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ABSTRACT

The temperature dependence of the activation enthalpy (ΔH) with temperature is compared for LiF and MgO. The non linearity in ΔH vs T plot for MgO can be corrected by taking into account contributions from long range internal stresses in the temperature range 77 - 300°K. This correction gives a linear temperature dependence of activation enthalpy for MgO in agreement with the observed behaviour of LiF.

INTRODUCTION

Thermally activated deformation in solids is usually expressed by the relation

$$\dot{\epsilon} = \dot{\epsilon}_o \exp\left(-\frac{\Delta G}{KT}\right) \tag{1}$$

where $\dot{\epsilon}$ is the deformation rate, $\dot{\epsilon}_o$ the pre exponential factor which is unique for a particular deformation mechanism, and ΔG the change in the Gibbs free energy of activation for overcoming a local obstacle by a dislocation in motion.

The laws of thermodynamics give

$$\Delta H = \Delta G + T\Delta S \tag{2}$$

where ΔH is the change in activation enthalpy and ΔS is the change in entropy. Both ΔG and ΔH can be determined experimentally using strain rate cycling techniques[1-3]. If there is no entropy contribution to the deformation process ($\Delta S = 0$) then eqn (1) can be written as

$$\dot{\epsilon} = \dot{\epsilon}_o \exp\left(-\frac{\Delta H}{KT}\right) \tag{3}$$

A linear ΔH vs T plot indicates that $\dot{\epsilon}_o$ is constant and that deformation is governed by a single rate controlling mechanism[4,5]. If, however, ΔH vs T plot exhibits deviations from linearity, this is attributed to the possible effects of a non zero entropy term in eqn (2), assuming $\dot{\epsilon}_o$ to be constant.

Entropy effects have recently been invoked to explain the observed non linearity in the ΔH vs T plot for MgO single crystals[6,7]. In this paper, the results of a thermally activated deformation study of high purity LiF single crystals are compared with those in MgO. It is shown that non linearity in ΔH vs T plot for MgO can also arise due to the contributions of finite long range internal stresses at higher temperature[8,9].

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RESULTS AND DISCUSSION

An experimental ΔH vs T plot for LiF single crystals is given in Figure 1 showing a linear dependence of activation enthalpy (ΔH) with temperature. Figure 2 shows the replotted[6, 7] ΔH vs T data for MgO single crystals showing a positive curvature above 200 K.

These results indicate that entropy contributions are important in the thermally activated deformation of MgO above 200 K whereas LiF remains relatively unaffected by entropy changes. This difference is surprising because both LiF and MgO are NaCl structure ionic crystals with $\{110\}\langle 1\bar{1}0\rangle$ type slip systems and which in general have similar deformation characteristics[10]. According to Cagnon[2] the most important source of entropy effects in crystal deformation arises from changes in atomic vibrational spectra with temperature, all other contributions to entropy changes being negligible. This is manifested in the variation of shear modulus (μ) with temperature. Comparing $\Delta\mu$ for MgO and LiF in the temperature range 77 - 473 K, it is seen that $\Delta\mu$ is about 9% for MgO and 20% for LiF. Furthermore, the melting point of MgO is 3123 K and of LiF is 1123 K. These observations suggest that entropy effects should be more important in LiF than in MgO, which is contrary to the experimental results under discussion. Cagnon has, however, observed a non-linear ΔH - T plot for irradiated LiF and has attributed it to entropy effects. However, since his results are on irradiated specimens, comparisons with the present work are not justified. Further, Guiu and Langdon[11] have recently reported a linear temperature dependence of activation enthalpy for LiF single crystals of varying impurity content in agreement with the present results.

In MgO the deviation from linearity in the ΔH - T plot can be explained if it is considered that more than one thermally activated deformation mechanism is probably operative in the temperature range 77 - 473 K. Possible mechanisms could include dislocation-vacancy and dislocation-impurity-vacancy dipole interactions, which are easily overcome by thermal energy[12]. Other mechanisms could be due to dislocation-dislocation dipole or multipole interactions such that the effect is equivalent to a non-vanishing periodic internal stress (τ_μ) with a dislocation defect spacing such that it cannot be surmounted by thermal energy[8]. In ionic crystals, the density of dislocation dipoles or multipoles increases with increasing temperature due to the relative ease of the multiple cross-glide of screw dislocations, providing the bulk of the internal stress[13].

The contribution of τ_μ to deformation in MgO can be estimated using the method of Arsenault and Li[8]. Taking $m = 55$ at room temperature[14] and $\frac{\tau_\mu}{\tau} = 0.30$ where τ = applied stress, one can obtain $\Delta H_a^{Expt} - \Delta H = .07$ ev where ΔH_a^{Expt} is the aparent activation enthalpy and ΔH is the activation enthalpy if $\tau_\mu = 0$. This gives a corrected $\Delta H = 0.97$ ev at room temperature, so that a linear ΔH - T plot can be obtained for MgO in the temperature range 77 - 300 K. Arsenault and Li[8] and Arsenault[9] have used similar arguments to account for the effects of internal stress fields in thermally activated deformation of irradiated LiF and neutron irradiated copper, respectively.

Below 300 K, $\frac{\tau_\mu}{\tau}$ decreases with decreasing temperature so that applied correction is negligible. At higher temperatures on the other hand because of the lack of data, no correction is invoked. In any case at higher temperature curvature can arise in ΔH vs T plot due to the increase in pre-exponential factor in equation(3)[7].

