

## Diffusivity and neutron scattering study of the Li-defect conversion in $\text{MgF}_2$

J. Toulouse

*Physics Department, Lehigh University, Bethlehem, Pennsylvania 18015*

D. E. Cox

*Physics Department, Brookhaven National Laboratory, Upton, New York 11983*

(Received 6 April 1987)

Lithium in  $\text{MgF}_2$  has been shown to exist in the form of tightly bound pairs below room temperature. By contrast, at high temperatures ( $\geq 900^\circ\text{C}$ ), Li is present mostly as interstitials and diffuses rapidly. In the present study we have attempted to determine the temperature range within which the defect conversion occurs and possible structural reasons for this conversion. We report here diffusivity results for lithium in a single crystal of  $\text{MgF}_2$ , between 650 and 1100°C. The diffusivity,  $D_{\text{Li}}$ , exhibits a change of slope around 800°C for both components, respectively parallel and perpendicular to the  $c$  axis. Isochronal annealings followed by internal-friction measurements also indicate that the Li pairs may extensively dissociate and convert to interstitials above 700°C. In order to investigate possible causes for the Li-defect conversion, we have used neutron powder diffraction to measure the lattice parameter as a function of temperature, and have carried out structure refinements at 20 and 849°C. These measurements show no change in the positional parameters of the fluorine ions and only a small change in lattice parameters between 20 and 849°C, giving no evidence for a lattice disordering in  $\text{MgF}_2$  similar to that in  $\text{CaF}_2$ . On the other hand, a large increase in the vibrational amplitude of the F ions is observed. It is suggested that this increase may well result in a decrease of the Li-pair binding energy, thereby enhancing the dissociation of Li pairs above 700°C and the conversion to interstitials, resulting in the high diffusivity.

### INTRODUCTION

Several systems crystallizing in the cubic fluorite structure ( $\text{PbF}_2, \text{CaF}_2$ ) exhibit a Faraday transition to a "fast-ion" phase at a temperature<sup>1</sup>  $T_c$  several hundred degrees below the melting point  $T_m$ . In the case of  $\text{CaF}_2$ , for example,  $T_c$  and  $T_m$  are respectively 1157 and 1423°C. The appearance of this phase is accompanied by a drastic enhancement in diffusivity and ionic conductivity due to a large increase in the anion mobility.<sup>1</sup> Structurally this high-temperature phase appears to be characterized by the formation of a relatively large concentration of permanent anion Frenkel pairs (interstitial anions and vacancies). Recently an inelastic neutron scattering study<sup>2</sup> has revealed the presence of short-lived clusters comprising Frenkel pairs in a smaller concentration ( $\sim 5\%$ ) than earlier thought, but with a relaxed or distorted lattice region around them. The appearance of the fast-ion phase is also marked by a Schottky-type anomaly in the specific heat.<sup>3</sup>

The behavior of chemically related  $\text{MgF}_2$  is quite different. This compound crystallizes with the tetragonal rutile structure, space group  $P4_2/mnm$  ( $D_{4h}^{14}$ ) with Mg in the  $2a$  site at (0,0,0) and F in the  $4f$  site at  $(x,x,0)$ . Its specific heat does not show an anomaly similar to that of  $\text{CaF}_2$  (Ref. 3) and, as a result,  $\text{MgF}_2$  is regarded as being structurally stable all the way up to its melting point (1260°C). Nothing seems to be known about the fluorine-anion self-diffusion in  $\text{MgF}_2$ , but lithium has been shown to rapidly diffuse at high tempera-

tures.<sup>4</sup> This is a surprising result in view of the low-temperature lithium defect.

A detailed analysis of the internal-friction (IF) peak in Li-doped  $\text{MgF}_2$ , and the absence of a corresponding dielectric loss peak, led Kim and Nowick<sup>4</sup> to propose that, at low temperatures, two Li ions substitute for a  $\text{Mg}^{2+}$  ion to form a  $(\text{Li}^+ - \text{Li}^+)^0$  dumbbell pair, which is therefore a neutral defect relative to the perfect crystal. This defect is represented in Fig. 1. Theoretical calculations<sup>5</sup> have estimated the bonding energy of such pairs to be approximately 1.2 eV. Above 850°C, a recent study<sup>6</sup> has shown that manganese only diffuses appreciably in  $\text{MgF}_2$  with simultaneous Li diffusion. This result indicates that Li, at high temperature, is mostly present as interstitials, thereby explaining the observed fast lithium diffusivity. The question then arises as to when and how the tightly bound Li pairs convert to highly mobile interstitials. To answer this question, we have carried out measurements of the lithium diffusivity  $D_{\text{Li}}$ , the results of which are presented in Sec. I. In particular, we observe a change of slope of  $D_{\text{Li}}$  around 800°C which appears to coincide with the conversion of the Li defect to its high-temperature form. We have found this conversion to be suggestive of a possible structural lattice change and have carried out a structural study by neutron-powder-diffraction techniques as a function of temperature. The results of this latter study are reported in Sec. II. Section III consists of a general discussion of the meaning of the neutron scattering results towards explaining the defect conversion and hence the change in diffusivity around 800°C.

