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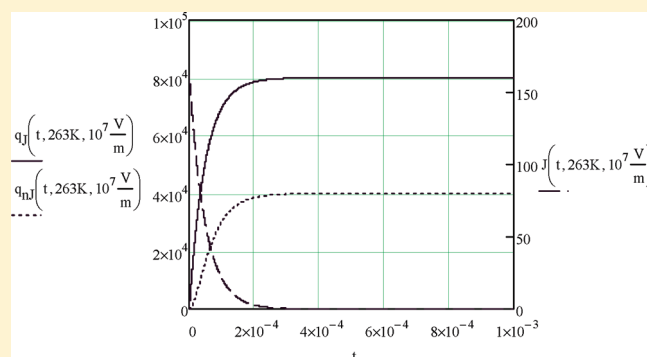
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ABSTRACT: We theoretically predict and calculate non-Joule heating/cooling caused by a direct electric current in ordinary crystalline ice *Ih*. The cause of this effect is related to partial ordering/disordering occurring in the proton subsystem of ice when protons either drift or diffuse in the ice. Depending on relative directions of the electric current and the configuration vector of ice, the non-Joule effect can be either positive, that is, heat generation, or negative, that is, heat absorption, and its absolute magnitude is usually comparable with that of normal Joule heating. The magnitude of this phenomenon is also approximately inversely proportional to the ice temperature and, thus, is more pronounced at low temperatures.



INTRODUCTION

All crystalline forms of ice have an ordered lattice of oxygen atoms, but their hydrogen atoms may or may not be arranged in an orderly manner. Thus, in an ordinary ice, *Ih*, the oxygen atoms are arranged in a wurtzite lattice (hexagonal form of ZnS), but the hydrogen atoms demonstrate a significant degree of disorder due to the fact that each hydrogen atom may occupy one of two possible positions in a hydrogen bond, as shown in Figure 1, which depicts a layer of ordinary ice *Ih* projected on the (10 $\bar{1}$ 0) plane.¹

That allows numerous possible configurations of the hydrogen subsystem and a significant configuration entropy. In a defect-free ice *Ih* lattice, the number of such configurations is limited by two Bernal–Fowler rules: there is one hydrogen atom per hydrogen bond and there are two hydrogen atoms per water molecule.² Pauling³ showed that the number of the ice configurations for an ice crystal consisting of N water molecules is $(3/2)^N$, and the corresponding configuration entropy is equal to $Nk_B \ln(3/2)$. Pauling's prediction agrees very well with experimental results obtained by Giaque and Ashley.⁴

In defect-free ice *Ih*, a lattice transition from one Bernal–Fowler configuration to another is not possible because any translation of a hydrogen atom either along a hydrogen bond or in between two hydrogen bonds would create point defects. In fact, such point defects are always present due to either thermal excitation or a presence of specific dopants. Moreover, contemporary theories of electrical properties of ice and ice elastic relaxation are based on the existence of “proton point defects” and their fluxes.¹ The mobile hydrogen atoms are stripped of their electrons and, as such, are protons. For that reason, we will refer to the above-mentioned point defects as “proton” defects.

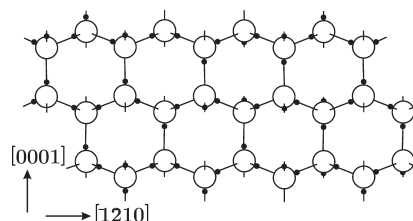


Figure 1. A layer of the ice *Ih* structure projected on the (10 $\bar{1}$ 0) plane.

There are four such defects of particular importance. Two involve the H_3O^+ and OH^- ions, and two others are defects of hydrogen bonds, known as L and D defects. The latter ones are also called “Bjerrum defects”.⁵ These four defects are schematically shown in Figure 2. In undoped ice, the ionic and Bjerrum defects are formed in pairs, and the corresponding energies of formation of the pairs are approximately 1.0 eV for ions and 0.7 eV for Bjerrum defects. After they are formed, the defects can easily migrate through the crystal lattice under the action of either an electric field, elastic stress, or a concentration gradient of the defects.¹

The ionic and Bjerrum point defects are considered to be the main charge carriers in ice, and the latter is often called a proton semiconductor because what is actually moving in ice when an electric current flows are protons. Under specific conditions, the

