THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

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Effect of Temperature and Potassium Chloride Impurity on the Relative ⟨10$\bar{1}$0⟩ Tilt Grain Boundary and Surface Free Energies in Ice

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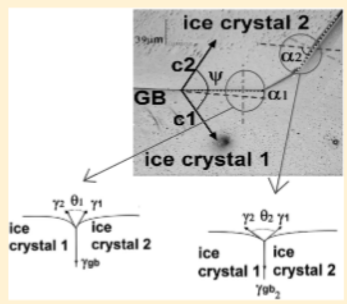
ABSTRACT: The ratio of the grain boundary free energies relative to the surface free energies γ_{gb}/γ_s can be determined by measuring the root angles of the grooves formed at the intersection of the grain boundary with the free surface. The grooves were copied by plastic replicas, and the topographic details were revealed with a laser confocal 3D microscope. Values of γ_{gb}/γ_s were determined for high purity and potassium chloride doped ice bicrystals annealed at −5 and −18 °C. The studied samples were ⟨10$\bar{1}$0⟩/ψ tilt grain boundaries with ψ between 10 and 180°. The used KCl concentrations were 1 and 10 μmol/l, and the conductivity of the pure ice was 0.3 μS. ⟨10$\bar{1}$0⟩/60° grain boundary relative energies were also determined for different grain boundary inclinations. All the γ_{gb}/γ_s obtained values were analyzed and compared using the CSL (coincidence site lattice) theory. For pure samples annealed at −18 °C, an important variation of γ_{gb}/γ_s with the grain boundary inclination was found. In general, a remarkable correspondence between CSL planar density Γ and γ_{gb}/γ_s was observed. Results also showed that the increase of temperature and the impurity changes significantly γ_{gb}/γ_s.



1. INTRODUCTION

It is well-known that grain boundaries (GBs) have an important role in determining the properties of materials, especially at temperatures close to the melting point such as those normally observed in the processes that take place in glaciers and atmospheric ice. In 2010, Brandon[1] presented a summary of how, in metallurgy, the understanding of grain boundaries has advanced and today's new technologies make it possible to virtually see the atoms forming the grain boundaries. A similar summary of what has been observed in ceramics can be seen in the work of Harmer (2010).[2] In ice, the understanding of grain boundaries and surface processes has improved due to the use of new techniques, such as laser confocal microscopy combined with differential interference contrast microscopy,[3] scanning electron microscopy (SEM),[4−6] and environmental scanning electron microscopy (ESEM)[7] to cite a few. However, currently there are very few studies, experimental or simulated, of the structure of grain boundaries in pure and doped ice, especially in the conditions of purity found in glaciers (≈1 μmol/L).[8]

Unique experimental works carried out to determine the energy of the ice GB were made by Ketcham and Hobbs (1969)[9] (KH) and Suzuki and Kuroiwa (1972)[10] (SK). These authors measured this energy at temperatures near the melting point (0 °C KH and −5 °C SK), and the exact GB misorientations of the analyzed samples were not informed. In fact, they only specified the angles Ψ between the *c*-axes of each crystal and it must be noted that, to specify a GB misorientation, five independent parameters must be provided, three specifying the rotation between the two lattices and two to describe the orientation of the GB plane.[11] The results obtained by KH show that GB energies vary relatively little when Ψ varies between 20 and 150°. On the other hand, SK results also show that the GB relative energies vary little when Ψ varies between 20 and 80° but decrease rapidly when Ψ tends to 0, 90, or 180°.

