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VACUUM VAPORIZATION STUDIES OF LITHIUM FLUORIDE SINGLE CRYSTALS

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ABSTRACT

The vacuum sublimation kinetics of the (100) face of lithium fluoride single crystals are investigated in the temperature range of 690°C to 820°C by means of a microbalance. Pure LiF sublimes at about 1/6 of the calculated maximum rate. It has an activation enthalpy of sublimation of 66.7 kcal/mole that is equal to the equilibrium enthalpy of sublimation (ΔH_s = 66.3 kcal/mole). The dependence of the sublimation rates on cation impurities (Ca^{2+} and Al^{3+}) that were incorporated in the LiF single crystals is studied. Calcium-doped samples have lower sublimation rates and aluminum-doped samples have higher sublimation rates than the sublimation rates of pure LiF crystals. The sublimation rates are independent of the dislocation density in the various sublimed crystals. The results of this study when combined with the sublimation kinetics studies of other alkali halides (NaCl, KCl) show that surface non-stoichiometry rather than ion diffusion is the rate controlling process of the sublimation.

INTRODUCTION

Alkali halides represent an important group of ionic crystals. They have cubic structures and have melting points in the range of 988°C for NaF to 450°C for LiI. Monomer and dimer molecules are the vapor species formed when NaCl and KCl sublime. LiF has an appreciable (~4 mole%) trimer concentration in the vapor phase in addition to the monomer and dimer concentrations.[1]

The sublimation kinetics of NaCl have been studied[2] in order to reveal the mechanism by which ion pairs break away at the subliming surface. The activation enthalpies of sublimation have been determined and correlations between the sublimation rate and both the divalent cation impurity concentration and the concentration of dislocations in NaCl crystals have been established. In order to further elucidate the sublimation mechanism of alkali halides and to verify whether the sublimation characteristics of other alkali halides are similar to that of NaCl the sublimation kinetics of LiF single crystals have been investigated. We have measured the vacuum sublimation rate of the (100) crystal face of LiF as a function of temperature. We have also studied the sublimation rate as a function of impurities in the crystal lattice (Ca^{2+} and Al^{3+}) and the effect of dislocation density on the sublimation rates.

EXPERIMENTAL

The samples used in this study were pure and impurity-doped lithium fluoride single crystals. The pure, and the calcium- and aluminum-doped lithium fluoride crystals were obtained from the Harshaw Chemical Corp.

Studies of the vacuum sublimation of other alkali halides indicate marked effects of small amounts of selected impurities on the sublimation characteristics.[2] The results of spectroscopic analyses of the pure and doped LiF crystals are given in Table 1. Analysis was made only for possible cation impurities. Other work on alkali halides has shown that monovalent anion impurities at various concentration levels had no effect on the sublimation rate.[3] Although the accuracy of the analysis is ±30%, this was judged to be satisfactory, since previous alkali halide studies showed detectable changes in the sublimation rate only with order of magnitude changes in impurity concentration.[2]

Lithium fluoride was obtained as large single crystals and these were cleaved to prepare the samples for sublimation. The samples used in sublimation runs were about 2 x 3 x 5 mm.

In order to clean the crystal of oil films and possible chemical contamination each lithium fluoride sample was rinsed in a 90% methanol, 10% water solution. The sample crystal to be sublimed was then wrapped in a non-reactive (3 mil Pt) metal foil leaving only the face to be sublimed exposed.

A correlation between sublimation rate and dislocation density has been found in studies of the vacuum sublimation of sodium chloride. In order to measure the dislocation density of lithium fluoride an etching

solution, consisting of equal parts concentrated hydrofluoric acid and glacial acetic acid and a one volume percent of concentrated HF saturated with $FeCl_3$, was used that specifically developes dislocations as square etch pits.[4] This etchant brings out all of the different types of dislocations equally well regardless of crystal history. The dislocation etch pits were counted before and after the sublimation. Etch pit counts were made using a Zeiss Metalograph. The crystal faces did not have a uniform distribution of etch pits, rather there were regions of large and small etch pit densities. The average value of the etch pit densities could, however, be calculated. A detailed description of the vacuum and microbalance systems are found elsewhere.[3]

The background pressure was kept much lower than the apparent pressure from the subliming sample ($p = 7.4 \times 10^{-4}$ torr) by at least a factor of a hundred ($\sim 10^{-6}$ torr) so that molecules, reactive or nonreactive, in the ambient would rarely impinge on the subliming surface. The capacity of the balance[3] is 1 gram and weight changes as small as 1μg have been detected. In determining rate through weight loss per time measurements, the balance was used as a null device. A set of wire calibration weights were used to determine the balance's sensitivity. The sensitivity for the balance was about 13.5 millivolts per milligram.

