Teutsch for his critical reading of the first draft of this paper.

APPENDIX

It is possible to give a simple physical argument for expecting the effective K value to be non-constant as the applied electric field is varied over the region covered in the experiments in this paper.

The distance from the emitting surface of the potential energy maximum for emitted electrons varies with the electric field in the oxide adjacent to the emitting surface. This distance x_m is given by the equation:

$$x_m = (16\pi K\epsilon_0 E/e)^{-1/2}. \quad \text{(A1)}$$

If it is assumed initially that there is a constant value of K, then x_m can be computed. By assuming that the electron velocity in traversing the distance x_m is about thermal velocity, the transit time can be obtained. The value of K should be comparable to that for electromagnetic radiation of roughly the same period as the transit time.[15] For 10^7 V/m$<E<1.5\times10^8$ V/m the corresponding wavelength range is in the near infrared region and $n=K^{1/2}$ for silicon dioxide in this region is not constant, violating the initial assumption.

Furthermore, at high fields ($E\gtrsim1.5\times10^8$ V/m), the value of x_m is at most only a few times the nearest-neighbor distance in silicon dioxide casting some doubt upon the use of the dielectric-constant concept based on polarization of a homogeneous medium.

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[15] Similar reasoning has been employed by S. M. Sze, C. R. Crowell, and D. Kahng, J. Appl. Phys. 35, 2534 (1964).

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Transport Properties of LaF_3

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We report measurements of the lattice and bulk thermal expansion, fluorine nuclear magnetic resonance, and electrical conductivity of single-crystal LaF_3 in the temperature range 300–1000°K. In the lower portion of this temperature range, the measurements yield activation energies for the formation of Schottky defects of ~0.07 eV and for fluorine ion diffusion of ~0.45 eV. The activation energy for diffusion appears to decrease at higher temperatures. We propose a model for the crystal with low activation energy for the formation of neutral defects, and a higher energy for defect dissociation and diffusion. The apparent changes of activation energy are ascribed to the excitation of lattice vibrations near the Debye temperature.

I. INTRODUCTION

The temperature dependences of the electrical conductivity, thermal expansion and fluorine nuclear magnetic resonance of LaF_3 crystals have been measured. These experiments have produced a wealth of data with several unusual features. The data exhibit many interesting details but the principal characteristics are:

(1) Thermal expansion measurements have been made both with a dilatometer and with x-rays from 300–1000°K. The bulk of the crystal expands faster than the unit cell, which is indicative of Schottky defect formation. The measured activation energy (see Fig. 4) for the creation of Schottky defects is $E_S=0.069$ eV. This is an exceedingly low activation energy. It is especially surprising in view of the 1760°K melting point of LaF_3 crystals. Furthermore E_S increases linearly with increasing temperature, which is contrary to the behavior of most other crystals.

(2) The activation energy for diffusion below 360°K, as measured both by magnetic resonance and by conductivity, is 0.46 eV. Since the fluorine magnetic resonance line narrows,[1] the fluorine ions must be moving. Moreover, since the activation energy for diffusion is about the same for the magnetic resonance line narrowing and the conductivity, the fluorine ions apparently make the principal contribution to the ionic conduction.

(3) Above ~350°K the rate of increase of the conductivity with temperature (see Fig. 6) becomes smaller than the 0.46 eV measured below 350°K. The high-temperature data can be fitted by an activation energy of 0.082 eV, or by a T^{-9} temperature dependence entering into the conductivity. The bend over occurs at the effective Debye temperature of LaF_3.[2]

The model assumes that a large fraction of the Schottky defects are bound as neutral "molecular" holes. Mott and Gurney[3] point out that if the activation

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[1] K. Lee and A. Sher, Phys. Rev. Letters 14, 1027 (1965).

[2] W. M. Yen, W. C. Scott and A. L. Schawlow, Phys. Rev. 136, 271 (1964).

[3] The possibility of this phenomenon is mentioned in N. F. Mott and P. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 41. The measured dielectric constant of LaF_3 is $\epsilon=14$. The Coulomb energy of a LaF_2^+ and an F^- separated by 2.3 Å, a La^{3+}-F^- distance, is 0.45 eV.

energy for the creation of Schottky defects is small compared to the dissociation energy, bound defects may be present. In view of the extremely low measured E_S in LaF_3 it is reasonable to assume that most of the defects are neutral. Hence they do not contribute to the conductivity, and since the activation energy for diffusion of a large neutral defect is likely to be high they should not contribute to motional narrowing of the fluorine-magnetic-resonance line width. It is assumed that dissociation of the defects is governed by a law of mass action. The resulting charged defects are the principal contributors to the conductivity and to the motional narrowing of the magnetic-resonance line width. The break in the conductivity versus $1/T$ curve is tentatively ascribed to the excitation of lattice degrees of freedom near the Debye temperature.