Regarding the ice GB structure and its variation with impurity concentration, theoretical studies have been performed at temperatures close to the melting point[12,13] and optical scattering measurements have been carried out on ice GB.[14] Thomson et al.[14] noted that the GB thickness increases with the impurity concentration and decreases for small angle twist grain boundaries. Small angle GBs are special grain boundaries, i.e., GBs with properties which differ drastically from those of general GBs. Misorientational dependencies of surface energy, GB diffusion parameters, GB migration, etc., have a sharply nonmonotonic character with extremes on special GBs.[15,16]

The coincidence site lattice (CSL) is widely used to study GB structures, and it is observed that boundaries with a high density of coincidence sites on the GB plane (Γ) are probably boundaries with low energies.[1] The CSL theory was satisfactorily used in ice to interpret some ice GBs with special properties.[17−20] It was also shown[20] that the movement of ⟨10$\bar{1}$0⟩/Ψ (⟨10$\bar{1}$0⟩/Ψ represents a GB obtained by matching two crystals obtained through a rotation Ψ around the ⟨10$\bar{1}$0⟩

Special Issue: Physics and Chemistry of Ice 2014

Received: April 28, 2014
Revised: August 7, 2014
Published: August 7, 2014

   dx.doi.org/10.1021/jp504134v | J. Phys. Chem. B 2014, 118, 13365−13370

axis) ice grain boundaries could be satisfactorily explained assuming that the GB energy depends on the GB inclination, and that the GB energy is minimized when the GB coincides with a plane that has a high density of coincidence sites.

Furthermore, in a previous study of the GB movement in ⟨10$\bar{1}$0⟩/60° bicrystals grown from KCl water solution (1 and 10 μmol/L),[21] it was observed that the GB mobility systematically decreases with temperature when temperatures are greater than −15 °C. However, the GB mobility jumps to a greater value when the samples are annealed at −20 °C. In the cited study,[21] following Gottstein and Shvindlerman,[15] this behavior was interpreted as a change in the GB structure: from a disordered quasi-liquid structure at high temperatures (> −15 °C) to a more ordered structure with less impurity concentration at lower temperatures.

The only studies of ice GB energies γ_{gb} were performed 40 years ago using plastic replicas of the ice surface, and these values are still used today. However, the results of these studies do not explain the dependence of the GB energy on the GB structure. Unfortunately, new technologies to study γ_{gb} are not yet available to us; therefore, in this work, γ_{gb} was studied using the old method of plastic replicas and values of the ratio γ_{gb}/γ_s, where γ_s is the ice−air surface free energy, were determined for high purity and potassium chloride doped ice bicrystals annealed at −5 and −18 °C. The studied samples were ⟨10$\bar{1}$0⟩/ψ tilt grain boundaries with Ψ between 10 and 180°. GB relative energies were specially determined for ⟨10$\bar{1}$0⟩/60° and ⟨10$\bar{1}$0⟩/45° tilt GBs with different GB inclinations. In this way, we aimed to determine the magnitude of γ_{gb}/γ_s variations and establish if the CSL theory can be used to explain them.

2. METHODS

High purity ice samples (water conductivity 0.3 μS) and KCl doped ice samples (1 and 10 μmol/L), with ⟨10$\bar{1}$0⟩/ψ tilt boundaries, were obtained following the method described by previous works.[22,23] The ice surfaces were prepared to a mirror-like finish by polishing them with a microtome in a cold chamber at −10 °C, and were allowed to evaporate for 3 h at constant temperature, in a dry airtight container with silica gel. The temperatures used were −5 and −18 °C. Subsequently, each sample surface was replicated with a 4% solution of Formvar in 1−2 dichloroethane. Acrylic rings of 1.5 cm in diameter were placed on the intersection of the sample surfaces with the GB grooves, and fixed amounts of Formvar solution were placed inside the rings. Then, samples were left in the refrigerated dry airtight container for 24 h, in order to evaporate completely the 1−2 dichloroethane and partially the ice surface. After these 24 h, a plastic sheet, approximately 0.1 mm thick, could be easily removed from the sample and stored to be analyzed later at ambient temperature. This procedure ensured that the thermal and chemical attack times were the same in the replicas of all the samples analyzed, so that any differences observed would be entirely due to differences between the samples. From the plastic replicas, Ψ and α angles were measured with a precision of ±1°. As shown in Figure 1, Ψ is the smaller of the angles formed between the c-axes lying on the {10$\bar{1}$0} prismatic plane of both crystals and α is that formed between the GB and the ψ bisector.