Oven calibration to determine temperature gradients was carried out and similar results to previous studies[3] were obtained. After a constant temperature was attained in the hot zone the sample was lowered into the oven and hooked to the balance. Weight loss measurements were then taken.

The sublimation runs at the slowest rates took about seven hours (Rate = 3×10^{-2} mg min^{-1} cm^{-2}), and at the fastest about twenty minutes (Rate = 7×10^{-1} mg min^{-1} cm^{-2}).

The measurements carried out using the vacuum microbalance give the absolute weight loss of a sublimating crystal as a function of time. This weight loss is normalized by dividing the rate of weight loss by the geometrical surface area of the subliming crystal face. The rate of weight loss, R_s (mg cm^{-2} min^{-1}) is then plotted as the logarithm of R_s versus the reciprocal temperature, 1/T°K. This plot gives a straight line where the slope yields the activation enthalpy of sublimation, ΔH_s^*.

Experiments in this study utilized three crystal samples from each of the pure, calcium- and aluminum-doped LiF single crystals being used in the sublimation runs. Results reported for the evaporation rates of each type of crystal are the average of those sublimed.

RESULTS

A plot of the vacuum sublimation rate, log R_s, versus 1/T(°K) for pure LiF (undoped) is shown in Fig. 1 along with a curve of the logarithm of the maximum sublimation rate for LiF for comparison. The maximum sublimation rate curve was calculated from the equilibrium vapor pressure data of Pugh and Barrow[5] and the kinetic theory using the formula $R_{max} = P(2\pi mRT)^{-\frac{1}{2}}$ where T is the absolute temperature, R is the gas constant, and m is the molecular weight of the subliming species taken as the weighted average of the various LiF vapor molecules. The weighting factors were obtained from the work of Eisenstadt, Rothberg and Kusch.[1]

The vacuum sublimation rate as a function of temperature for LiF crystals that were doped with 250 ppm calcium is plotted in Figure 2.

LiF-AlF_3 mixed crystals were from a 0.15 mole % Al-doped parent crystal. Plots of the vacuum sublimation rates as a function of temperature for the LiF-AlF_3 mixed crystals is shown in Fig. 1. Since, unlike the other crystals some of these samples gave different rates there are two curves shown in Fig. 1. We believe that the changing sublimation rate from sample to sample reflects the variation of the aluminum concentration from sample to sample.

In other studies of alkali halide vacuum sublimation the etch pit density at the subliming face was found to influence the rate (i.e., the NaCl sublimation rate increased with increase in etch pit density). Unlike for NaCl the etch pit density for LiF was found to decrease during an experimental run. The etch pit density decreased from 1 - 5 x 10^7 per cm^2 to 1-6 x 10^6 per cm^2. The sublimation rates could be reproduced for all of the LiF crystals regardless of their initial dislocation density, indicating that the dislocation density had adjusted to a constant level shortly after the sublimation experiment commenced. Thus, the variation of the dislocation density in the different samples had no effect on the sublimation rates.

The activation enthalpy of sublimation, ΔH_s^*, was calculated for each crystal from the experiment. These activation enthalpies are given in Table 2. It should be noted that absolute weight loss measurements determine an average activation enthalpy (per mole of vapor) for the combined vapor flux (monomers, dimers and trimers).

DISCUSSION

The sublimation characteristics of lithium fluoride single crystals are summarized by the following statements.

1. The vacuum sublimation rates of the (100) crystal faces of high purity lithium fluoride were lower by about a factor of six ($\alpha_s(730°C)$ = 0.17) than the vacuum sublimation rates that can be calculated using the equilibrium vapor pressure data.[5] The average activation enthalpy of sublimation (i.e., the weighted average of monomer, dimer, and trimer activation enthalpies) determined by the microbalance studies is ΔH_s^* = 66.7 kcal/mole. This is comparable to the equilibrium enthalpy of sublimation, ΔH_s = 66.3 kcal/mole.