Crystals of LaF_3 doped with various trivalent rare-earth ions have been investigated by a number of groups. These studies have included electron spin resonance,[4] optical spectroscopy,[2,5] and lasers.[6] There has been a controversy about the crystal structure of LaF_3.[4,5,7] Recently L. O. Andersson and W. G. Proctor[8] have completed a crystal structure determination by a study of the La nuclear quadrupole resonance. They conclude that the space group is $P6_3/mcm$ with twelve formula units per unit cell. They find six magnetically nonequivalent La sites and four nonequivalent F sites. The crystal structure is depicted in Fig. 1. Two papers[9] have recently been presented on the crystal growth, physical and optical properties of LaF_3.

A description of the experiments and their results are presented in Sec. II. Section III is devoted to a discussion of the model which best fits the known facts. Section IV contains a brief listing of mechanisms and other models which have been considered. The conclusions are presented in Sec. V.

II. EXPERIMENTS

A. Thermal Expansion

Measurements of the thermal expansion of both the unit cell and bulk dimensions were made from 300 to 1350°K. The former were made on a polycrystalline sample with x-rays and the latter on a single crystal with a dilatometer.

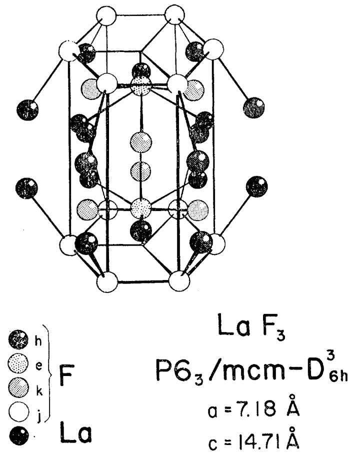

FIG. 1. Half of the unit cell of LaF_3. The four different F sites are marked in Wyckoff notation. The top and bottom hexagonal planes are mirror planes and the center c axis is a screw hexad (6_3) with a translation of one-half the c-axis period.

The thermal expansion of the unit cell was observed using standard high-temperature x-ray diffractometer techniques. A Norelco x-ray diffractometer, with a wide range goniometer and a Stone high temperature furnace designed for the Norelco goniometer were used. The polycrystalline sample was heated in a dry nitrogen atmosphere and the temperature was monitored with a platinum-platinum 10% rhodium thermocouple. Average values of the lattice constants l_a and l_c were calculated at each temperature by introducing the measured 2θ values and the corresponding hkl values into an IBM-7094 computer. Although measurements were made up to 1300°K, only the data below 1000°K were reliable enough to use.

The measurements of the thermal expansion of the bulk dimensions of a single crystal, that is the measurement of the coefficients of expansion of LaF_3, were made on a standard dilatometer which uses an electrical

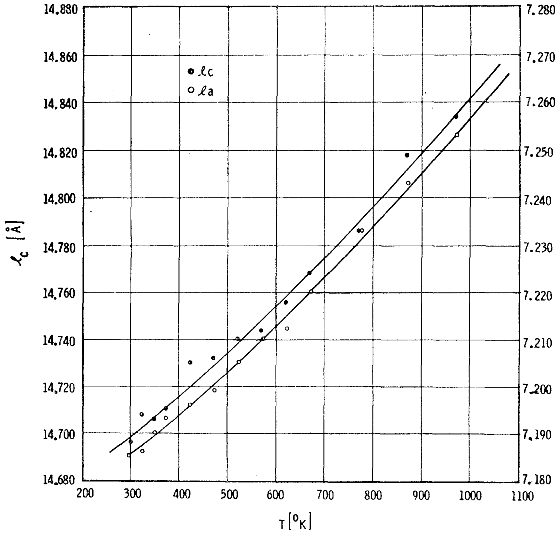

FIG. 2. Unit cell dimensions l_a, l_c along the a and c axis from x-ray data as a function of temperature.

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[4] See for example, D. A. Jones, J. M. Baker and D. F. D. Pope, Proc. Roy. Soc. (London) **A74**, 249 (1959).

[5] See, for example, W. M. Yen, R. L. Green, W. C. Scott, and D. L. Huber (unpublished), and H. H. Caspers, H. E. Rast, and R. A. Buchanan, J. Chem. Phys. **42**, 3214 (1965).

[6] R. Solomon and L. Mueller, Appl. Phys. Letters **3**, 135 (1963). W. F. Krupke and J. B. Gruber, J. Chem. Phys. **41**, 1225 (1964).

[7] I. Oftedal, Z. Phys. Chem. **5B**, 272 (1929); **13B**, 190 (1931). H. H. Caspers, R. A. Buchanan, and H. R. Martin, J. Chem. Phys. **41**, 94 (1964). E. Wong, O. Stafsudd, and D. Johnson, *ibid.* **39**, 786 (1963); Phys. Rev. **131**, 990 (1963).

[8] L. O. Andersson and W. G. Proctor (unpublished).