## I. Li DIFFUSIVITY AND THE Li-DEFECT STABILITY

### A. Experimental techniques

The presence of lithium in  $\text{MgF}_2$  can be detected conveniently by means of an internal-friction peak, the height of which has been shown to be proportional to the Li concentration.<sup>4</sup>

The diffusion coefficient of Li has been measured both by in- and out-diffusion experiments, as described below. The first method was initially chosen because it was also the one used to dope the crystals with lithium at high temperature. The second method was subsequently found to be more precise, and also more practical at lower temperatures.

#### 1. In-diffusion experiment

In this case a crystal block is sealed in a quartz tube with LiF powder and treated for a given time and temperature. The block is then cut up and internal-friction specimens prepared from material at different depths. These are chosen away from the side walls so as to simplify the diffusion problem to one dimension. The diffusion coefficient  $D$  is calculated from the solution to Fick's law for a parallel slab with a constant concentration at the boundary.<sup>7</sup>

#### 2. Out-diffusion experiment

This experiment begins with a thin slab having a given LiF concentration which is then heated for a given time and temperature in flowing argon, then quenched by

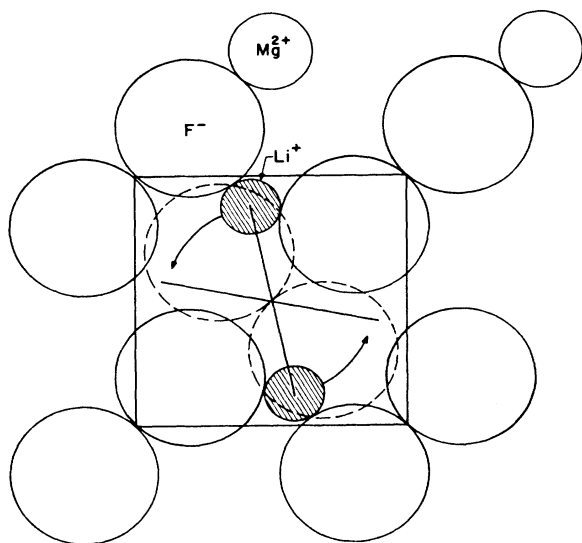


FIG. 1. Model of the  $(\text{Li-Li})^0$  defect at low temperature, in the  $(001)$  plane. Dashed atoms are located at  $\pm c/2$ .

blowing cold air on it. For the boundary condition we assume  $C_{\text{Li}}=0$  at the surface. Although this condition cannot be perfectly satisfied at the lowest temperatures investigated, it is nevertheless believed to be a reasonable one for reasons to be discussed in the following section. In order to obtain  $D$ , the IF peak height is measured before and after the out diffusion. Some corrections are required<sup>8</sup> to take into account the concentration gradient present in the sample after diffusion. This method has the advantage that  $D$  can be calculated from a ratio of two IF peak heights only, since the peak height is proportional to the Li concentration. The expression used for the concentration  $C(t)$  is again the solution to the diffusion equation,<sup>7</sup> this time for an initial concentration  $C(0)$  and a surface concentration fixed at zero.