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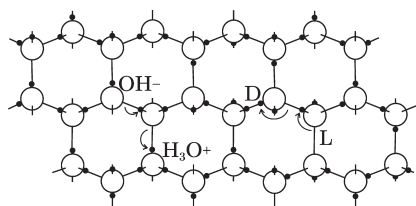


Figure 2. Ionic and Bjerrum defects introduced into the structure of Figure 1.

effects of an electric current in ice can drastically differ from what occurs for normal conductors. We show in this paper that heat generated in ice by an electric current is generally not equal to the well-known Joule heating. In fact, under some conditions, an electric current can cool ice. This departure from Joule heating is due to the change in the zero-point entropy that the fluxes of point defects produce.

Herein, we will derive the governing equations that describe the heat generated by an electric current in ice, estimate the magnitude of the effect, and also specify particular conditions under which the effect differs the most from Joule heating. It is worth stressing that while the configuration entropy can be changed by fluxes of point defects, those fluxes can be induced by a number of factors, such as an electric field, mechanical stress, proximity to an ice/solid interface or to a free ice surface, proton injection into the ice, and so forth. Of course, thermal effects induced by a change in ordering of some subsystem inside of a solid-state material are well-known. One example is a magnetocaloric effect in paramagnetic salts.⁶ The magnetocaloric effect in cooperative paramagnetics has recently been discussed by Orendac et al.⁷ and by Ryzhkin.⁸ However, the effect that we discuss here differs significantly from the magnetocaloric effect because in ice, there is a very strong correlation in orientation of molecular dipoles, which in turn can be changed by fluxes of the defects. Moreover, the constants in the equations describing the two effects differ greatly, and that results in a different temperature range where the non-Joule heating of ice can be observed and in quite different orders of magnitude of those effects.

■ NON-JOULE HEATING GOVERNING EQUATIONS

To describe electrical properties of ice, we use the theory developed by Jaccard⁹ and further developed by Hubmann.¹⁰ We will also use the most recent refinement of the theory suggested by Ryzhkin and Whitworth.¹¹ In Jaccard's theory, a so-called "configuration vector", $\vec{\Omega}$, is used to quantify the degree of ordering in the hydrogen subsystem. The configuration vector can be defined in two ways. It is worth noticing that motion of either of the four defects changes the orientation of water molecules in the ice lattice. Because of that, the configuration vector can be defined in terms of defect fluxes

$$\vec{\Omega}(t) - \vec{\Omega}(0) = \int_0^t (\vec{j}_1 - \vec{j}_2 - \vec{j}_3 + \vec{j}_4) dt' \quad (1)$$

where t is time, j_i are defect's fluxes, and the indices $i = 1, 2, 3$, and 4 refer to H_3O^+ , OH^- , D , and L respectively.

The configuration vector is proportional to the total dipole moment of the unit volume and is 0 for a totally disordered configuration. For any given value of $\vec{\Omega}$, one can calculate a number of configurations having that value and, thus, an entropy that corresponds to the value of the configuration vector. Such

calculations lead to the following relationship between the configuration part of the entropy, S_c , and the configuration vector $\vec{\Omega}$

$$S_c(\vec{\Omega}) = S_c(0) - \frac{\Phi}{2T} \vec{\Omega}^2 + O(\vec{\Omega}^4) \quad (2)$$

where $\Phi = (8/\sqrt{3})ak_B T$, T is temperature, and a is the mean length of a hydrogen bond in ice *Ih* (0.2764 nm at $T = 253$ K). The entropy in eq 2 represents an expansion of a more complex formula derived by Ryzhkin and Whitworth.¹¹ We will see later that the first two terms of that expansion can provide a good approximation. For instance, even in the extreme case of total alignment of molecular dipoles along the hexagonal axis c , the first two terms in the expansion of eq 2 imply a value of $k_B \ln(1.27)$ per water molecule, which is close to the precise value of $k_B \ln(1.175)$ found by Auvert and Villain.¹² Because of this, we will use the first two terms to make order-of-magnitude estimates of the thermoelectrical effects in ice even for strongly ordered proton configurations in ice.

