_p and a wider atomic periodicity, both consistent with the idea of a reduced atomic density and lower electron density at the GB.
6. Tilting experiments performed on a $38.7^\circ\langle 111 \rangle$ tilt GB show that the effective delocalization diameter depends on the thickness and orientation of the sample due to contributions from double-scattering effects.
7. The FWHM of plasmon peak from the matrix, oriented on a $[111]$ ZA, was found to be lower compared to a $[110]$ ZA orientation. This anisotropy in the dampening behavior of the bulk plasmon in Al, or any other cubic system, has not been reported in the literature. According to empirical pseudopotential calculations [72], the anisotropy could be due to band structure effects.
8. A decrease in plasmon intensity at and near to a GB can be attributed to the following processes that occur simultaneously:
 - i) A decrease in inelastic scattering due to a lower electron density.
 - ii) An intensity loss from the volume plasmon as a *begrenzungs* peak.

- iii) Partial recovery of the lost intensity as a GB response.
9. Sample thickness has a negligible effect on the change in plasmon energy (ΔE_p) and the change in FWHM ($\Delta FWHM$) as a large fraction of energy-loss electrons are collected through the 2mm entrance aperture. Thickness moderately affects the width of the plasmon valley and FWHM hill, due to beam divergence and probe broadening inside the sample.
 10. It is possible to access inelastically scattered electrons, that have scattered to higher angles by tilting the sample relative to the Kikuchi lines. Keeping low-order Kikuchi bands in view while tilting the sample, should allow one to explore momentum space associated with different sets of planes.

6.2. EXELFS

11. This study demonstrates that EXELFS can be used to accurately measure the average increase in nearest neighbor (n.n.) distance of atoms at a GB. EXELFS studies from three GB's revealed that an increase in GB energy occurs directly proportional to an increase in n.n. distance, as well as to the deficit in electron density and the width of the deficit region as mentioned above.
12. Fourier filtering to isolate the frequency associated with the 1st RDF peak only, revealed an increase in the Debye-Waller factor (σ) at the GB compared to the matrix. The Debye-

Waller factor was found to increase with increasing GB energy, which means static disorder increases proportional to the GB energy.

13. The total volume expansion at a GB, calculated using the EXELFS n.n. distance and the plasmon profile is in good agreement with values reported using other experimental techniques [93][23]. Based on these results, it can be concluded that the electron density variation as obtained from the plasmon profile is proportional to the average increase in n.n. distance, or the atomic volume obtained from EXELFS analysis.
14. The results of this study show that EXELFS analysis at a GB could be a powerful technique to determine the volume expansion and potentially the GB energy, for an unknown GB.
15. The results of this investigation experimentally and conclusively demonstrate that the GB energy increases proportional to the decrease in electron density and concomitant increase in specific volume expansion at a GB.

7. References

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