The topology of the replicas was analyzed with an Olympus Laser Confocal Microscope (LEXT OLS4000 3D). Parts a and b of Figure 2 show the 3D and 2D confocal images of the groove corresponding to the sample ⟨10$\bar{1}$0⟩/83°. Figure 2c shows the GB groove profile extracted from line AB of Figure 2b. For each GB, the angle θ shown in Figure 2c was measured. Only GB planes normal to the surface were considered, so the values of γ_{gb}/γ_s were obtained using the simplified Herring equation[24,9] (eq 1), which results from the surface energy balance at the GB groove (see Figure 2d)

$$\frac{\gamma_{gb}}{\gamma_s} = 2\cos(\theta/2) \qquad (1)$$

Some surfaces of the pure ice samples, with the orientation angle Ψ = 60°, were replicated with a 4% solution of Formvar in chloroform and 4% solution of Formvar in 1−2 dichloroethane at −18 °C: The plastic replicas were studied, and as it can be seen in Table 1, no significant differences were observed in the angles θ measured on each replica.

To analyze the results by applying the CSL theory, the CSLs obtained for ice[25] corresponding to two grains obtained through a rotation Ψ^+ around the ⟨10$\bar{1}$0⟩ axis were used. In this work,[25] the CSL's primitive cells were obtained for samples with values of Σ (the volumetric density of CSL sites) less than 50; for each principal and diagonal plane of the CSL cell, the values of Γ (the planar density of coincident sites) were calculated. In the present work, the studied GBs with orientation angle Ψ were associated with a Ψ^+ CSL, following the commonly used Brandon criterion[26] (i.e., GBs were considered close to a CSL if differences between Ψ and Ψ^+ were lower than 10°). For each associated Ψ^+, the values of Γ corresponding to the principal or diagonal planes of the corresponding CSL cell were used.

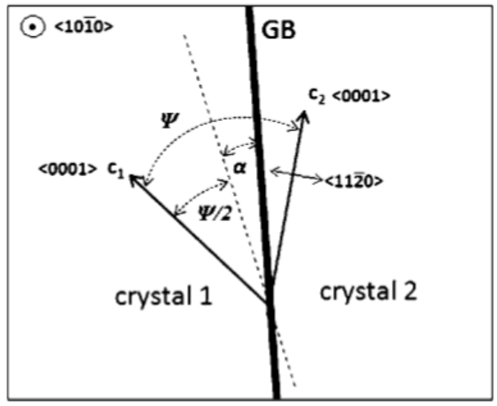


Figure 1. Schematic representation of a ⟨10$\bar{1}$0⟩/ψ GB, indicating the angles Ψ and α. c_1 and c_2 correspond to the ⟨0001⟩ axis of each crystal, and the common ⟨10$\bar{1}$0⟩ axis to each crystal is perpendicular to the figure plane. The ⟨11$\bar{2}$0⟩ prismatic axis is perpendicular to the ⟨0001⟩ axis and lies on the figure plane.

3. RESULTS AND DISCUSSION

3.1. Pure Samples. In this section, the values of γ_{gb}/γ_s for pure bicrystalline samples annealed at −5 and −18 °C are presented. The analyzed samples were ⟨10$\bar{1}$0⟩/ψ tilt GB with ψ between 10 and 90°.

3.1.1. Samples Annealed at −18 °C. The values of γ_{gb}/γ_s, with its corresponding standard deviation, obtained from eq 1 for all the samples annealed at −18 °C, are presented in Figure 3.