2. The sublimation rates of Ca-doped (250 ppm) LiF samples is reduced with respect to that of pure LiF crystals ($\alpha_s(730°C)$ = 0.07). The activation enthalpy of sublimation is ΔH_s^* = 62.6 kcal/mole for these doped crystals.

3. High purity LiF crystals that had different dislocation densities (in the range of 10^6 to 10^7 dislocations/cm^2) exhibited identical sublimation rates.

4. LiF-AlF_3 mixed crystals (LiF doped with 0.15 mole% Al) exhibit sublimation rates that are higher than that for undoped samples.

The vacuum sublimation rates of high purity LiF crystals are lower than the maximum rates, similar to the behavior of NaCl and KCl crystals. Also, the activation enthalpies of sublimation are nearly identical to the enthalpies of sublimation for all of these alkali halide crystals. It would appear that the sublimation mechanisms of these ionic compounds should be similar.

Ca-doped LiF and NaCl exhibit lower sublimation rates than that of the undoped crystals. On the other hand, Ca-doped KCl crystals have been found to have higher sublimation rates.[6] Ca-doping introduces cation vacancies in the alkali-halide crystals in addition to the equilibrium concentration of vacancies that are present in the pure crystal. Although the calcium concentration is in the ppm range it has major effect on the rates of sublimation. The calcium concentration in the crystals is too low to block a large fraction of the surface to prevent sublimation and there is no experimental evidence for the accumulation of calcium at the surface. Therefore it appears that calcium ions in the alkali halide crystals influence the sublimation rate by changing the vacancy concentrations at the surface, i.e., the surface stoichiometry.

There is strong evidence from the work of T. E. Gallon, et al.[7] that the chemical composition of different alkali halide crystal surfaces does not reflect the stoichiometry of the bulk phase. Auger Electron Spectroscopy studies of LiF and NaF surfaces freshly cleaved in ultra high vacuum or cleaved in air have detected the presence of much higher intensity Auger peaks due to the halogen than to the alkali metal.[7] Although calibration of the intensity peaks has not been carried out to permit quantitative surface chemical analysis, the data indicates that the halogen atom concentration is higher than the metal atom concentration.

For KCl, on the other hand, Auger Electron Spectroscopy studies showed roughly equal intensity peaks due to potassium and chlorine atoms at the surface. Clearly, as indicated by these studies, the alkali metal concentration was much higher at the KCl surface than at the LiF and NaF

surfaces. Mass-spectrometeric studies[7] have also revealed that upon cleavage the freshly created surface dissociates and alkali metal and halogen vapor atoms are detectable. Dissociation appears to be most marked for LiF and very small in the case of KCl.

These investigations indicate that non-stoichiometry exists exists at the surface of alkali halides.
NaT LiF, NaF, and NaCl (100) surfaces appear to be richer in halogen than in alkali metal atoms, i.e., they are likely to have a larger concentration of cation vacancies than anion vacancies. The introduction of calcium ions into these crystal lattices creates even more cation vacancies and results in an even greater deviation from stoichiometry. Since these ionic crystals sublime as ion pairs (NaCl, Na_2Cl_2, LiF, Li_2F_2, etc.) non-stoichiometry at the subliming surface could readily decrease the sublimation rates. This way, the lowering of the sublimation rates of NaCl and LiF when doped with calcium can be rationalized.

The effect of Ca-doping on the number of cation vacancies in a crystal can also explain the effect of Ca-doping on the sublimation rate of KCl where there was an <u>increase</u> in the sublimation rates obtained.[6] If one assumed that the potassium atom concentration is greater than the chlorine atom concentration at the (100) surface there is then a non-stoichiometry that implies a larger surface concentration of anion vacancies than cation vacancies. For this crystal (i.e., KCl), doping with calcium increases the cation vacancy concentration and improves the stoichiometry. Thus, the sublimation rates increase upon calcium doping of KCl crystals. Based on this model it is expected that the surface concentration of the ions in the minority will control the sublimation rate.