### B. Results

The graph of the diffusion coefficient  $D$  as a function of temperature is shown in Fig. 2. Both components,  $D_{\parallel}$  parallel to the  $c$  axis and  $D_{\perp}$  perpendicular to the  $c$  axis,

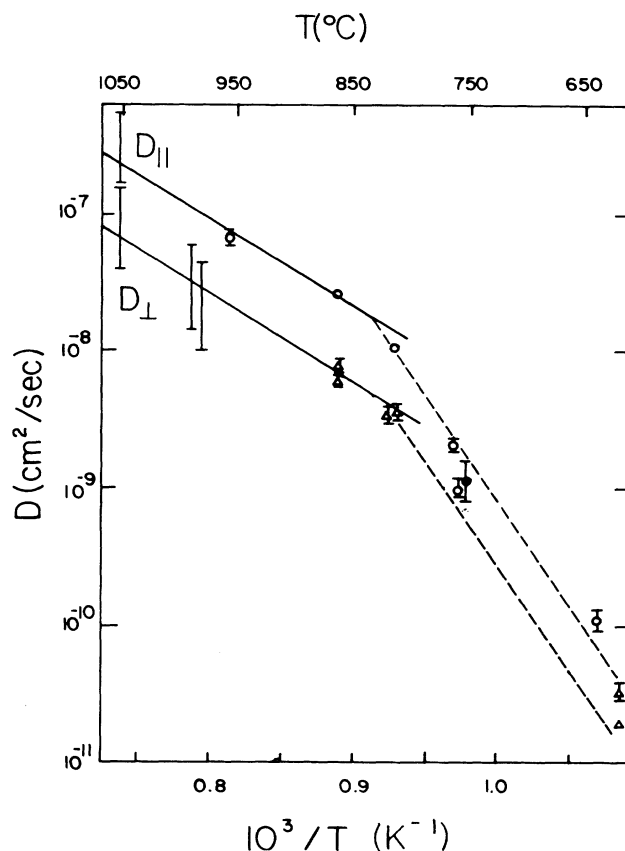


FIG. 2. Diffusion coefficient of Li in  $\text{MgF}_2$  versus temperature: ●,  $D_{\parallel}c$  axis, out diffusion from Ref. 19; ○,  $D_{\parallel}C$  and △,  $D_{\perp}C$ , both out-diffusion data points from this study. Above 975°C, the vertical bars indicate the range of  $D$  values obtained from in-diffusion measurements and assuming different surface concentrations between the two limits of 0.1% (upper end) and 10% (lower end). The dashed lines are only guides for the eye.

are separately represented. In-diffusion results are subject to a rather large uncertainty, a consequence of the corresponding uncertainty in the surface concentration. According to the  $\text{LiF}:\text{MgF}_2$  phase diagram,<sup>9</sup> this concentration should be approximately 30 mole % at 1000°C. However, if so, one would expect larger Li concentrations after in diffusion than those actually observed.

As expected from the easy doping of  $\text{MgF}_2$  with Li by solid-state diffusion at high temperature, both  $D_{\parallel}$  and  $D_{\perp}$  are unusually high, reaching beyond  $10^{-7}$   $\text{cm}^2/\text{sec}$  above 1000°C, and about  $10^{-6}$   $\text{cm}^2/\text{sec}$  near the melting point of 1260°C. A surprising result is the low anisotropy with the ratio  $D_{\parallel}/D_{\perp}$  being about a factor of 3 only.

For our present purpose, the most interesting result is the observation of a change in slope around 800°C exhibited by both components  $D_{\parallel}$  and  $D_{\perp}$ . Although the exact shape of the curve cannot be precisely determined due to the lack of data points below 600°C, a single straight line through all the existing points would certainly exceed the experimental error. The change of slope around 800°C may signal the conversion from the low- to the high-temperature Li defect.

At this point we should mention the assumption of zero Li concentration at the surface, particularly below 800°C. Specifically, if the diffusion rate of Li in bulk  $\text{MgF}_2$  were faster than the evaporation or sublimation rate of LiF from the surface, a layer of molecular LiF would form at the surface, thereby artificially suppressing the observed diffusivity. In the present case this is not thought to happen for two reasons.

(1) The lithium concentrations involved are relatively small ( $\sim 200$  ppm maximum), so that LiF is present on the surface in the form of adsorbed molecules rather than as a continuous liquid or a condensed layer.

(2) As discussed later in this paper, the conversion from the low- to the high-temperature defect occurs most likely via the formation of dissociated  $\text{Li}_i\text{-Li}_s$  pairs, with the diffusion rate controlled by the substitutional  $\text{Li}_s$ , i.e., effectively by Mg vacancies; the diffusion rate is then proportional to the probability of finding a Mg vacancy next to a substitutional  $\text{Li}_s$ , a probability which is expected to be low due to the small concentration of vacancies<sup>6</sup> below 800°C. A relatively fast evaporation rate of adsorbed molecules and a slower diffusion rate of substitutional lithium therefore justifies our assumption of a zero surface concentration.

