SHORT NOTES

METAMORPHISM OF AIR BUBBLES IN A SNOW CRYSTAL

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Abstract. Observations have been made of the modification produced by a temperature gradient in the shape of air bubbles in natural snow crystals, and also of the shrinkage of the bubbles with time. The rate of shrinkage is governed by a constant which is strongly temperature dependent with an activation energy of about 15·1 kcal./mole, a value sufficiently similar to the activation energy for diffusion of tritium, dielectric relaxation and mechanical relaxation to suggest that atomic diffusion processes may be responsible for all of these phenomena.

Résumé. *Métamorphisme des bulles d'air dans un cristal de neige.* Des observations ont été faites de la modification de la forme des bulles d'air produit par un gradient de température dans des cristaux de neige naturelle, et aussi du rétrécissement des bulles avec le temps. La vitesse de rétrécissement est gouvernée par une constante dépendant fortement de la température avec une énergie d'activation d'environ 15,1 kcal/mole, valeur suffisamment similaire à l'énergie d'activation de la diffusion du tritium, de la relaxation diélectrique et mécanique pour suggérer que les processus de diffusion atomique pourraient être responsables de tous ces phénomènes.

Zusammenfassung. *Veränderungen von Luftblasen in einem Schneekristall.* Die Formänderung von Luftblasen in natürlichen Schneekristallen, hervorgerufen durch ein Temperaturgefälle, sowie die zeitliche Schrumpfung der Blasen wurden beobachtet. Die Schrumpfgeschwindigkeit wird von einem Parameter gesteuert, der stark temperaturabhängig ist, mit einer Atkivierungsenergie von ca. 15·1 kcal/Mol. Dieser Wert ist der Aktivierungsenergie für Tritium-Diffusion, dielektrische Relaxation und mechanische Relaxation so ähnlich, dass die Annahme gerechtfertigt erscheint, atomare Diffusionsvorgänge seien für alle diese Erscheinungen verantwortlich.

Natural snow crystals contain a number of tiny air bubbles oriented in the $<11\bar{2}0>$ or $<10\bar{1}0>$ directions. The existence of air bubbles or gas enclosures in snow crystals has been noticed by Bentley and Humphreys (1931), but no detailed observation has been made. Recently, Maeno and Kuroiwa (1966) observed carefully the metamorphism of the air bubbles in snow crystals and found some interesting phenomena.

Figure 1a shows a typical snow crystal containing air bubbles symmetrically distributed in the $<11\bar{2}0>$ directions. This snow crystal was placed on a slide glass and allowed to sublime at $-6°$ C. The sublimation occurred heterogeneously as shown in Figure 1b; it was faster in the left part of the crystal than the right. Therefore, the left part should be colder than the right, because more heat of sublimation would have been released at the left. The difference in the rate of sublimation thus produces a thermal gradient through the crystal as indicated by the arrow. The modification in the shape of the air bubbles can be seen in Figure 1b. Hexagonal crystal faces were revealed on their warmer sides while their colder sides were still rounded. This phenomenon is very similar to the metamorphism of vapour figures investigated by Nakaya (1956), though vapour figures are different from air bubbles in snow crystals. Vapour figures in a single crystal of ice produced by internal melting can be considered to be vacuum voids containing only water vapour, while air bubbles in a snow crystal may be filled with the atmospheric air appropriate to the high altitude where the snow crystal grew.

In order to observe the rate of shrinkage of the air bubbles, a snow crystal was soaked in ice-saturated kerosene to keep it from sublimation. For this purpose, a brass plate with a hole (1 cm. in diameter) in its centre was used. A cover glass was attached to the base of this hole and the periphery of the hole was sealed completely with ice, then the hole was filled with kerosene. After a snow crystal had been immersed in the kerosene, the hole was covered with another cover glass and tightly sealed with ice so that the kerosene could be kept saturated with water vapour in respect to ice. Figure 2a shows a snow crystal after 57 hr. immersion. At this stage the complicated structures on the surface have vanished and only the air bubbles are seen to be distributed in $<11\bar{2}0>$ directions. Figure 2b is the same crystal which has been kept for another 390 hr. As seen in this picture, most of the air bubbles tended to spheres and shrunk in size. Some tiny air bubbles (a few microns in diameter) disappeared.