Barr[8] has suggested that the bulk diffusion of more slowly diffusing ions controls the sublimation rate of alkali halides. This suggestion was based on the good agreement found between the activation enthalpies of bulk diffusion of the more slowly diffusing Cl-ion and the activation enthalpy of sublimation for NaCl.[8]

The activation enthalpies of sublimation, the activation enthalpies of anion and cation diffusion, and the energies of forming a vacancy pair for NaCl, KCl, and LiF are listed in Table 3. Barr's model cannot easily explain the opposite effect of calcium doping on the vacuum sublimation rates of LiF and NaCl on the one hand, and KCl on the other since the more slowly diffusing ion is Cl^- in KCl as well. However, this disagreement can be rationalized since Fuller[9] reported that cation diffusion, which is enhanced by Ca-doping, makes an important contribution to the total diffusion flux in KCl and in fact is dominant at low temperatures ($< 500°C$).

Inspection of Table 3 reveals that the average activation enthalpy of LiF sublimation (66.7 kcal/mole) is much higher than the activation enthalpies of either anion (50.6 kcal/mole) or cation (43 kcal/mole) diffusion in LiF. The activation enthalpy of sublimation of the monomer (~62 kcal/mole)[1] is already markedly greater than the activation enthalpies of diffusion for either ion.

Thus Barr's model of ion diffusion as a rate determining step of the sublimation cannot explain the sublimation mechanism of LiF. There must be another step that has a greater energy requirement that controls the rate of sublimation.

Since sublimation involves the formation of ion pairs at the surface that subsequently desorb, the energy of forming a vacancy pair at the surface may also be a rate determining step. From Table 3 one can see that for NaCl the energy of forming a vacancy pair (Schottky defect) is less than the activation enthalpy of anion diffusion. On the other hand, for KCl and LiF the energy of vacancy pair formation is greater than ΔH_D^* (anion). Although the energy of vacancy pair formation of LiF (53.7 kcal/mole) was estimated from low temperature ionic conductivity studies and may be in error, it has to be increased by at least 10 kcal/mole to be of importance in the sublimation mechanism of LiF single crystals.

It appears that the sublimation mechanism of all alkali halides cannot be explained by the simple slow ion diffusion mechanism proposed by Barr.[8] Since sublimation takes place via several consecutive reaction steps that include bulk and surface ion diffusion, bond breaking and desorption, it is not surprising that small changes in the energy requirements of any of these reaction steps can change the rate determining reaction step. It is apparent, however, from our studies and from studies of calcium doped NaCl and KCl crystals that point defects at the crystal surface play an all important role in the sublimation of alkali halides. Minute changes in the ion vacancy concentrations can markedly change the sublimation rate. The non-stoichiometry at the surface that is characteristic of the ionic compound or that is created by the incorporation of impurities seems to control the sublimation rates.

Variation of the dislocation density of LiF apparently has not changed the sublimation rate. Similar insensitivity of the sublimation

rate to changes of dislocation density was found for KCl.[6] On the other hand it was shown that for NaCl the increased concentration of dislocation has increased the sublimation rate. It appears that the annealing rate of excess dislocations that were introduced by stress determines whether high dislocation densities can be maintained at the subliming surface. The annealing rates of excess dislocations are probably more rapid in LiF and KCl crystals than in NaCl.

We have found that the sublimation rate of LiF-AlF_3 mixed crystals is higher than that of pure LiF. The vaporization of LiF changes drastically in the presence of AlF_3, the majority vapor species is $LiAlF_4$ while the presence of Li_2AlF_5 and Li_3AlF_6 molecules also becomes detectable.[12] Thus the mechanism of sublimation of pure and Ca-doped LiF cannot be compared with the sublimation mechanism of these mixed crystals that must follow a different reaction path.

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TABLE 1

Spectroscopic analysis for LiF crystals used in experiments

Crystal Impurity	Pure LiF	Al-doped LiF	Ca-doped LiF
Ag	ND	2	1
Al	25	0.15%	25
B	1	10	1
Ba	50	ND	50
Ca	50	ND	250
Cu	1	2	1
Fe	20	25	20
Mg	22	60	10
Pb	ND	20	ND
Si	100	90	10
Sn	ND	20	ND

All concentrations are in ppm unless otherwise noted.

ND = not detected

TABLE 2

Activation enthalpies of sublimation of the (100) face of pure and doped lithium fluoride single crystals.

Crystal	ΔH_s^* (kcal/mole)
pure LiF	66.7
$LiF-AlF_3$ (1)	80.4
$LiF-AlF_3$ (2)	81.4
Ca-doped LiF	62.6

Enthalpy of sublimation of LiF $\Delta H_s = 66.3$ kcal/mole

TABLE 3

The activation energies of sublimation, ΔH_s^*, anion and cation diffusion, ΔH_D^* anion and ΔH_D^* cation, and the energies of vacancy pair formation ΔE, of NaCl, KCl and LiF.