In order to further investigate the temperature range of stability of the Li pairs and the conversion of the Li defect, we performed a series of successive isochronal annealings. Lithium was first diffused into a piece of  $\text{MgF}_2$  single crystal at 900°C for 6 h. The IF peak height measured thereafter was  $13 \times 10^{-5}$ . The sample was then annealed at 800°C for 1 h and slowly cooled in the furnace, a treatment that removed the peak almost entirely. A further 1-h annealing of 800°C followed by a fast quench more than restored the peak, to a height of  $50 \times 10^{-5}$  (185 at. ppm Li). These results, shown in Fig. 3, indicate that Li impurities can combine to form defects of a higher order than pairs, which then do not contribute to the IF peak. We also note that if such an apparent loss of lithium occurred during the diffusivity

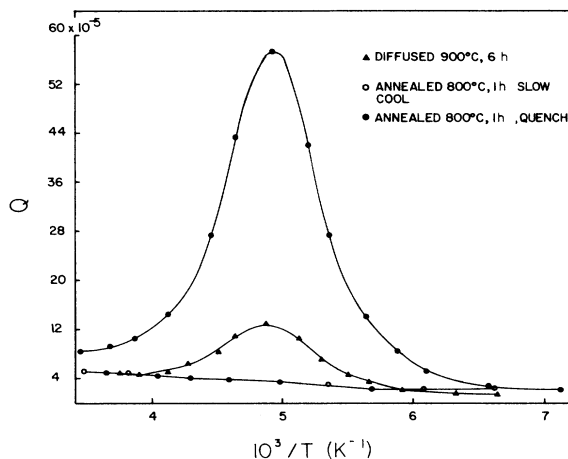


FIG. 3. Internal friction peaks due to  $(\text{Li-Li})^0$  pairs for three different treatments.

measurements reported above at 650 and 750°C, it would only result in an artificially high  $D_{\text{Li}}$ ; corrections for this occurrence would lower  $D_{\text{Li}}$  below 800°C and make the change in diffusivity sharper. Following the above preparation, the peak height was measured after 1-h annealings at successively higher temperatures. It can be seen in Table I that the IF peak height remained unchanged up to approximately 600°C. At higher temperatures the peak decreased and, as already mentioned, it can be completely removed by a 1-h annealing at 800°C followed by slow cooling. In this particular series, the first Li annealings, up to 550°C, were followed by quenching (sample pulled out of the furnace) while the last two were followed by furnace cooling (furnace turned off). Other measurements of the IF peak, as well as ionic conductivity measurements,<sup>8</sup> have shown, however, that the cooling procedure does not matter up to approximately 550°C. The series of annealings thus indicates that dissociation of the Li pairs becomes significant above 600°C and is complete at 800°C. This dissociation coincides, in temperatures, with the change in slope of the diffusivity and is therefore reminiscent of the Faraday transition observed in  $\text{CaF}_2$  at 1157°C and accompanied by the creation of a large concentration of interstitial fluorine ions. For this reason we have undertaken measurements of lattice parameters and atomic vibrational amplitudes as a function of temperature, by neutron-diffraction techniques.

## II. NEUTRON DIFFRACTION

### A. Experimental techniques

Neutron-diffraction measurements were carried out at the Brookhaven High Flux Beam Reactor on a compacted pellet of pure polycrystalline  $\text{MgF}_2$  about 2 cm high

TABLE I. Internal-friction peak heights for successive isochronal annealing; Q denotes quenched, FC furnace cooled, SC slowly cooled (4.5 h).

IF peak height ( $10^{-5}$ )	Annealing temperature ( $^{\circ}\text{C}$ )
13	900 diffused
~0.5	800 SC
50	800 Q
53	250 Q
53	355 Q
53	450 Q
53	550 Q
42	622 FC
32	685 FC

and 1 cm in diameter, obtained by grinding some single-crystal fragments. The experimental configuration consisted of pyrolytic-graphite monochromator and analyzer crystals in the (002) and (004) settings, respectively, with collimation 20' (in-pile), 40' (sample-analyzer), and 20' (analyzer-detector). The neutron wavelength was 2.38 Å and higher-order harmonics were suppressed with a pyrolytic-graphite filter.