The rate with which heat is generated by an electric field, \vec{E} , can be written in the following way

$$TS = TS_n + TS_c = \vec{j} \vec{E} - \Phi \vec{\Omega} \dot{\vec{\Omega}} \quad (3)$$

where S_n and S_c are the nonconfiguration and the configuration parts of the entropy, respectively

$$\vec{j} = \sum_{i=1}^4 e_i \vec{j}_i \quad (4)$$

is total density of electric current that is due to the point-defect motion, and e_i are the effective charges of the defects; $e_{1,2} \approx \pm 0.62e$ and $e_{3,4} \approx \pm 0.38e$, where e is a charge of a proton e .^{13,14} The $(\vec{j} \vec{E})$ term in eq 3 is, of course, the Joule heating, while the $(-\Phi \vec{\Omega} \dot{\vec{\Omega}})$ term originates from the second term of the expansion of eq 2 and, thus, is due to variations of the configuration entropy. Substitution of eq 1 into eq 3 leads to

$$TS = \sum_{i=1}^4 (e_i \vec{E} - \eta_i \Phi \vec{\Omega}) \vec{j}_i = \sum_{i=1}^4 \vec{X}_i \vec{j} \quad (5)$$

where $\eta_i = 1, -1, -1$, and 1 for $i = 1, 2, 3$, and 4 and $\vec{X}_i = e_i \vec{E} - \eta_i \Phi \vec{\Omega}$ are the generalized thermodynamic forces that cause the defect's fluxes. One can then write an equation for the defect fluxes as

$$\vec{j}_i = \frac{\sigma_i}{e_i^2} \vec{X}_i = \frac{\sigma_i}{e_i^2} (e_i \vec{E} - \eta_i \Phi \vec{\Omega}) \quad (6)$$

where kinetic coefficients σ_i are the specific partial conductivities of the charge carriers in ice.¹⁰

■ DISCUSSION AND ANALYSIS OF RESULTS

We now discuss in detail the difference between Joule heating and heat generated by an electric current in ice. For the derivative of the nonconfigurational part of ice entropy, eqs 3–5 yield

$$T\dot{S}_n = T\dot{S} - T\dot{S}_c = \sum_{i=1}^4 \frac{\sigma_i}{e_i^2} (e_i \vec{E} - \eta_i \Phi \vec{\Omega})^2 + \Phi \vec{\Omega} \dot{\vec{\Omega}} \quad (7)$$

The sum in eq 7 corresponds to conventional Joule heating, while the term $\Phi \vec{\Omega} \dot{\vec{\Omega}}$, describes heat generation associated with changes in configuration entropy. It should be noted that the

nonconfiguration entropy density S_n is a monotonically rising function of temperature so that the sign of its derivative \dot{S}_n corresponds to rising or falling temperature of the ice crystal. Ordering, that is, the growth of $|\vec{\Omega}|$, corresponds to $\vec{\Omega} \cdot \vec{\Omega} > 0$, so that both terms on the right-hand side of eq 7 are positive. Alternatively, in the case of disordering, the term $\Phi \vec{\Omega} \cdot \vec{\Omega}$ can be negative, but only for a certain amount of time. After crossing 0, the vector $\vec{\Omega}$ will grow again, and the product $\Phi \vec{\Omega} \cdot \vec{\Omega}$ will again become positive. From the discussion above, one can see an asymmetry in the effect of direct current on heat generation in ice. If the current direction is such that it increases the order in the proton subsystem (increasing $\vec{\Omega}$), then the heat generation rate is higher than that for the opposite direction of the current. That simply means that the proton subsystem releases heat during its ordering and absorbs heat during system disordering. An interesting question is if there are conditions at which ice will be cooled by a direct electric current. To find the answer to that question let us substitute $(\vec{j}_1 - \vec{j}_2 - \vec{j}_3 + \vec{j}_4)$ for $\vec{\Omega}$ (see eq 1) in eq 7 and then apply eq 6 and the relations between the effective electric charges of the point defects $e_1 = -e_2$, $e_3 = -e_4$. We will then arrive at the following result

$$TS_n = (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \vec{E}^2 + \left(\frac{\sigma_3 + \sigma_4}{e_3} - \frac{\sigma_1 + \sigma_2}{e_1} \right) \Phi \vec{\Omega} \cdot \vec{E} \quad (8)$$