	ΔH_s^*	ΔH_D^* anion	ΔH_D^* cation	ΔE vacancy pair
NaCl	55 ± 2 (2)	55 (8)	41.4 (8)	45.5 (10)
KCl	47 ± 2 (6)	48.8 (8)	39.9 (8)	53.1 (9)
LiF	66.7 ± 2	50.6 (11)	43 (11)	53.7 (11)

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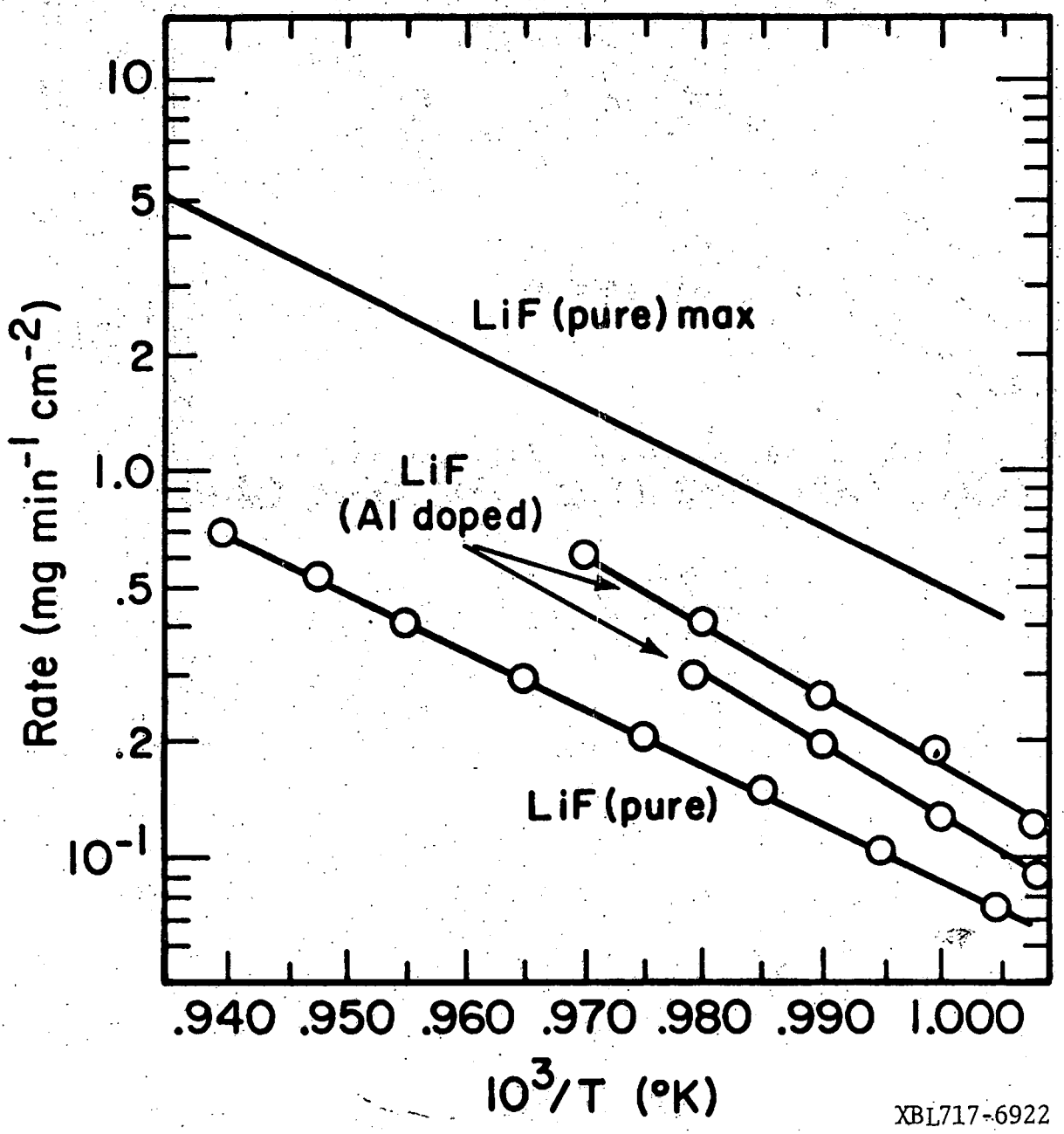

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Fig. 1

Sublimation rates of pure and AlF_3-LiF mixed crystals.