For the lattice-parameter measurements as a function of temperature, the pellet was wrapped in a piece of platinum foil and supported on a boron nitride pedestal in a Nichrome-wound split-hemisphere furnace which was evacuated to about  $10^{-6}$  Torr. Short scans were made at selected temperatures over roughly  $3.5^{\circ}$  ranges centered about the (220) and (002) reflections at  $2\theta$  values of about  $93^{\circ}$  and  $102^{\circ}$ . Extended data sets suitable for Rietveld refinement were collected out to  $140^{\circ}$  in  $2\theta$  at  $20^{\circ}\text{C}$  before and after the temperature-dependence measurements with the sample not in the furnace, and at 12 and  $849^{\circ}\text{C}$  with the sample mounted in the furnace.

In addition, accurate lattice-parameter measurements were made by synchrotron-X-ray powder techniques<sup>10</sup> with Si used as an internal standard before and after the neutron measurements in order to correct for small errors in the neutron wavelength.

### B. Results

The values of the lattice parameters  $a$  and  $c$ , and the  $c/a$  ratio, are listed in Table II and plotted in Fig. 4. These figures were derived with a correction factor of 1.000 61 applied to the neutron wavelength based on the measured x-ray parameters  $a = 4.6215$  Å,  $c = 3.0507$  Å at  $25^{\circ}\text{C}$ . The corresponding x-ray values obtained after the temperature measurements show a very slight increase to  $a = 4.6222$  Å,  $c = 3.0512$  Å.

While the general trend of the results is very similar to that previously reported,<sup>11,12</sup> the thermal expansion coefficient perpendicular to the  $c$  axis is about 10% smaller at  $600^{\circ}\text{C}$ .

Rietveld refinement of the four extended data sets was carried out with a local version<sup>13</sup> of the standard Rietveld program<sup>14,15</sup> in which the peak shapes are fitted by a convolution of Gaussian and Lorentzian functions.<sup>16</sup> In the local version of the code, the Gaussian peak widths [full width at half maximum (FWHM)] are

TABLE II. Lattice parameters for  $\text{MgF}_2$  from neutron-diffraction data collected as a function of temperature. Observed values have been scaled to the x-ray values obtained at  $25^{\circ}\text{C}$  by a factor of 1.000 61 to allow for a small error in the neutron wavelength. Estimated errors are 0.0003 Å, 0.0002 Å, and 0.000 08 in  $a$ ,  $c$ , and  $c/a$ , respectively.

$T$ ( $^{\circ}\text{C}$ )	$a$ (Å)	$c$ (Å)	$c/a$
12	4.6213	3.0500	0.659 98
182	4.6281	3.0572	0.660 56
384	4.6391	3.0684	0.661 41
582	4.6513	3.0804	0.662 26
687	4.6579	3.0872	0.662 78
769	4.6637	3.0928	0.663 16
849	4.6691	3.0980	0.663 50
722	4.6608	3.0899	0.662 95
475	4.6448	3.0749	0.662 00

represented by the usual expression

$$\Gamma_G = (U \tan^2\theta + V \tan\theta + W)^{1/2}$$

and the Lorentzian widths by the expression

$$\Gamma_L = X \tan\theta + Y/\cos\theta,$$

where  $U$ ,  $V$ , and  $W$  are instrumental parameters,  $X$  is a strain-disorder-type broadening term, and  $Y$  is a

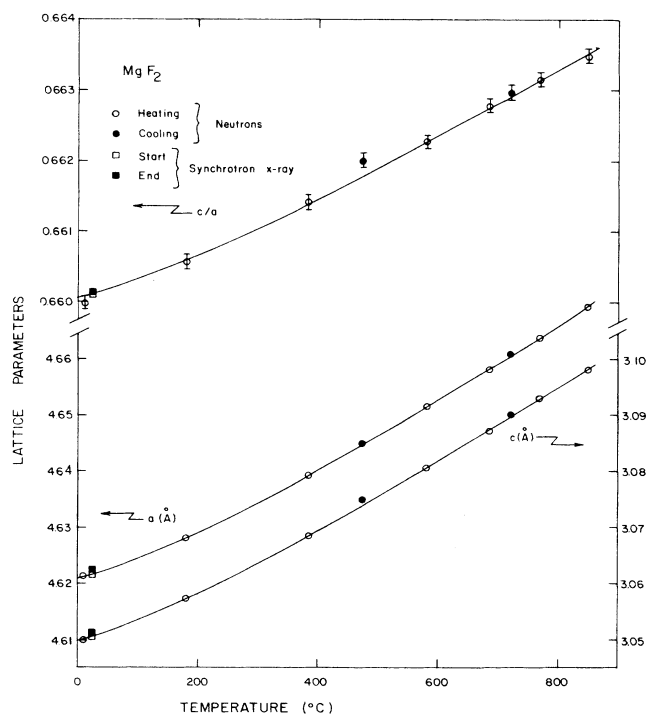


FIG. 4. Variation of  $\text{MgF}_2$  lattice constants with temperature from neutron-diffraction data. The values have been normalized to the synchrotron x-ray values obtained at  $25^{\circ}\text{C}$  as described in text.

