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Experimental Determination of $\langle 10\bar{1}0\rangle/\Psi$ Tilt Grain Boundary Energies in Ice

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Abstract

Ice grain boundary energies γ_{gb} relative to the free surface energy γ_s were determined by studying the topographic details revealed by plastic replicas of the ice grain boundary groove-free surface with a Laser Confocal 3D Microscope. The samples analyzed were high purity ice bicrystals, with ‹1010›/Ψ tilt grain boundaries, annealed at –18 °C. Values obtained of γ_{gb}/γ_s were analyzed using coincidence site lattice (CSL) theory. Significant correspondence was found between the γ_{gb}/γ_s values and the planar density Γ of coincident sites on the interface plane. The results show that γ_{gb}/γ_s depends on the GB inclination and may be up to one order of magnitude different.

Keywords: ice, grain boundary energy, grain boundary groove, coincident site lattice (CSL), laser confocal 3D microscope

1. Introduction

Ice cores provide the most detailed records of climate over the past several hundred thousand years (Petit et al., 1999). For example, water-soluble impurities have been used as proxies for atmospheric chemistry (Alley, 2000; Thompson et al., 2013). However, numerical models warn that distributions of the trace constituents are significantly altered by rapid diffusion through grain boundaries (GB) and liquid veins along triple junctions during ice sheet flow (Thompson, 2013; Rempel & Wettlaufer, 2003; Johnsen et al., 2000; Nye, 1998; Rempel, Waddington, Wettlaufer, & Worster, 2001).

Studies on deep ice cores have revealed the development of highly lattice-preferred orientations with most of the c-axis of the grain perpendicular to the slip direction, ie with a preponderancy of low-angle GBs (Gow & Williamson, 1976; Herron & Langway, 1985; Lipenkov, Barkov, Duval, & Pimienta, 1989; Gundestmp & Hansen, 1984; Pimienta, Duval, & Lipenkov, 1987; Budd & Jacka, 1989; Paterson, 1991). It is known that low-angle GBs have low GB energies (Paterson, 1991), so, as the lattice-preferred orientation develops through the ice sheet depth, the proportion of low-energy GBs is increased. GBs with low energies may have a low segregation factor (Smith, 1992) and in consequence low impurity concentration, which in turn would reduce impurity diffusion along the GB. Grain boundaries with low energies are not only low-angle GBs but also high-angle GBs with special properties (Sutton & Balluffi, 1987), and this kind of grain boundaries in ice have not been studied extensively.

The coincidence site lattice (CSL) and Σ, the reciprocal density of coincidence sites, have been widely used to study GB structures. Crystalline samples with high Σ values were first used to characterize GBs with special properties. However, it was then found (Paterson, 1991) that not all low energy GBs have high Σ values, and it was shown that the orientation of the boundary planes within the CSL, and the boundary coincidence density Γ are a more physically useful tool to recognize grain boundaries with low energies.

It is known that there are some questions about CLS theory validity, but, as Davies and Randle (2001) said, “the CSL approach retained its position as a cornerstone of grain boundary research”.

The CSL theory was satisfactorily used in ice by Kobashashi and Furukawa (1975, 1976, 1978), Hondho and

Higashi (1979) and Di Prinzio and Nasello (1997) to interpret some ice GBs with special properties. However, the authors do not know of a systematic determination of ice GB energies and their relation with the CSL theory.

GB energy measurements are generally carried out by observing the geometry of interface junctions assumed to be in thermodynamic equilibrium (Rohrer, 2011). Herring's theory described the equilibrium between interfacial forces at a triple line as a vector balance of forces tangential and normal to the interfaces. However, the simplified Herring equation, which does not take into account the normal forces, is usually used. In these cases, Herring's theory states that, when the surface energy γ_s is isotropic and the GB energy γ_{gb} is independent of the GB inclination, the following relation is satisfied.

$$\frac{\gamma_{gb}}{\gamma_s} = 2\cos\left(\frac{\theta}{2}\right) \quad (1)$$

where θ is the angle of the GB groove root (see Figure 1).
On the other hand, when the surface energy is anisotropic (Davies & Randle, 2001) it is

$$\frac{\gamma_{gb}}{\sin\theta} = \frac{\gamma_l}{\sin\theta_r} = \frac{\gamma_r}{\sin\theta_l} \quad (2)$$

where θ_r and θ_l are the right and left groove angles, formed where the GB emerges on the surface, $\theta = \theta_r + \theta_l$ and γ_r and γ_l are the respective γ_s energy.