Figure 3 shows that the maximum and minimum values of γ_{gb}/γ_s corresponding to the same orientation are statistically different. As we will see later, this fact is connected with the GB inclination. In Figure 3, it is observed that for Ψ angles from 0

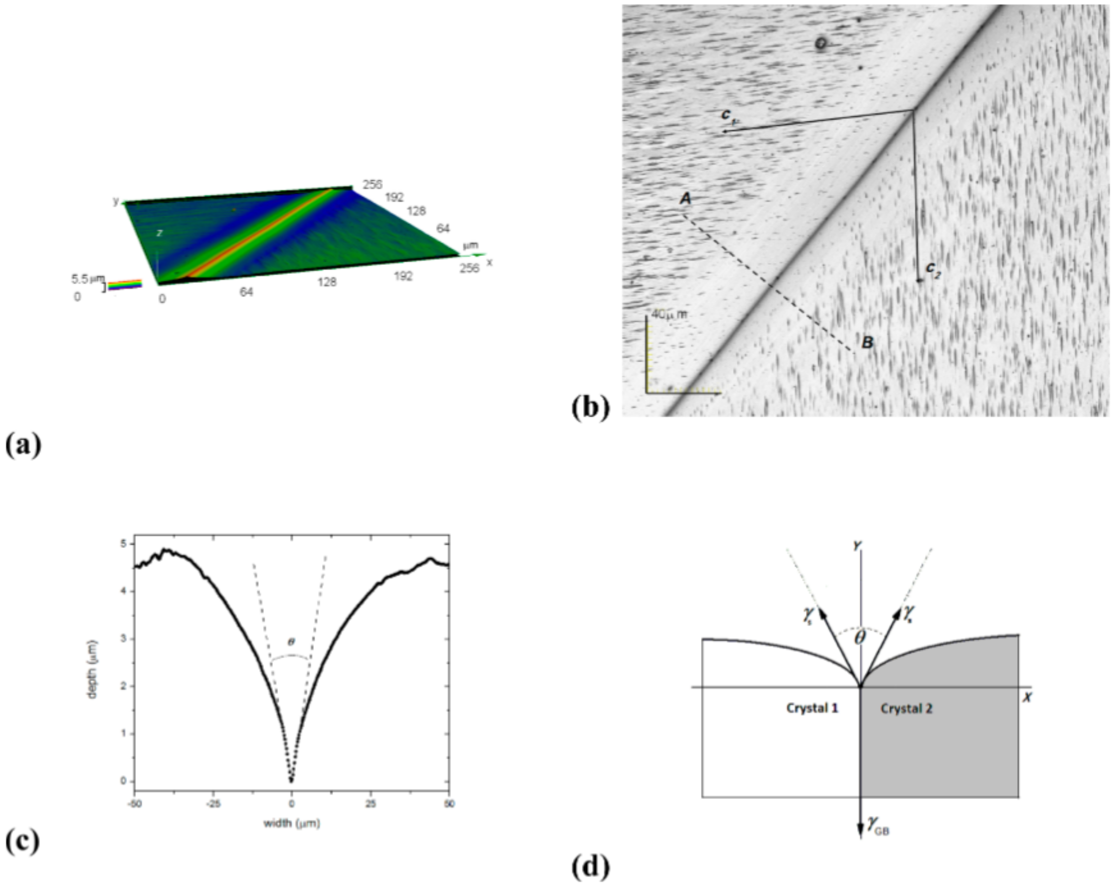


Figure 2. (a, b) 3D and 2D confocal microscope image of the plastic replica corresponding to the $\langle 10\bar{1}0\rangle/83°$ sample. (c) GB groove profile, extracted from line AB of image b. (d) Schematic representation of the surface energy balance at the GB groove.

Table 1. θ Values Obtained from Plastic Replicas of the Same Sample, Performed with Solutions of Formvar in 1−2 Dichloroethane and Chloroform