particle-size-type broadening term. The Lorentzian function, not normally included in neutron refinement, was necessary here because of the imperfect fit obtained with a simple Gaussian to the tail of the high-angle peaks. This appears to be due to strain effects in the freshly crushed crystal which are annealed out at higher temperatures. The quality of the fit is seen by the  $R$  and  $S^2$  factors listed in Table III,<sup>17</sup> where a purely statistical distribution of the data (i.e., no systematic discrepancies) would give for  $S^2$  a value of 1.

The results of the final round of refinements are summarized in Table IV. The results of the refinement of the 12°C data set are omitted, since they are essentially identical to those of the initial 20°C refinement. The latter (column I, Table IV) are in good agreement with previous neutron single-crystal results,<sup>18</sup> the average discrepancy being about two estimated standard deviations (ESD), a typical figure for Rietveld analyses. Between 20 and 849°C, the  $x$  parameter is unchanged, while the thermal parameters increase by a factor of 3 to 4 (column II, Table IV). The results obtained after cooling to 20°C (column III, Table IV) indicate a small increase in the in-plane vibrational amplitudes and a small decrease in the  $x$  parameter relative to the initial 20°C refinement. This could possibly be due to a small amount of static disorder, but the significance of this result cannot be regarded as conclusive.

### III. DISCUSSION

In the following we shall first discuss the diffusivity results, and then the possible role of the structural features observed by neutron diffraction.

#### A. Diffusivity

The most likely explanation of the change in slope of the diffusivity can be obtained by considering the nature of the defect at low temperature<sup>4</sup> on the one hand and recent results<sup>6</sup> obtained concerning the enhancement of the diffusion of  $\text{Mn}^{2+}$  in  $\text{MgF}_2$  crystals by the presence of lithium on the other hand. As mentioned in the Introduction and shown in Fig. 1, the low-temperature Li defect in  $\text{MgF}_2$  consists of two lithium ions substituted for a  $\text{Mg}^{2+}$  ion to form a  $(\text{Li}^+-\text{Li}^+)$  dumbbell pair of monoclinic symmetry, with its axis perpendicular to the  $c$  axis of the crystal. This pair can be regarded as composed of a substitutional,  $\text{Li}'_s$ , and an interstitial lithium ion,  $\text{Li}'_i$ , bound together by a Coulombic force. This

TABLE III.  $R$  factors from Rietveld refinement of neutron data from  $\text{MgF}_2$ .  $R_I$  and  $R_{\text{WP}}$  are based upon integrated intensity and weighted-profile fits, respectively,  $R_E$  is the expected or statistical value, and  $S_p^2 (=R_{\text{WP}}^2/R_E^2)$  is the goodness of fit (Ref. 17).

	20°C (start)	849°C	20°C (end)
$R_I$	0.025	0.022	0.032
$R_{\text{WP}}$	0.069	0.070	0.070
$R_E$	0.047	0.052	0.046
$S_p^2$	2.1	1.8	2.3

may be called a self-compensated defect since no other intrinsic defect is required for charge neutrality. Because of the strain imposed by a lithium pair on its atomic environment and conversely the constraints placed on the Li pair, it is unlikely that it will diffuse as a pair. Consequently, in order to diffuse we expect the pair to dissociate into  $\text{Li}'_s$  and  $\text{Li}'_i$  (Kröger's notation), the respective defects now being of opposite charge. This is a case of "ambipolar" diffusion and both must diffuse simultaneously, diffusion of substitutional  $\text{Li}'_s$  being necessarily rate limiting since it must diffuse via Mg vacancies.<sup>19</sup> However, such a diffusion process can hardly explain the high diffusivity observed above 800°C. Thus if the Li pairs do dissociate at high temperature, as shown by the annealing treatments, they must do so differently than by producing  $\text{Li}'_i$  and  $\text{Li}'_s$ .