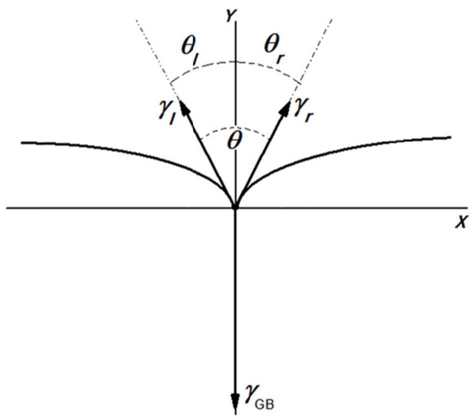

Figure 1. Sketch of the triple junction between the GB and the sample surface

The first important work concerning ice GB energy was written by Ketcham and Hobbs (1969) (KH). They determined GB energies experimentally using Equation (1) and measuring the groove angles θ in polycrystalline ice samples annealed at 0 °C. They made plastic replicas of the ice surface (Formvar 5%), which were then metalized and the angles θ were visualized using an interferometric microscope. For adjacent ice crystals, only the angles (Ψ) between the c-axes of each crystal were measured, so the GB misorientations were not exactly determined (to specify a GB misorientation, five independent parameters must be provided, three specifying the rotation between the lattices and two describing the orientation of the GB plane (Paterson, 1991)). The results obtained by KH show that angles θ and in consequence the GB energies vary relatively little for Ψ between 20º and 150º, being in average θ = 145º ± 2º.

After KH's work, Suzuki and Kuroiwa (1972) (SK) measured the angles θ in tricrystalline ice samples annealed at –5 °C. The crystallographic orientations of the crystals were controlled by varying the c-axes of adjacent crystals. They replicated the GB groove by pressing a 0.3 μm metal sheet on the ice surface and then measured the groove angles θ using an interferometric microscope. Their results show that the angles θ vary little for Ψ between 20º and 70º and between 110º and 160º (θ = 135º ± 5º), but increase rapidly when Ψ tends to 0º, 90º, or 180º. They also measured the same samples using the plastic replicas method used by KH. In general, they observed that the angles measured on plastic replicas were slightly higher (~10°) than those obtained with the metal film. The differences observed were attributed to the effect of chemical corrosion caused by the solvent used to produce plastic replicas. They did not consider these differences to be significant and concluded that their results were consistent with those obtained by KH. SK also observed that the Read-Shockley equation for GB energy (Paterson, 1991) is valid for ice GBs tilted between 0° and 15°.

GB energy may be strongly dependent on GB plane orientation, temperature and impurity concentration (Smith 1992; Sutton & Balluffi, 1987; Hondho & Higashi, 1979). As we saw before, the GB energy values reported by KH and SK showed no dependence on the GB misorientation apart from that of low-angle boundaries. It should be noted that these authors studied GB energy at temperatures of –5 °C and 0 °C. It is known that GB structure can suffer structural transformations similar to the ice-vapor surface (Benatov & Wettlaufer, 2004; Dash, Rempel, & Wettlaufer, 2006; Thomson, Hendrik, Wilen, & Wettlaufer, 2013; Thomson, Wettlaufer, & Wilen, 2009) where there has long been evidence of the existence of a liquid-like surface on ice samples at temperatures near melting point, Hence, the GB energies determined by KH and KS could be affected by the presence of a liquid-like layer.

In an ice core, the change in GB energy with depth may significantly change the climate proxies. In spite of the importance of GB energy in ice polar processes, there are few studies about the dependence of ice GB energy on GB misorientation, impurity concentration or temperature.

The main objective of this paper is to determine experimentally the variations of relative ice GB energy with crystallographic misorientation and use CLS theory to identify ice GBs with low energies. For this purpose, GB energies were studied corresponding to tilt ‹$10\bar{1}0$›/Ψ boundaries annealed at –18 ºC, to be sure that GB melting is not possible. The simplified Herring's theory was used to obtain the relative variations of γ_{gb}/γ_s and the results were analyzed using the ice coincidence site lattice (CSL) calculated in a previous work (Gonzalez Kriegel, Di Prinzio, & Nasello, 1997). In this way, we aimed to determine the magnitude of γ_{gb}/γ_s variations and establish which special ice GBs have low energies.