1−2 dichloroethane	chloroform
$\theta = 154 \pm 2°$	$\theta = 158 \pm 2°$

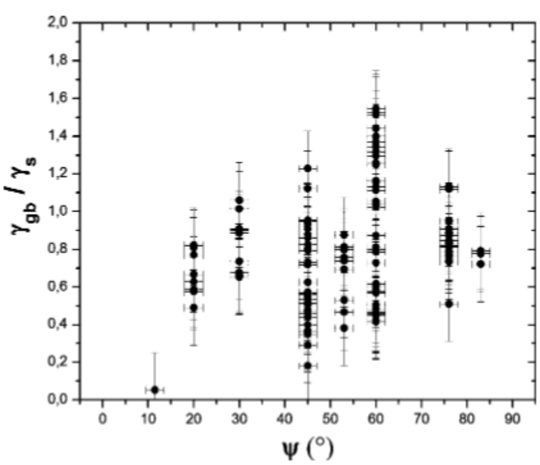


Figure 3. Values of γ_{gb}/γ_s for pure ice $\langle 10\bar{1}0\rangle/\psi$ tilt GBs annealed at −18 °C.

to 60° the maximum values of γ_{gb}/γ_s show a tendency to increase with the orientation and for Ψ angles from 60 to 90° a tendency to decrease. This behavior in ice was also found by Suzuki and Kuroiwa,[10] and it is modeled very well with the GB dislocation model.[1]

For the orientations Ψ = 60° and Ψ = 45°, experimental values of γ_{gb}/γ_s corresponding to different GB inclinations (α) were obtained.

Figures 4 and 5 show, respectively, the value of γ_{gb}/γ_s for Ψ = 60° and Ψ = 45° as a function of α (α = 0 represents the symmetric GB). In these figures, the values of 1/Γ obtained

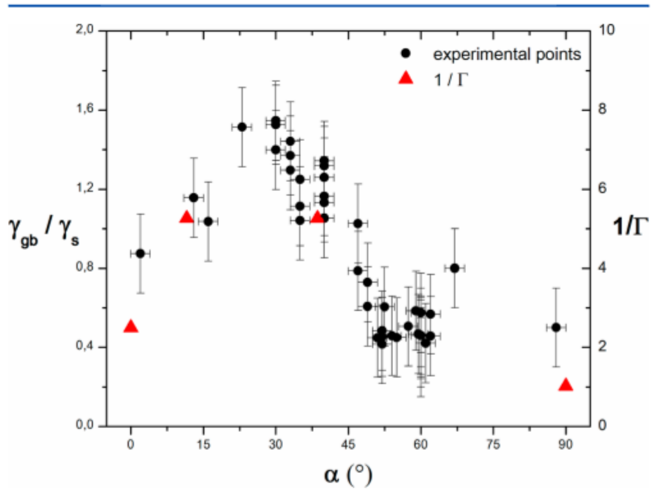


Figure 4. Values of γ_{gb}/γ_s as a function of α for pure ice $\langle 10\bar{1}0\rangle/60°$ tilt GB annealed at −18 °C.

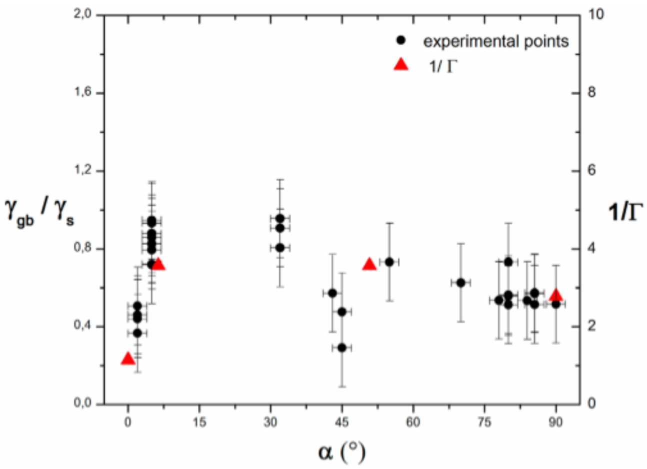


Figure 5. Values of γ_{gb}/γ_s as a function of α for pure ice $\langle 10\bar{1}0\rangle$/45° tilt GBs annealed at −18 °C.

from Gonzalez et al.[25] for Ψ^+ = 63° and Ψ^+ = 45° are also included.