A recent study of Mn diffusion<sup>6</sup> in  $\text{MgF}_2$  points to the creation of interstitial lithium. In this study  $D_{\text{Mn}}$  was observed to be 25 times higher when Li was present. Because Mn is very similar in size and charge to Mg, it most likely diffuses via a vacancy mechanism. An enhanced diffusivity of Mn in the presence of Li indicates that lithium introduces Mg vacancies. This can only occur if a Li pair dissociates into two interstitials  $\text{Li}'_i$ . The change in slope of the Li diffusivity would consequently signal the conversion of the Li impurities from self-compensated defects to mostly interstitials. Energetically, such a conversion is surprising in that it now creates three defects,  $2\text{Li}'_i + 1V_{\text{Mg}}$ , instead of two otherwise. The neutron results provide elements for an explanation of this point.

#### B. Structural features

The two most significant results of the structural part of the study are the constancy of the positional parameter  $x$  of fluorine in the temperature range 20–849°C, and the large and anisotropic increase in the vibrational amplitude of the fluorine ions in this same range.

First, our present results clearly indicate the absence of anion lattice disordering in  $\text{MgF}_2$  up to 850°C, in contrast to  $\text{CaF}_2$  and isostructural fluorides. As seen from the value of  $x$  (Table IV), the relative average position of the fluorine ions does not change at high temperature. We note, however, an increase of 3.7% in the volume of the unit cell between 20 and 849°C. Concurrently, the  $c/a$  ratio increases by 0.5%. This in itself, however, is not believed to be sufficient to explain a major conversion from dumbbell pairs to mostly interstitial  $\text{Li}'_i$ .

The second important result of the structural part of the study is more likely to be significant in explaining this conversion. It concerns the thermal or atomic mean-square displacement factor which, in the principal representation, is written as  $U_1S_1^2 + U_2S_2^2 + U_3S_3^2$ , where  $U_i = \langle u_{ii}^2 \rangle$  and  $S_i$  is the component of the scattering vector along the  $i$ th principal axis of the tensor. It is relatively straightforward to show that the principal axes, in the  $(x, y)$  plane, lie along the Mg—F bond and perpendicular to it, and that, correspondingly,  $U_1 = U_{\parallel} = U_{11} + U_{12}$  and  $U_2 = U_{\perp} = U_{11} - U_{12}$ . In Table V we summarize the diagonal  $U$  values for both  $\text{Mg}^{2+}$  and

TABLE IV. Results of Rietveld refinement of  $\text{MgF}_2$ . ESD's are given in parentheses.  $\langle u_{ij}^2 \rangle = a_i a_j \beta_{ij} / 2$  (Ref. 2), where  $\beta_{ij}$  is defined in the Debye-Waller exponent  $\exp[-(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23})]$ ,  $a_i, a_j$  are the unit-cell parameters and  $hkl$  are the Miller indices. All values for  $\langle u_{ij}^2 \rangle$  are in  $\text{\AA}^2$ .

		20°C (start)	849°C	20°C (end)	300° K
		I	II	III	(Ref. 10)
F	$x$	0.30310(10)	0.30313(11)	0.30274(11)	0.3032(2)
Mg	$\langle u_{11}^2 \rangle$	0.0099(7)	0.0291(7)	0.0134(7)	0.0053(3)
	$\langle u_{33}^2 \rangle$	0.0031(7)	0.0119(10)	0.0038(7)	0.0036(3)
	$\langle u_{12}^2 \rangle$	0.005(5)	-0.0018(5)	0.0001(5)	-0.0004(2)
F	$\langle u_{11}^2 \rangle$	0.0104(5)	0.0373(5)	0.0150(5)	0.0087(2)
	$\langle u_{33}^2 \rangle$	-0.0081(6)	0.0239(10)	0.0075(6)	0.0062(2)
	$\langle u_{12}^2 \rangle$	-0.0029(4)	-0.0149(4)	0.0046(4)	-0.0034(2)

$\text{F}^-$ . At 20°C, the mean-square vibration amplitude of fluorine in the basal plane is about twice as large perpendicular to the  $\text{MgF}$  bond as it is in the parallel direction [110]. This ratio increases 25% between 20 and 849°C. The most striking result is, however, that the absolute amplitudes increase by a factor of 4 in one and 3 in the other direction. The increase in the third direction, [001], is also by a factor of 3. Such large increases are likely to play an important role in the dissociation of the lithium pairs into lithium interstitials.