2. Methods

In the present study, the simplified Herring's theory was used to obtain the relative variations of γ_{gb}/γ_s corresponding to tilt ‹$10\bar{1}0$›/Ψ boundaries annealed at –18 ºC.

High purity bicrystalline ice samples (water conductivity 1.3×10^8 Ω), with tilt ‹$10\bar{1}0$›/Ψ boundaries were obtained following the method described a previous work (Di Prinzio & Nasello, 1997). The ice surfaces were prepared to a mirror-like finish by polishing them with a microtome in a cold chamber at –10 ºC, and allowed to evaporate for 3 hours at –18 ºC in a dry airtight container with silica gel. Subsequently, each sample surface was replicated with a 4% solution of Formvar in 1-2 dichloroethane. An acrylic ring was placed on the sample surface in the region of the GB groove and a fixed amount of Formvar solution was placed inside this ring. This procedure ensured that the thermal and chemical attack times were the same in the replicas of all the samples analyzed, so that any differences observed would be entirely due to differences in the samples. Figure 2 shows a photograph of a plastic replica of a ‹$10\bar{1}0$›/57º sample. From the plastic replicas, the angles (Ψ) formed between the c-axes of both crystals, and the angles β_r and β_l formed between each crystal's c-axis and the GB, were obtained.

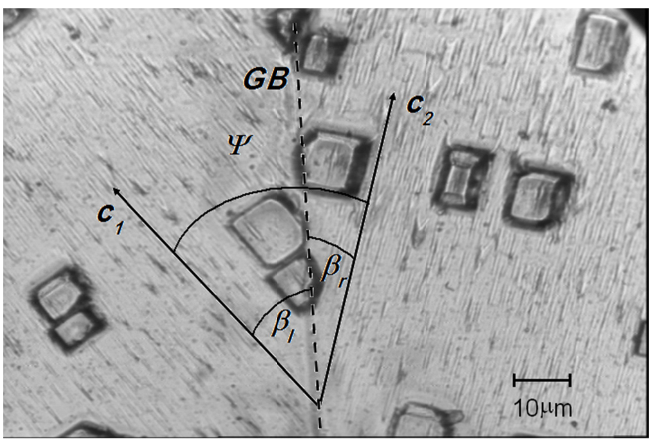

Figure 2. Plastic replica of a ‹$10\bar{1}0$›/57º ice surface sample

Angles Ψ and β were measured with a precision of ±1º. Only GB planes normal to the surface were considered. The topology of the replicas was analyzed with an Olympus Laser Confocal Microscope (LEXT OLS4000 3D). Figures 3(a) and (b) show the 3D and 2D confocal images of the groove corresponding to the sample ‹$10\bar{1}0$›/83º. Figure 3(c) shows the GB groove profile extracted from line AB of Figure 3(b). For each GB, angles θ_r, θ_l and θ

($\theta = \theta_r + \theta_l$) shown in Figure 3 (c) were measured.