The disappearance and shrinkage of small air bubbles in a snow crystal may suggest the dissolution

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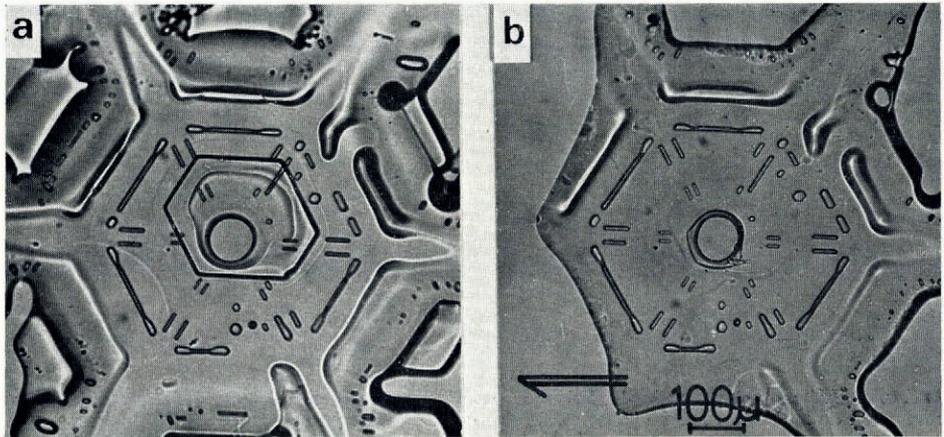
Fig. 1. *Metamorphism of air bubbles under a thermal gradient. A snow crystal (a) sublimed heterogeneously at −6° C. to result in a thermal gradient (indicated by an arrow in b) after about 10 min.*
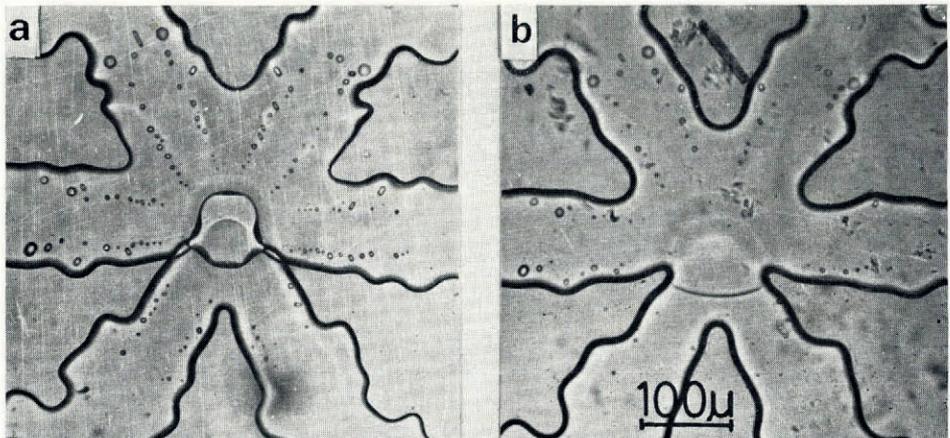
Fig. 2. *Metamorphism of air bubbles in an isothermal condition. The photographs show a snow crystal which has been kept in kerosene at −5° C. for 57 hr. (a) and 447 hr. (b)*

of molecules from the air into ice. The dissolution into ice seems quite likely because the existence of air in ice crystals has been confirmed by many chemical analyses and we often observed the appearance of tiny air bubbles from a snow crystal or ice block melting in kerosene under a microscope. The essential point to note is that the lattice configuration of ice crystal is very spacious.