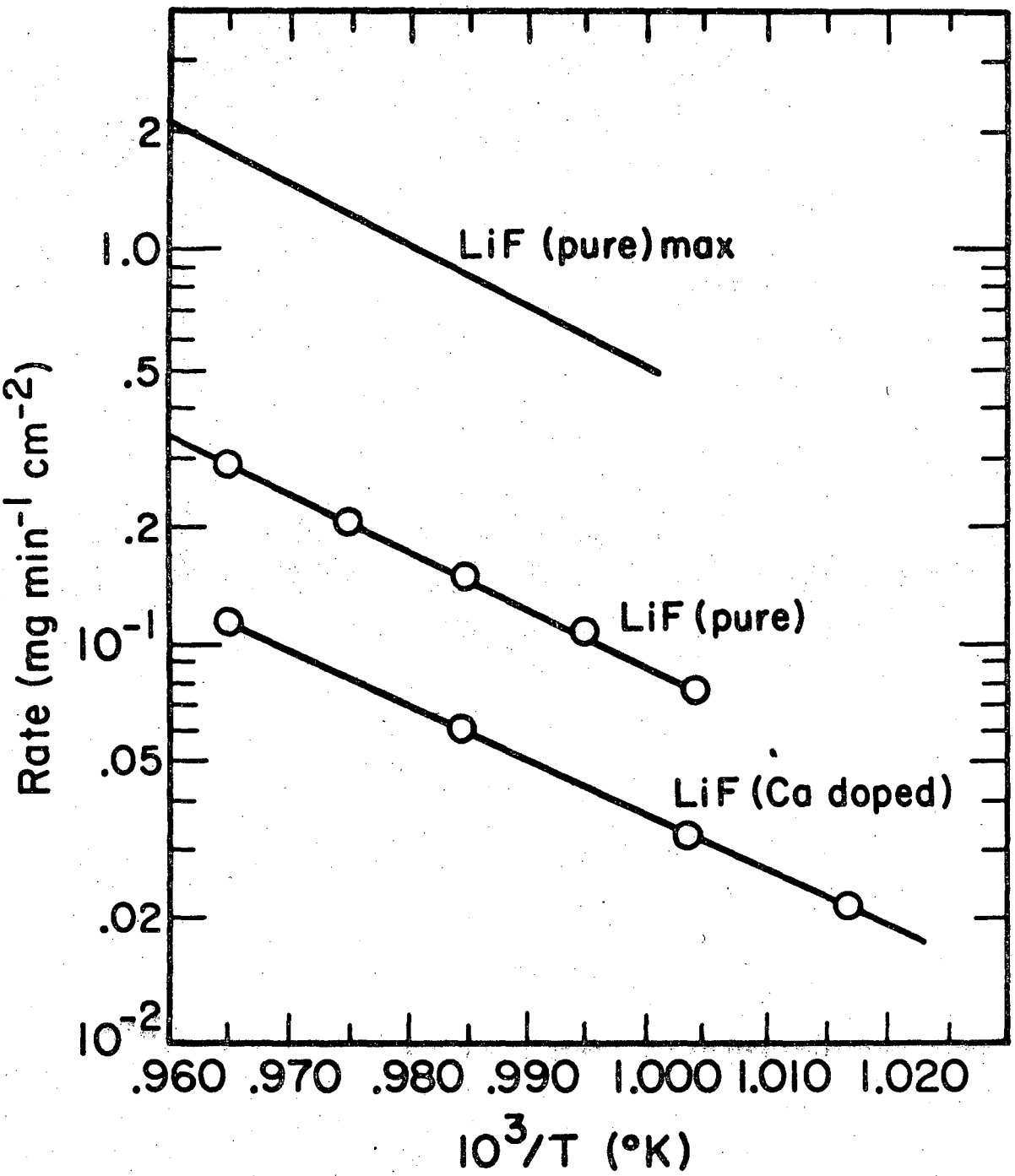

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Fig. 2

Sublimation rates of pure and Ca-doped LiF crystals.

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