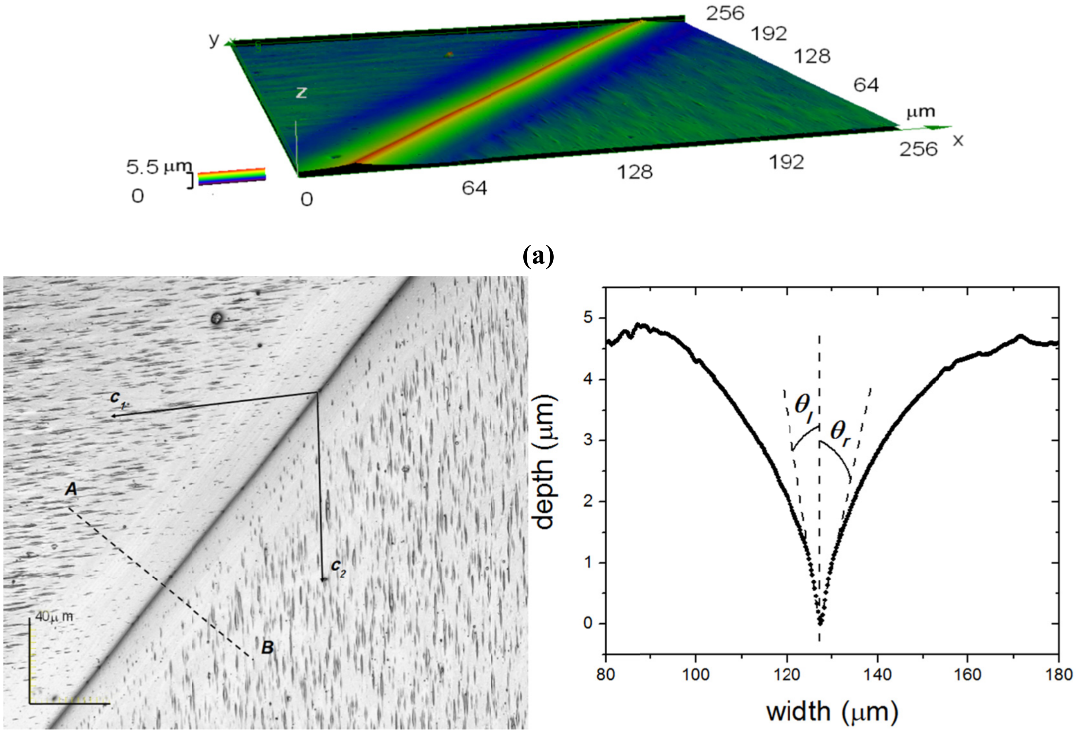

Figure 3. Confocal microscope image of the plastic replica corresponding to the sample ‹$10\bar{1}0$›/83º. (a) (b) 3D and 2D microscope images respectively (c) GB groove profile, extracted from line AB of image (3b)

In general, GBs were not a straight line, so different β angles were found along the same sample. In these cases angles θ_r and θ_l were measured for each different pair of β values observed.

In general, θ_r and θ_l values were different, so Equation (2) indicates that for each sample there were two different values of γ_{gb}/γ_s. To avoid this problem, we note that the prismatic and basal planes of the hexagonal ice (Ih) have lower surface energies than the other crystal planes and these are therefore defined as “special”. When surface crystallographic planes are not “special”, they have similar surface energy, so, when the β angles were between 20º and 70º or 110º and 160º, it was considered that surface planes near the groove root have no “special” property, and their surface energies γ_s were considered equal. Then, defining angle θ^* as the θ right or left angle, corresponding to the side of the sample that presented the greatest angle $\beta\,(\beta^+)$, from Equation (2) we obtained:

$$\frac{\gamma_{gb}}{\gamma_s} = \frac{\sin\theta}{\sin(\theta - \theta^*)} \tag{3}$$

The angles β^+ were also used to represent the GB inclinations and the GBs were considered symmetric when $\beta^+ = \Psi/2$.

3. Results and Discussion

The mean values of γ_{gb}/γ_s with its corresponding standard deviation obtained from Equation (3), for each different β^+ value of all the samples analyzed, are presented in Figure 4. In this figure, the values corresponding to symmetric GBs are represented by crosses.