The rate of shrinkage of air bubbles in snow crystals was measured at the temperatures, −5° C., −15° C. and −34° C. The time dependence of the shrinkage could be expressed by the formula;

$$r - r_\infty = (r_0 - r_\infty) \exp(-\lambda t)$$

where, r_0 and r_∞ are the initial and final diameters of the air bubble, t is time and λ is a constant. The constant λ was strongly temperature dependent. Figure 3 shows the relation between $\log \lambda$ and reciprocal of absolute temperature. Though the observed data are fairly scattered around a straight line, A–A, the temperature dependence of λ may be expressed by $\lambda = \lambda_0 \exp(-E/RT)$, where E is the activation energy, R the gas constant, and λ_0 a constant. The activation energy E can be calculated roughly as $15 \cdot 1$ kcal./mole from the slope of the line A–A.

The shrinkage of air bubbles in snow crystals can be also explained in the same manner as that of

voids in metals. If we assume an existence of molecular vacancies in crystal lattices of ice, their concentration may be increased in the vicinity of a small air bubble in proportion to its curvature. These vacancies may diffuse towards the regions of lower concentration and at the same time result in mass transport in the opposite direction to shrink the air bubble. The precise behaviour of such defects in ice crystals have not been understood well, but they may play an important role in diffusion processes.

The obtained value of the activation energy is roughly similar to those for the diffusion of tritium ($13 \cdot 5 \pm 1 \cdot 1$ kcal./mole, Dengel and Riehl, 1963), dielectric relaxation ($13 \cdot 25$ kcal./mole, Auty and Cole, 1952) and mechanical relaxation ($13 \cdot 1$ kcal./mole, Kuroiwa, 1965). The similarity of the activation energies suggests that the atomic diffusion process may be responsible for the shrinkage of air bubbles and relaxation phenomena.
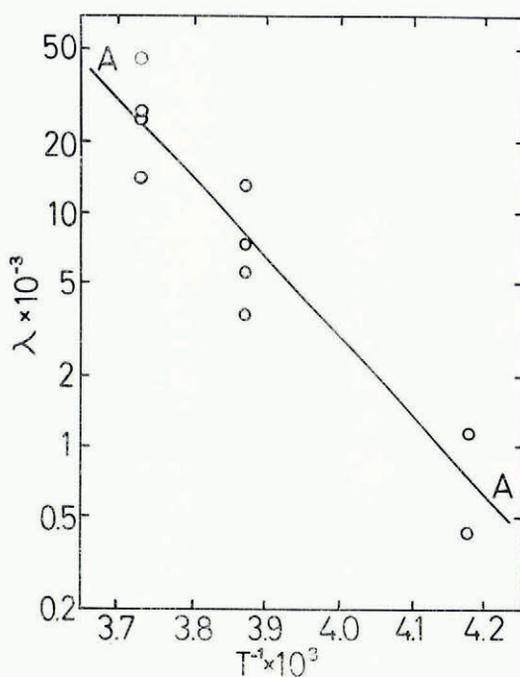
Fig. 3. *Logarithm of λ versus reciprocal of absolute temperature*

The shrinkage of vapour figures in a single ice crystal under isothermal conditions was observed by Nakaya (1956). He found that the rate of shrinkage of vapour figures was represented by an exponential function of time. The exponential factor, k, was also strongly temperature dependent. If we assume $k = k_0 \exp(-Q/RT)$, and calculate the activation energy, Q, from his data, we obtain $Q \simeq 10 \cdot 23$ kcal./mole. From the similarity between temperature dependence of k and the saturation vapour pressure of ice, he concluded that the metamorphism of vapour figures may be made through vapour phase. He assumed that the total volume of the vapour figure was constant during the metamorphism, but in our case the shrinkage and disappearance of small air bubbles occurred.

The derivation of activation energy from the shrinkage of air bubbles seems to be somewhat crude in this case. More elaborate experiments are under way and the results will be published in the future.

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