The first term on the right side of eq 8 is always positive and proportional to the square of the applied electric field. The second term there (the non-Joule heat effect) can be either positive or negative and is proportional to the applied electric field. Therefore, non-Joule heat effects are most prominent when the applied electric field is weak and the initial proton ordering is sufficiently high. Thus, the following condition must be satisfied to cool ice in an electric field

$$E < \Phi \vec{\Omega} \cdot \left(\frac{\sigma_1 + \sigma_2}{e_1} - \frac{\sigma_3 + \sigma_4}{e_3} \right) / (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \quad (9)$$

where $\vec{\Omega}$ and E are the magnitudes of these vectors. According to eq 8, the sign of the effect is determined by the interplay between the partial conductivities of point defects, the direction of the electric field, and the direction of the configuration vector. Notice that the second term in the right side of eq 8 may be either negative or positive. For instance, when Bjerrum defects are the majority charge carriers (as they usually are), that is, $(\sigma_1 + \sigma_2)/e_1 < (\sigma_3 + \sigma_4)/e_3$, the term $((\sigma_3 + \sigma_4)/e_3 - (\sigma_1 + \sigma_2)/e_1) \Phi \vec{\Omega} \cdot \vec{E}$ in eq 8 is negative when an electric field and a configuration vector are antiparallel. However, even for parallel $\vec{\Omega}$ and E , that term in eq 8 can be negative when H_3O^+ and OH^- ions become dominant charge carriers. In that case $((\sigma_1 + \sigma_2)/e_1 > (\sigma_3 + \sigma_4)/e_3)$. The ions indeed may become the majority charge carriers in doped ice, for example.¹⁵

We now discuss other properties particular to electric heating of ice. First, let us notice that, regardless of the type of majority charge carriers, the heat generation rate exceeds Joule heating when a direct current is induced in a nonpolarized ice crystal, that is, when $\vec{\Omega}(0) = 0$. That can be seen in eq 7, where the first term on the right side of the equation is positive for the discussed case. If after first passing a current in one direction we then reverse the current direction, the total heat generation rate would fall below

Joule heating. Of course, alternating current would generate as much heat as Joule heating does.

Let us now investigate the relationship between Joule and non-Joule heating of ice in more detail. When a constant electric field is applied to a nonpolarized ice crystal for the first time, the electric current decays from its high initial value, which is characteristic of the high-frequency conductivity of ice, to a lower magnitude that is specific to the static conductivity of ice. A solution to that time-dependent problem can be easily found by combining eqs 1, 4, and 6. By solving a system of ODE with the initial condition of $\vec{\Omega}(0) = 0$, we will find that the total electric current and the configuration vector are the following functions of time

$$J(t) = E \cdot \left[(\sigma_\infty - \sigma_s) \cdot \exp\left(-\frac{t}{\tau_D}\right) + \sigma_s \right] \quad (10)$$

$$\vec{\Omega} \cong \frac{\left(\frac{\sigma_1 + \sigma_2}{e_1} - \frac{\sigma_3 + \sigma_4}{e_3} \right)}{\Phi \left(\frac{\sigma_1 + \sigma_2}{e_1^2} + \frac{\sigma_3 + \sigma_4}{e_3^2} \right)} \vec{E} \cdot \left(1 - \exp\left(-\frac{t}{\tau_D}\right) \right) \quad (11)$$

where

$$\sigma_\infty = \sum_{i=1}^4 \sigma_i \quad (12)$$

is the ice high-frequency conductivity

$$\sigma_s = \frac{e^2}{\frac{e_1^2}{\sigma_1 + \sigma_2} + \frac{e_3^2}{\sigma_3 + \sigma_4}} \quad (13)$$

is ice static conductivity, and

$$\tau_D = \left[\Phi \cdot \left(\frac{\sigma_1 + \sigma_2}{e_1^2} + \frac{\sigma_3 + \sigma_4}{e_3^2} \right) \right]^{-1} \quad (14)$$

is Debye relaxation time. The Joule part of the heat generated over time t is equal to

$$q_J(t) = \int_0^t J(\zeta) \cdot E \, d\zeta = E^2 \cdot \left[(\sigma_\infty - \sigma_s) \cdot \tau_D \cdot \left(1 - \exp\left(-\frac{t}{\tau_D}\right) \right) + \sigma_s \cdot t \right] \quad (15)$$

and the non-Joule part of the heat generated over time t is equal to

$$q_{nJ}(t) = \frac{\Phi \vec{\Omega}(t)^2}{2} = \frac{\left(\frac{\sigma_1 + \sigma_2}{e_1} - \frac{\sigma_3 + \sigma_4}{e_3} \right)^2}{2 \Phi \cdot \left(\frac{\sigma_1 + \sigma_2}{e_1^2} + \frac{\sigma_3 + \sigma_4}{e_3^2} \right)} \vec{E}^2 \cdot \left(1 - \exp\left(-\frac{t}{\tau_D}\right) \right)^2 \quad (16)$$