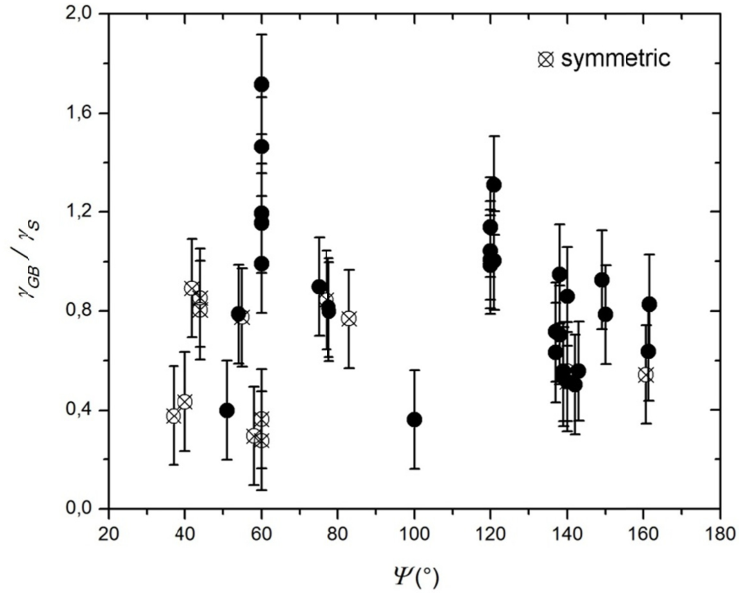

Figure 4. Values of γ_{gb}/γ_s with its corresponding standard deviation obtained from Equation (3). Values corresponding to symmetric GBs are represented by crosses

In Figure 4, it can be noted that the symmetric GBs in general have the lower value of γ_{gb}/γ_s. This agrees with Sutton and Balluffi (1987), who concluded that a good argument for an extreme in boundary energy is one based on symmetry.

The values of γ_{gb}/γ_s show an empirical dispersion but the experimental error bars show that all γ_{gb}/γ_s values are practically similar, with the exception of those corresponding to $\Psi = 60°$.

Figure 5 shows the values of γ_{gb}/γ_s for $\Psi = 60°$ as a function of β^+ where $\beta^+ = 30°$ represents the symmetric GB. The plot shows that the GB with $\beta^+ = 30°$ has the lowest γ_{gb}/γ_s value and that γ_{gb}/γ_s increases as the GB inclination increases with respect to the symmetric GB. In consequence, the current results show that, at –18 ºC, ice GB energy also depends on the GB inclination.

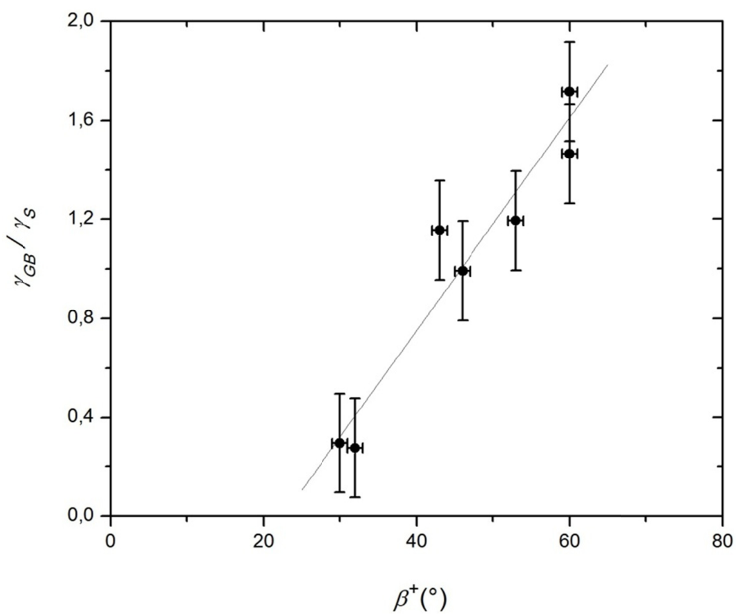

Figure 5. Values of γ_{gb}/γ_s for $\Psi = 60°$ as a function of β^+ where $\beta^+ = 30°$ represents the symmetric GB

As seen in this Figure, γ_{gb}/γ_s as a function of β^+ varies up to an order of magnitude. In a previous work (Di Prinzio & Nasello, 1997), we showed that at –10 ºC small differences in the GB energy with GB inclination could explain significant differences in GB velocity. The results obtained in this work show that at –18 ºC the dependence of GB energy on GB inclination is more important than supposed in the results obtained previously, and thus GB migration at –18 ºC could be more significantly affected by GB anisotropy in GB energy.

Gonzalez Kriegel, Di Prinzio and Nasello (1997) studied the ice CLS corresponding to rotation angles Ψ^+ around the axis ‹1010›. The values obtained of Σ (the volumetric density of CSL sites) and Γ (the planar density of the corresponding symmetric plane) are presented in Table 1.

