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THE EFFECT OF DISLOCATIONS ON THE VAPORIZATION RATE OF NaCl SINGLE CRYSTALS

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December, 1967

The Effect of Dislocations on the Vaporization Rate of NaCl Single Crystals

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We have observed that an increase in the dislocation density[1] of NaCl single crystals increases the steady state vaporization rate of the (100) face into vacuum. This behavior has been postulated by several theoretical papers.[2,3] Dislocations are known to cause transient rate of evaporation[4] during the initial period of vaporization. This is the first report, to our knowledge, of dislocations controlling the steady state vaporization rate from a solid surface. Crystals with etch pit densities greater than about $1 \times 10^7/cm^2$ had vaporization rates, J_{exp}, equal to the maximum thermodynamic rate, J_{ther}

$$J_{exp} \cong J_{ther} = P_{eq}(2 \Pi mkT)^{-1/2}$$

within experimental error (±5%) in the temperature range 770-900°K. Crystals with lower etch pit densities ($\sim 1 \times 10^6/cm^2$) had evaporation rates lower by a factor of 2 to 2.5.

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Sodium chloride vaporizes according to the dominant reaction, $NaCl(solid) \rightarrow (1-X)\ NaCl(vapor) + X/2\ Na_2Cl_2(vapor)$. In the temperature range of our investigation the dimer concentration is roughly 5-30 mole % of the total vapor concentration and increases with increasing temperature. Mass spectrometric studies which have been carried out simultaneously indicate that the vapor composition (monomer-dimer ratio) over the different dislocation density samples remains virtually unchanged at a given temperature. The single crystals of the highest commercially available purity were obtained from Harshaw Chemical Co.[5] All of the crystals used were from the same lot, and had almost identical impurity concentrations. When desired, dislocations were introduced by compressively straining a crystal into the plastic flow region. Samples for the vaporization experiments were cleaved from the deformed or from the unstrained crystals and etch pit counts made on the mirror image cleavage face of the vaporizing crystal surface. Previous investigations had found a one to one correspondence of etch pits on mating surfaces.[6] This eliminated the possibility of Hg^{++} contamination of the vaporizing surface by the etching solution. Etch pits were also counted on the sample after vaporization. A slight decrease ($\sim \div 2$) in etch pit density was noticed in the most highly strained samples after vaporization ($1.5 \times 10^7\ cm^{-2}$). The average of the two counts (before and after evaporation) was used as the characteristic dislocation density value during vaporization. The sample was tightly wrapped with Pt foil so that only one crystal face was exposed. Vaporization rates were measured with a quartz microbalance at a residual pressure of $\sim 10^{-7}$ torr.

The evaporation rates of the (100) face of low and high dislocation density sodium chloride crystals are given in Figure 1. The equilibrium data are those of Zimm and Mayer,[7] corrected for the dimer concentration as given by Miller and Kusch.[8] By using only crystals from one lot and preparing all samples by identical procedures (except for straining) we have sought to eliminate all causes for the rate change except a change in the dislocation density. We have been unable to obtain crystals with etch pit densities below $\sim 5 \times 10^5/cm^2$, thus the range of dislocation densities over which we have data is, at present, limited. Further experiments are in progress in an attempt to extend the range of dislocation densities and to develop a quantitative relationship between the evaporation rate and the dislocation density.

The introduction of chloride ion or sodium ion vacancies in excess of their equilibrium concentrations, had no effect on the vacuum evaporation rates. These point defects diffuse out of the crystal rapidly at the evaporation temperatures. The surface becomes roughened during vaporization.

Computations indicate[9] that the mean free path of neutral molecules on alkali halide surfaces is, at most, a few lattice spacings before they desorb into vacuum. Thus, steady state ledge concentration at the vaporizing surface can be different for crystals with low dislocation densities ($\leqslant 10^6$ cm^{-2}) from that for high dislocation density ($\sim 10^7$ cm^{-2}) samples.

The results of these experiments certainly indicate that dislocations may have a pronounced effect on the vaporization rates of many solids into vacuum and should be given more attention in the preparation and characterization of samples. It is likely that other ionic crystals especially among the alkali halides will show similar dislocation controlled vaporization kinetics.

Acknowledgment. This work was performed under the auspices of the United States Atomic Energy Commission.