The plots of the time-dependent functions of $J(t)$, $q_J(t)$, and $q_{nJ}(t)$ calculated from eqs 10, 15, and 16, respectively, are shown in Figure 3.

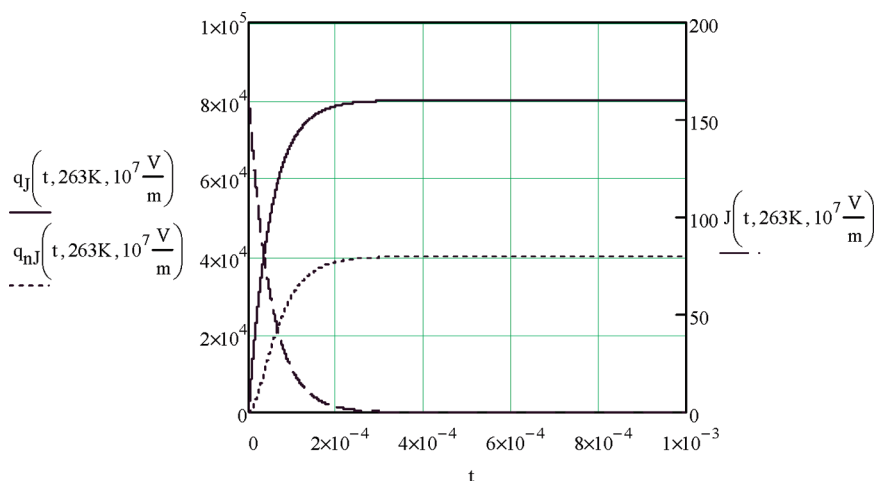


Figure 3. The Joule and non-Joule heat transfer in J/m^3 of pure ice and also the current density, J , in A/m^2 versus time, t , in s. A static electric field strength of $E = 10^7 \text{ V/m}$ was applied at $T = 263 \text{ K}$.

Notice that with $t \rightarrow \infty$, the configuration vector approaches the following limit

$$\vec{\Omega}(\infty) \cong \frac{\left(\frac{\sigma_1 + \sigma_2}{e_1} - \frac{\sigma_3 + \sigma_4}{e_3} \right)}{\Phi \left(\frac{\sigma_1 + \sigma_2}{e_1^2} + \frac{\sigma_3 + \sigma_4}{e_3^2} \right)} \vec{E} \quad (17)$$

To compare the magnitudes of q_J and q_{nJ} , let us consider $t \gg \tau_D$ and neglect the small $\sigma_S \cdot t$ term in eq 15. Using for τ_D eq 14, we arrive at the following result

$$\frac{q_{nJ}}{q_J} \cong \frac{1}{2} \quad t \gg \tau_D \quad (18)$$

Thus, neglecting the usually very small Joule heating due to the static conductivity of ice, we found that a rectangular pulse of an electric field of duration longer than the Debye relaxation time generates 50% more heat than it would generate in a usual electrical conductor. When an opposite-direction pulse of electric field is applied, it generates 50% less heat until the polarization vector vanishes. Of course, if the current lasts for a sufficiently long time, the small static conductivity term, $E^2 \cdot \sigma_S \cdot t$, in eq 15 becomes important.