Table 1. Misorientations Ψ and Ψ^+ corresponding to the closest dense CLS of each symmetrical boundary studied. Σ and Γ are the volumetric and planar density of CSL from (Gonzalez Kriegel, Di Prinzio, & Nasello, 1997) respectively

Ψ	Ψ^+	Σ	γ_{gb}/γ_s	Γ
37	34.05	35	0.38	0.55
42	44.42	14	1.23	0.36
55	57.12	35	0.60	0.23
60	62.96	11	0.28	0.98
83	78.46	10	0.76	0.60
121	62.96	11	0.80	0.46
140	44.42	14	0.54	0.87
160.7	23.07	25	0.52	0.46

In this table, all the symmetric GBs studied in this work were associated to a rotation Ψ^+, following the commonly used Brandon criterion (Brandon, 1966), ie GBs were considered close to a CLS if differences between Ψ and Ψ^+ were lower than 10º. In this table, it is possible see that the values of γ_{gb}/γ_s are not related to Σ, but may be related to Γ. In fact, in figure 6 where the values of 1/5 Γ and of the associated γ_{gb}/γ_s are plotted as a function of Ψ^+, it is observed that there is a significant correspondence between the values γ_{gb}/γ_s for symmetrical GBs and 1/5 Γ, ie when γ_{gb}/γ_s increases 1/5 Γ increases and vice versa. Thus it can be seen that the planar density of the corresponding CSL—planes can help to understand the ice GB energy.

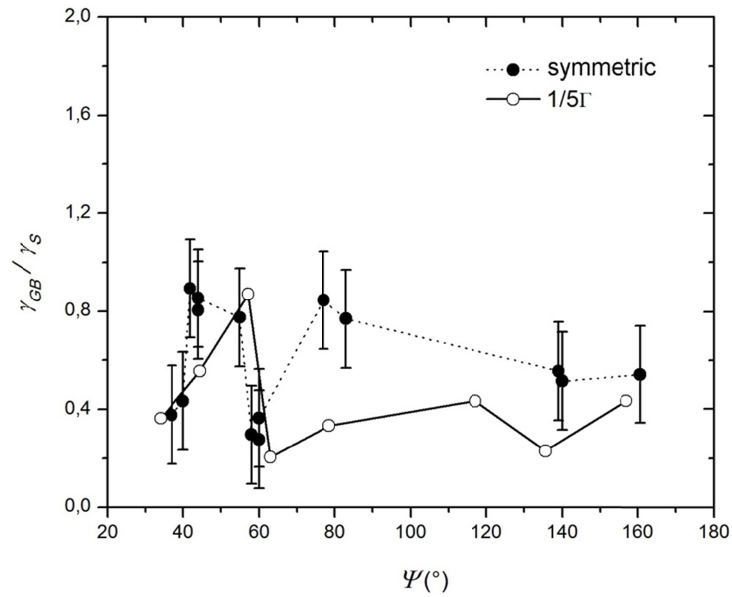

Figure 6. Values of 1/5 Γ and of the associated γ_{gb}/γ_s are plotted as a function of Ψ^+

4. Summary

In this paper, ice GB energies γ_{gb} relative to that of the free surface energy γ_s were determined by studying the topographic details of the groove formed at the GB intersection with the free surface.

Values of γ_{gb}/γ_s corresponding to tilt $\langle 10\bar{1}0\rangle/\Psi$ boundaries annealed at –18 ºC were obtained using the simplified Herring's theory, supposing that, when surface crystallographic planes at the GB groove root are not near the prismatic and basal planes, they have similar surface energy γ_s.

It was found that:

- symmetrical GBs, in general, have a lower value of γ_{gb}/γ_s compared to asymmetric ones;
- given an orientation β^+, γ_{gb}/γ_s depends on GB inclination and increases as the asymmetry increases;
- γ_{gb}/γ_s values may vary by up to one order of magnitude as a function of β^+. Thus, in general, the GB energy of high-angle ice GBs cannot be taken as a constant;
- the values of angle θ at the GB groove root obtained in the present work show a higher dispersion than those presented by KH and HS, indicating that at –18 ºC the GB may not be quasi-liquid as it seemed to be at the temperatures studied by these authors ie 0 ^{o}C and –5 ^{o}C;
- a significant correspondence between the values γ_{gb}/γ_s and the planar density Γ of the interface plane was observed, therefore, Γ can help to identified identify GBs in ice with low energies.

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