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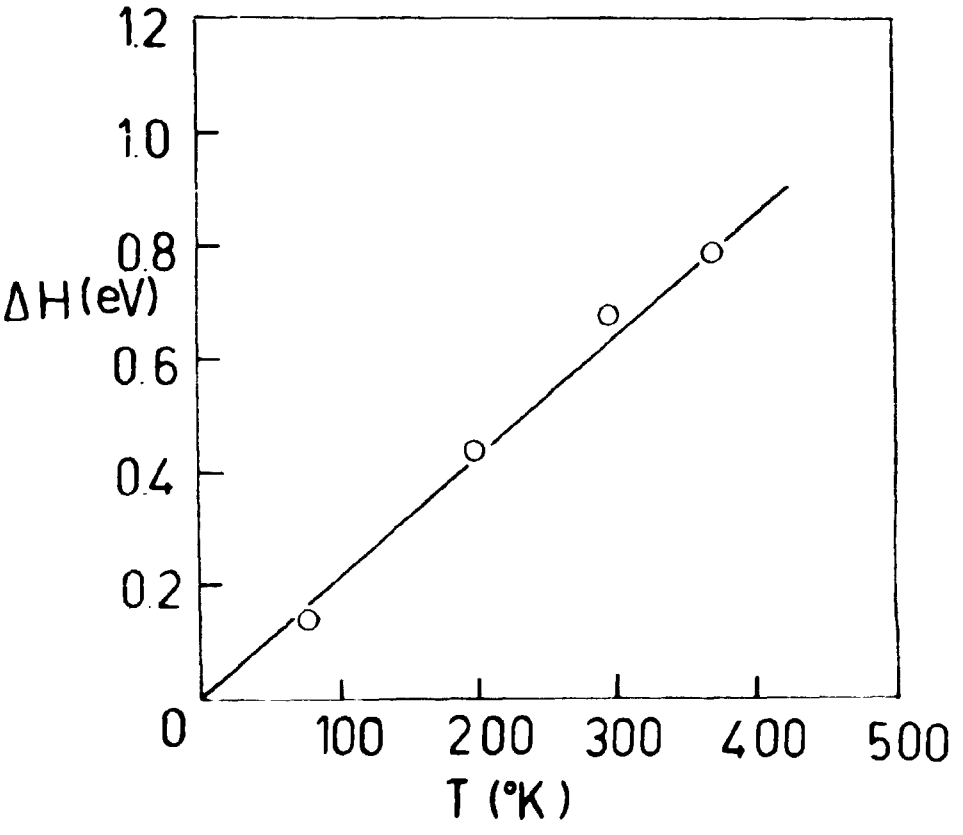

Figure 1 – Variation of activation enthalpy with temperature in LiF

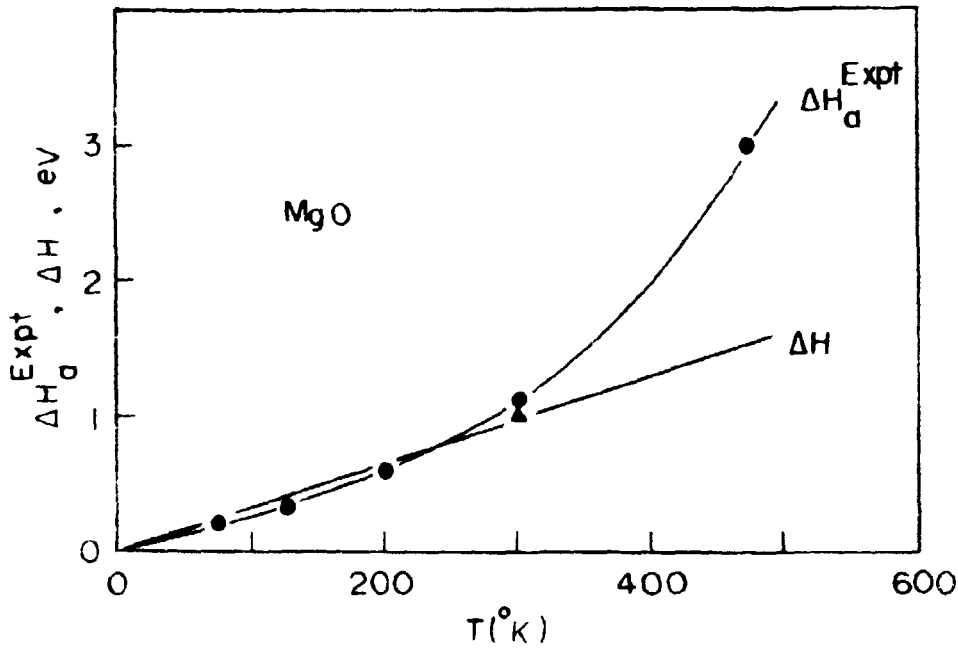

Figure 2 - Variation of activation enthalpies with temperature in MgO from refs 6,7 Observed values given by ( ), corrected value at room temperature by ( ) (See text)

RESUMO

A dependência na temperatura da entalpia da ativação (ΔH) é comparada para o LiF e MgO. A não linearidade do gráfico ΔH vs T para MgO pode ser corrigida levando em conta as tensões internas de longo alcance no intervalo de temperatura de 77 - 300°K. Esta correção resulta em uma dependência linear da entalpia de ativação na temperatura no MgO em concordância com o comportamento observado para o LiF.

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