Notice also that short-circuiting an ice sample after applying a DC pulse will cool the ice by q_{nJ} due to relaxation of the configuration vector through reversed defect fluxes. The configuration entropy there turns to its initial value for a nonpolarized crystal. Let us now estimate the maximum absolute magnitude of the effect. Assuming that ions are the majority charge carriers, we can find from eq 16

$$q_{nJ}(\infty) = \frac{\Phi \cdot \vec{\Omega}(t)^2}{2} \cong \frac{e_1^2}{2\Phi} E^2 \quad (19)$$

Substituting in eq 19 the electric strength of ice $E = 10^7 \text{ V/m}$ (the value that one of the authors, Petrenko, experimentally measured in ice single crystals for $T < -10^\circ \text{C}$) yields for a single electric relaxation pulse applied at -10°C

$$q_{nJ}(\infty) = 1.065 \times 10^5 \text{ J/m}^3 \quad (20)$$

Yet, that large amount of heat transfer per unit volume would

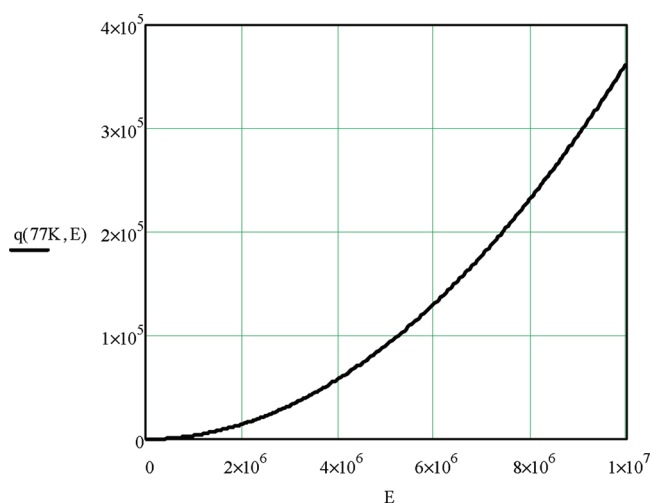


Figure 4. The non-Joule part of the heat transfer, q , in J/m^3 in ice doped with KOH at $T = 77 \text{ K}$ versus the static electric field strength, E , in V/m .

cause only very modest change in ice temperature

$$\Delta T = \frac{q_{nJ}(\infty)}{C_{\text{ice}} \cdot \rho_{\text{ice}}} \approx 0.06 \text{ K} \quad (21)$$

where $C_{\text{ice}} = 1962 \text{ (J/kg} \cdot \text{K)}$ is the specific heat capacity of ice and $\rho_{\text{ice}} = 920 \text{ kg/m}^3$ is ice density at -20°C .¹

Notice that because Φ is linearly proportional to the ice temperature, q_{nJ} and $\Delta T(\infty)$ are inversely proportional to the ice temperature. Because of this, one can expect greater non-Joule heating at low temperatures. Doping ice with KOH extends the temperatures at which the ice is electrically conductive to about 70 K .¹⁷ In ice heavily doped with KOH, OH^- ions are the majority charge carriers, and the dielectric relaxation time is about $\sim 1 \text{ s}$. The static conductivity in such ice is not detectable at 70 K .¹ There is some evidence that for temperatures above 200 K , Bjerrum defects become the majority charge carriers in KOH-doped ice. Figure 4 shows the calculated dependence of the non-Joule heat transfer as a function of the electric field strength applied to KOH-doped ice at 77 K . To calculate the temperature

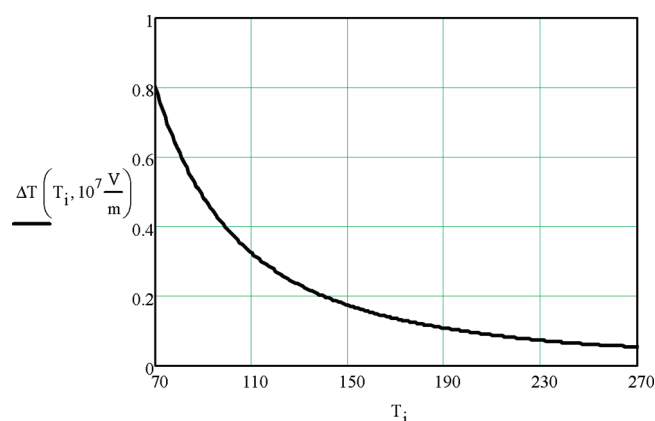


Figure 5. The non-Joule part of the temperature change, ΔT , per one application of static electric field $E = 10^7$ V/m in ice doped with KOH at $T = 77$ K versus the ice temperature in K.

dependence of $\Delta T(\infty)$ shown in Figure 5, we have used experimental data on the heat capacity of ice for temperatures above 25 K published by Haida et al.¹⁸

Notice that at $E = 10^7$ V/m, the configuration vector in eq 17 would only be equal to 1% of the configuration vector of a fully polarized ice structure, $\sim 1.3 \times 10^{19} \text{ m}^{-2}$ (see eq 23 below). Thus, our use of only the first two terms of the expansion of eq 2 appears justified.