The frequency of vibration of the Li ions in their respective wells is most probably higher than that of the much heavier F ions; the internal friction study indeed yields  $10^{14} \text{ sec}^{-1}$  for the attempt frequency of the lithium.<sup>4</sup> Also, the motion of the Li ions from one well to the other being primarily constrained by the two F ions located in the basal plane, an interwell transition of Li requires a transverse displacement of these F ions. It is interesting to note that their transverse vibration is associated with the general rotation of rigid  $\text{F}_6$  octahedra. This rotation is a mode of  $B_{1g}$  symmetry which has a particularly low frequency compared to the other vibrational modes,<sup>20</sup> approximately  $2.7 \times 10^{12} \text{ sec}^{-1}$  at room temperature. This frequency is about 50 times lower than the attempt frequency of the Li ions in the pair. Consequently, at higher temperatures, the large amplitude displacement of the F ions will appear as partially

static to them, resulting in a decrease of their binding potential energy. Thus the large vibrational amplitude should facilitate pair dissociation which, because of the large binding energy of the pairs, is expected to be the rate-controlling step for the conversion of most of the lithium to interstitials.

In several systems in which lithium is substituted for a larger ion, e.g.,  $\text{Li:KCl}$ ,<sup>21</sup> it forms an off-center defect because of its small size. In the present system, although Li has almost the same radius as Mg, the large vibrational amplitude of the surrounding fluorine ions and their comparatively low frequency may reduce the constraint placed on the lithium. This then makes it possible for the lithium to be displaced in the direction of an octahedral interstitial position at least part of the time. Thus, although the dissociation of pairs may initially form  $\text{Li}_i + \text{Li}_s$ , the substitutional  $\text{Li}_s$  could well be allowed off center by the fluorine vibrations and become interstitial. We therefore suggest that the change in slope of the diffusivity around 800°C corresponds to the extensive conversion  $\text{Li}_s \rightarrow \text{Li}_i$ . It is important to note that below 800°C the Li diffusivity would be controlled by the diffusion of  $\text{Li}_s$ , which itself depends upon the intrinsic concentration of magnesium vacancies, apparently low.<sup>6</sup> As soon as  $\text{Li}_s$  can go off center, such vacancies are created at a concentration level equal to half the to-

TABLE V. Bond lengths and mean-square displacements in  $\text{MgF}_2$  at 20°C and 849°C. Errors are estimated to be  $\sim 0.001 \text{ \AA}$  for the bond lengths and  $\sim 0.001\text{--}0.002 \text{ \AA}^2$  for the displacements.

	20°C (start)		849°C		20°C (end)	
Mg-F in plane ( $\text{\AA}$ )	1.981		2.002		1.979	
Mg-F out of plane ( $\text{\AA}$ )	1.996		2.022		1.998	
	20°C (start)		849°C		20°C (end)	
	Mg	F	Mg	F	Mg	F
$U_{\parallel}$ [110] ( $\text{\AA}^2$ )	0.0104	0.0075	0.0273	0.0224	0.0135	0.0104
$U_{\perp}$ [1 $\bar{1}$ 0] ( $\text{\AA}^2$ )	0.0094	0.0133	0.0309	0.0522	0.0133	0.0196
$U_{\perp}$ [001] ( $\text{\AA}^2$ )	0.0031	0.0081	0.0119	0.0239	0.0038	0.0075

tal lithium concentration and we should expect a sharp change in the Li diffusivity.

### CONCLUSION

The present study of the Li diffusivity in  $\text{MgF}_2$  has revealed an unexpected change in  $D_{\text{Li}}$  around  $800^\circ\text{C}$ . Internal-friction results also indicate a significant loss of peak height, i.e., Li pairs, in the same temperature range. Both results signal an extensive dissociation of the pairs and conversion to interstitials. A possible explanation for the changes in the nature of the Li defect is provided by the neutron-diffraction results. These show that the vibrational amplitude of the F ions con-

straining the lithium defects increase by a factor of 3 to 4 between 25 and  $850^\circ\text{C}$ . Based on a vibrational frequency argument we therefore suggest that this amplitude increase may lead to extensive dissociation and conversion of  $\text{Li}_i$  to  $\text{Li}_i$ .

### ACKNOWLEDGMENTS

We particularly wish to thank Dr. A. S. Nowick for his cooperation in this study. The diffusion and internal-friction experiments were carried out in his laboratory at Columbia University. D.E.C. was supported by the Division of Materials Science, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

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