Footnotes and References

(1) The chemical etch pit density on a (100) face surface was used as a measure of the dislocation density. A direct proportion between etch pits and dislocations terminating at the surface was assumed. Etching was performed using $HgCl_2$ in absolute ethanol as the etchant, per D. Krasnopolsky and A. Grinberg, Czech. J. Phys., 11, 609-10 (1961).

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(5) Chemical analysis of a typical sample showed only Cr, 4 ppm; K, 20 ppm; Li, 15; Br, 200 ppm; and O, 400 ppm at detectable levels above 1 ppm.

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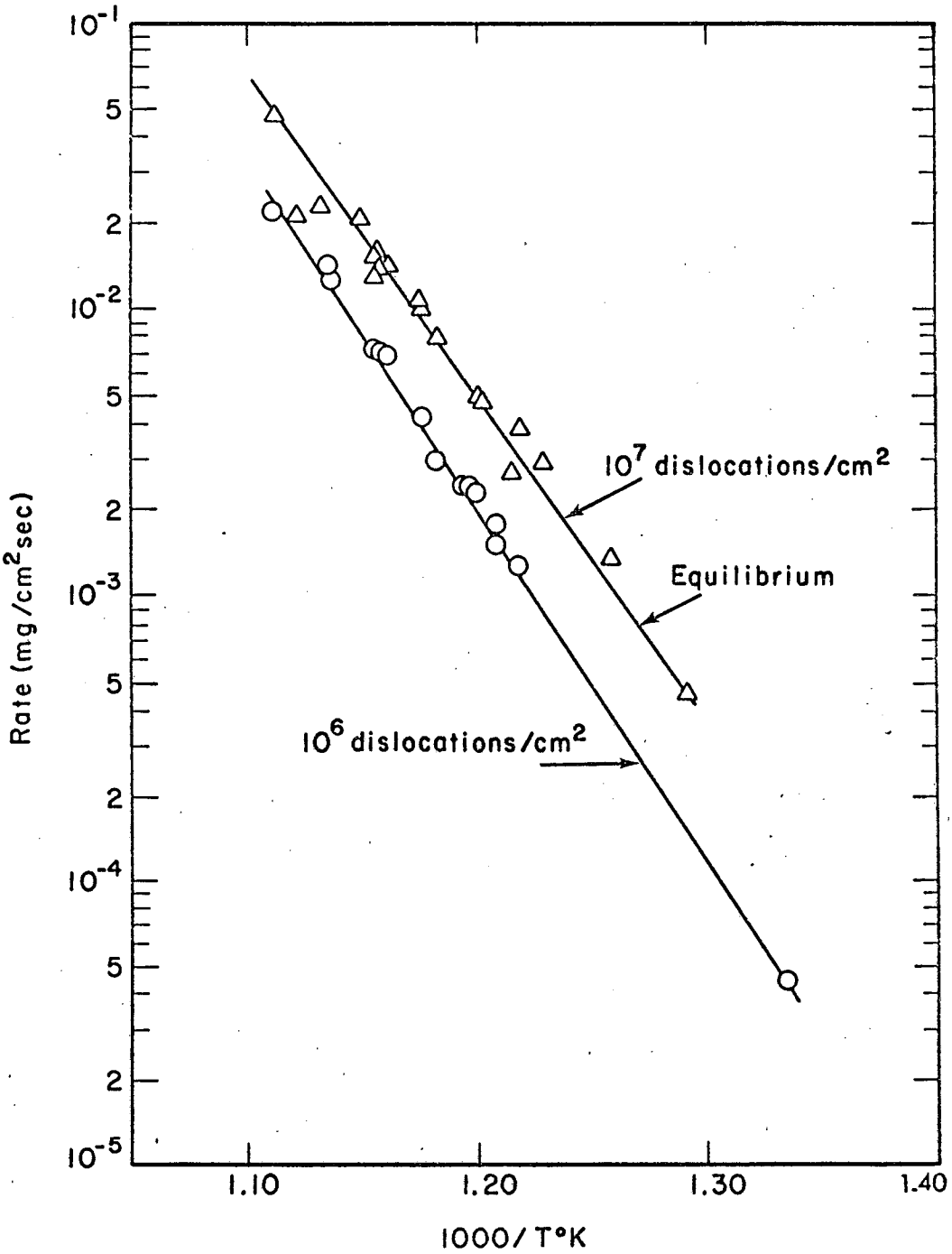

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Fig. 1 Vaporization rates of NaCl crystals with different dislocation densities. Etch pit densities are O, 1×10^6; Δ, 1×10^7.

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