Figure 4 shows that the maximum and minimum values of γ_{gb}/γ_s differ by approximately 1 order of magnitude. The plot also shows that the γ_{gb}/γ_s values are the lowest when α = 0° and when α is between 60 and 90° and they have a maximum around α = 30°. This figure also shows that there is a significant correspondence between the values of γ_{gb}/γ_s and 1/Γ. It is seen that when γ_{gb}/γ_s increases 1/Γ increases and vice versa; i.e., the ratio γ_{gb}/γ_s decreases when the density of atoms that occupy similar points in the crystals at both sides of the GB planes increases. Thus, it can be seen that grain boundary planes with a high density of coincident sites are good candidates to have low energy. Furthermore, Figure 4 shows that the highest GB relative energy is 1.6 and corresponds to the inclination where the GB coincides with a $\{11\bar{2}0\}$ prismatic plane of one of the crystals. This result indicates to us that the match between a prismatic plane and a nonindexed plane is very poor and in consequence γ_{gb} is near $2\gamma_s$; i.e., the GB energy is approximately the sum of the ice−air surface energy corresponding to each plane.

In previous work,[22] we showed that, at −10 °C, a variation in the GB energy with GB inclination by a factor of about 2 could account for significant changes in the GB velocity. The results obtained in this work show that at −18 °C the dependence of GB relative energy on GB inclination is more important than that supposed in the results obtained previously; thus, GB migration at −18 °C could be more significantly affected by GB relative energy anisotropy. The variations of the grain size with the depths in glaciers are ruled by the movements of the grain boundaries; thus, these results must be taken into account when glacial ices are analyzed.

Figure 5 shows a behavior very similar to that of Figure 4. The GB relative energy has a maximum between 10 and 30°, which is where the GB coincides with a $\{11\bar{2}0\}$ prismatic plane. As in Figure 4, it is observed that there is a significant correspondence between γ_{gb}/γ_s and 1/Γ.

3.1.2. Samples Annealed at −5 °C. The values of γ_{gb}/γ_s obtained, from eq 1, for the pure ice bicrystalline sample with Ψ = 60° annealed at −5 °C with its corresponding standard deviation are presented in Figure 6 as a function of α.

The Figure 6 plot shows a similar behavior to that of Figure 4, corresponding to the same sample annealed at −18 °C. In

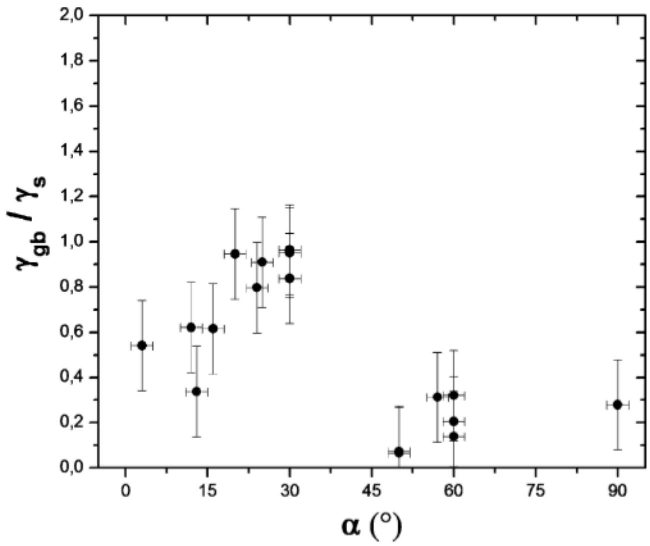


Figure 6. Values of γ_{gb}/γ_s as a function of α for pure ice $\langle 10\bar{1}0\rangle$/60° tilt GB annealed at −5 °C.

this case, however, the maximum values are approximately half of those observed at −18 °C. As the general trend is that surface tension decreases with the increase of temperature,[27] this behavior could be understood by considering that the GB energy also decreases as the temperature increases.

3.2. Doped Samples. In this section, the values of γ_{gb}/γ_s for doped bicrystalline samples annealed at −5 and −18 °C are presented. The samples had $\langle 10\bar{1}0\rangle$/60° tilt GBs and were grown from KCl water solutions of 1 and 10 μmol/L.