As seen in eq 16, the only case when non-Joule heating is absent is the so-called ice conductivity crossover

$$\frac{\sigma_1 + \sigma_2}{e_1} \approx \frac{\sigma_3 + \sigma_4}{e_3} \quad (22)$$

In all other cases, when the configuration vector results from an electric current, the magnitudes of non-Joule and Joule heat generation are comparable but may have opposite signs.

A very different relation between the Joule and non-Joule heat generation rates occurs when a very large configuration vector appears near an ice/solid interface as a result of specific boundary conditions. For instance, the condition of eq 9 can be easily satisfied near an ice/metal interface, where ordering in the proton subsystem can reach a very significant magnitude. One reason for the strong lattice polarization of ice near an ice/metal interface is that the concentration of electrically charged point defects can be much higher in the vicinity of a metal. The point defects moving from an ice bulk to the interface can then strongly polarize the ice structure according to the following equation

$$\vec{\Omega} = \frac{\sqrt{3}}{4a^2}(f_1 - f_2 - f_3 + f_4) \vec{n} \quad (23)$$

where f_i are the defects numbers per one surface molecule and \vec{n} is the unit vector normal to the surface of ice and pointing outward. As was shown in ref 16, a surface concentration of defects can approach 1. For instance, $f_1 = 1$ sets a maximum possible polarization in the $[1,1,1]$ direction. If, under these conditions, a weak electric field of appropriate polarity is applied, the net heating effect predicted by eq 7 is almost entirely determined by the second negative term on the right side of the equation, that is, $\dot{S}_n < 0$ (cooling). If the polarity is reversed, the effect becomes positive at a level significantly greater than the Joule heating. This shows that the heating by a weak electric field applied to an ice/metal interface depends strongly on its polarity.

In conclusion, let us estimate the maximum possible heating of ice due to the change of the configuration entropy. From eq 23, one can find that $\Omega_{\max} = 3^{1/2}/4a^2$, and the maximum changes of entropy and temperature are

$$\begin{aligned} \Delta S_{\max} &= \frac{\Phi}{2T} \cdot \frac{3}{16a^4} \\ &= \frac{\sqrt{3}k_B}{4a^3} \Rightarrow \Delta T_{\max} = \frac{\sqrt{3}k_B T}{4a^3 C_{\text{ice}} \rho_{\text{ice}}} \approx 40 \text{ K} \end{aligned} \quad (24)$$

This estimate is based on the largest possible preliminary ordering configuration vector. However, even if Ω_{\max} is reduced by a factor of 3 or 4, the temperature rise may still be significant, but very short-lived, because of heat diffusion to the ice bulk and to the metal electrodes. We can easily estimate that heat-dissipation time, t_{diff} assuming that the thickness of the heated layer is of the same order of magnitude as the Debye screening length in ice, l_D

$$t_{\text{diff}} = \frac{l_D^2}{\alpha} \quad (25)$$

where α is ice thermal diffusivity coefficient:

$$\alpha = \frac{k_{\text{ice}}}{C_{\text{ice}} \cdot \rho_{\text{ice}}} \quad (26)$$

where $k_{\text{ice}} = 2$ (W/K·m) is a thermal conductivity of ice.¹ For a typical range of $10^{-9} \text{ m} < l_D < 10^{-6} \text{ m}$, we will arrive at the range of heat-dissipation time of $7.5 \times 10^{-13} \text{ s} < t_{\text{diff}} < 7.5 \times 10^{-7} \text{ s}$. Because that time is much shorter than the time of electric heating (Debye relaxation time τ_D), we can conclude that the large ice heating predicted by eq 24 is unlikely to be observed. Instead, interfacial ice layers will always be in thermal equilibrium with the ice bulk and the metal.

CONCLUSIONS

We showed that, due to the changes that direct electric current induces in the configuration entropy of ordinary ice, electric heating of ice usually differs greatly from Joule heating. Similar non-Joule heating should also occur in other materials where partial ordering/disordering can be caused by an electric current.

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