In Figure 7, the GB relative energy γ_{gb}/γ_s values obtained from samples with a concentration of 1 μmol/L and annealed

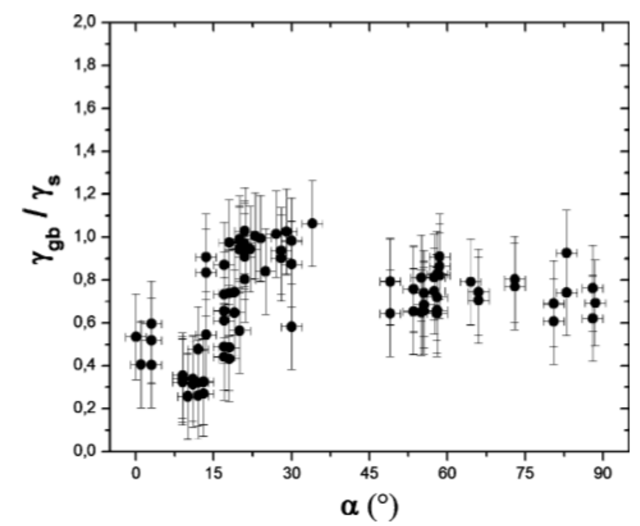


Figure 7. Values of γ_{gb}/γ_s, as a function of α, of $\langle 10\bar{1}0\rangle$/60° tilt GBs obtained from 1 μmol/L KCl water solutions and annealed at −18 °C.

at −18 °C are shown as a function of α. In this figure, it is observed that the variations of GB relative energy γ_{gb}/γ_s with the GB inclination (α) in the doped sample have the same behavior of the pure samples. However, it must be noted that the difference between the maximum and minimum values of γ_{gb}/γ_s are similar to those observed in Figure 6, i.e., corresponding to pure samples annealed at −5 °C. Thus, it may be said that the effect of increasing the impurity concentration is similar to the effect of increasing the temperature. This is consistent with the fact that solutes segregate to the GB and reduce the energy necessary to remove an atom from the surface.

In Figure 8, the GB relative energy γ_{gb}/γ_s values corresponding to a concentration of 10 μmol/L and −18 °C

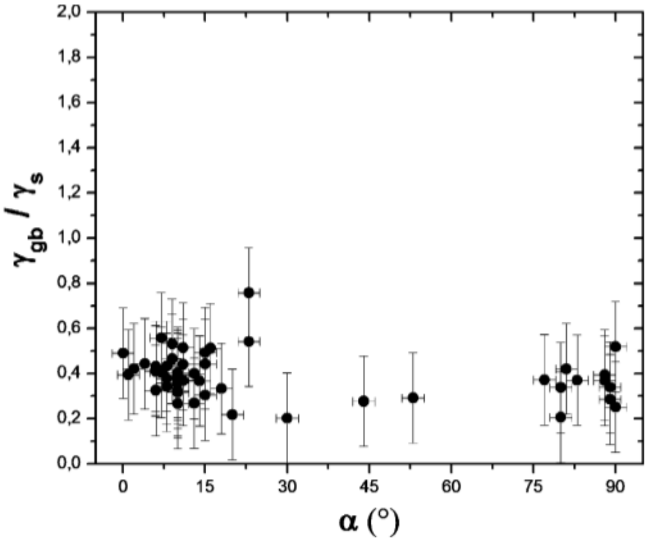


Figure 8. Values of γ_{gb}/γ_s for $\Psi = 60°$ as a function of α at −18 °C and with a concentration of 10 μmol/L.

are shown. Clearly, the figure shows that the experimental values do not change with the GB inclination and, in general, the values are lower than 0.5. The same results also were observed at −5 °C for both solute concentrations. In these cases, the replicas were very difficult to measure because the surface in general appears very clear and it looks like a liquid surface. The GBs were not always visible, and when a θ angle could be measured, it was very close to 180°. When the temperature of pure ice tends to 0 °C, the ice surface becomes quasi-liquid, and this effect is increased when soluble solvents are included. In these cases, evidently, the replica method is not appropriate to study the GB energy. However, in these cases, the replicas indicate that the GB structure changed with the GB inclination because, as it is seen in Figure 9, the grain boundary groove can be resolved only at some GB inclinations.

4. SUMMARY

In this paper, the ice GB energies γ_{gb} relative to 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 and values of γ_{gb}/γ_s were obtained using Herring's theory.

Pure ice bicrystals with $\langle 10\bar{1}0\rangle/\psi$ tilt boundaries were annealed at −18 and −5 °C.

At −18 °C, the following was found:

- γ_{gb}/γ_s values show a variation higher than the standard deviation, and the maximum values have a tendency to increase with the orientation angle Ψ from 0 to 60° and decrease from 60 to 90°.
- Given an orientation Ψ, γ_{gb}/γ_s depends on the GB inclination angle α. For $\Psi = 60°$, the highest GB relative energy corresponds to $\alpha = 30°$ where the GB coincides with a $\{11\bar{2}0\}$ prismatic plane of one of the crystals. In

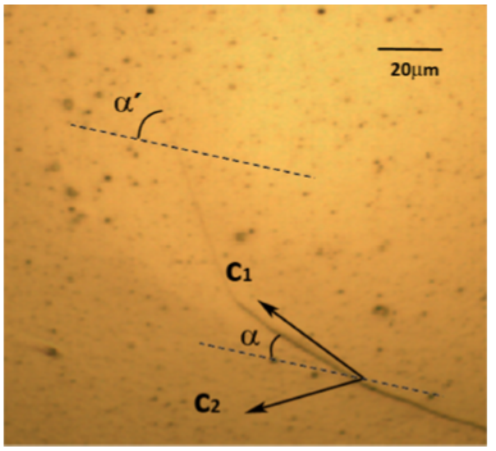


Figure 9. GB groove of the $\langle 10\bar{1}0\rangle/60°$ sample at −18 °C with a concentration of 10 μmol/L. The dashed lines indicate the Ψ bisector, and two different α values are presented.

this case, the GB relative energy is 1.6 times greater than the surface energy.
- For $\langle 10\bar{1}0\rangle/60°$ and $\langle 10\bar{1}0\rangle/45°$ tilt boundaries, there is a significant correspondence between the values γ_{gb}/γ_s and $1/\Gamma$, where Γ is the planar density of the principal and diagonal planes of the associated CSL. Therefore, it is concluded that the planar density of the corresponding CSL planes can be used to understand the ice GB energy.

At −5 °C, the following was found:

- γ_{gb}/γ_s values show a similar behavior to that observed at −18 °C.
- The maximum values are approximately half of those observed at −18 °C. This behavior indicates that the GB energy decreases as the temperature increases.

Doped ice bicrystals obtained from KCl water solutions of 1 and 10 μmol/L with $\langle 10\bar{1}0\rangle/60°$ tilt boundaries were studied at −18 and −5 °C.

In doped ice bicrystals, obtained from solutions of 1 μmol/L and annealed at −18 °C, it was found that the variations of GB relative energy γ_{gb}/γ_s with the GB inclination (α) behave the same as the pure samples. However, the differences between the maximum and minimum values of γ_{gb}/γ_s were lower than those observed in pure samples.

For 1 μmol/L doped samples annealed at −5 °C and for 10 μmol/L doped samples annealed at −5 and −18 °C, the replicas were very difficult to measure because the surface in general appears very clear as if it was the surface of a liquid. In these cases, the replica method is not appropriate to study the GB energy. However, in some cases, the replicas indicate that the GB structure changes with the GB inclination because the grain boundary groove could be observed at some but not all GB inclinations.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This paper was economically supported by CONICET (PIP No.: 11220090100537) and Secyt-UNC (2012−2013). We thank Mr. Jose Barcelona for the technical collaboration that was integral to the success of our measurements.

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