[9] H. M. Muir and W. Stein, in Proceedings of the Fifth Rare Earth Research Conference, 1965 (unpublished). J. B. Mooney, in Proceedings of the Thirteenth National Infrared Information Symposium (IRIS), 1965 (unpublished).

push rod transducer. The single crystal was heated in an argon atmosphere and the temperature was monitored with a chromel-alumel thermocouple. The expansion data were automatically plotted on a Varian F-80 X-Y Recorder. The measured values along both the c and a axes were verified by a mechanical indicator at selected temperatures.

Figure 2 is a plot of the unit cell dimensions as a function of temperature obtained from the x-ray measurements. Figure 3 is a plot of the fractional expansion along the a and c axes from both the dilatometer and the x-ray measurements as a function of temperature. No hysteresis in dimensions as a function of temperature was ever observed, i.e., there was never any indication of permanent shrinkage or expansion.

Table I gives the expansion coefficients for several temperature ranges. From these results we can obtain the concentration of Schottky defects as a function of temperature. The difference in expansion between the lattice and the bulk has been replotted in a form suitable for analysis in Fig. 4, and the analysis as well as the definition of the labeling for this figure are given in Appendix A. The analysis of course is made in terms of thermal activation of Schottky defects, and the best fit for the temperature dependence of the defect concentration is obtained with the relation

TABLE I. Expansion coefficients of LaF$_3$ in 10^{-6} deg^{-1}: values at 25°C and averages over various intervals.

Temperature region, °C	a axis	c axis
25	15.8	11.0
25–625	19.1	15.25
25–925	23.0	18.9
25–950	24.2	···
25–1080	···	20.1

$$\frac{S}{N}=\exp(-E_S/kT)\,, \tag{1}$$

where S is the number of defects, N the number of formula units in the sample, and

$$E_S=E_{S0}+\alpha_S kT\,, \tag{2}$$

with $E_{S0}=0.069$ eV and $\alpha_S=4.05$.

These extremely unusual values will be discussed in more detail in Sec. III, below.

B. F^{19} Nuclear Magnetic Resonance

The fluorine nuclear magnetic resonance (NMR) of a single crystal of lanthanum trifluoride LaF$_3$ has been investigated in the temperature range from 173 to 573°K. The resonance line was observed to begin motionally narrowing at 300°K. The results of these measurements were published earlier[1] and only a brief review of the measurements will be presented here.

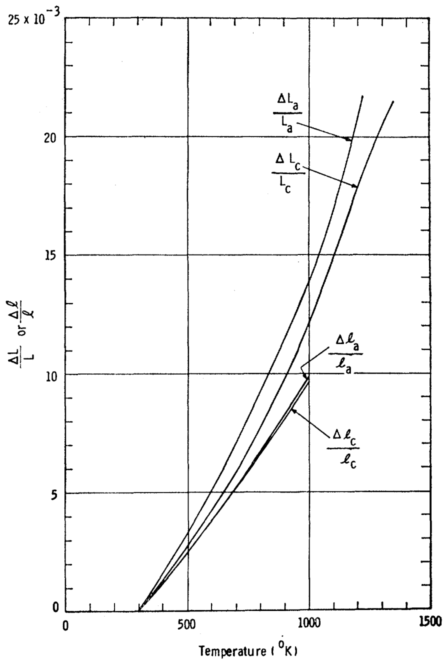

FIG. 3. Thermal expansion as a function of temperature. The $\Delta L/L$ curves and the $\Delta l/l$ curves are respectively from the dilatometer and x-ray measurements.

The experimental measurements were performed on a Varian V-4200 NMR Spectrometer operated at 16.00 Mc/sec. The temperature dependence was obtained using a Varian V-4540 variable temperature controller which controls and monitors the flow of cooled or

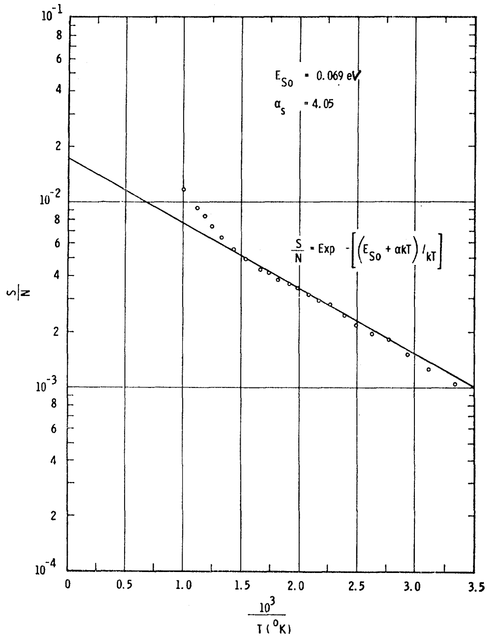

FIG. 4. Fractional concentration of Schottky defects as a function of temperature. The straight line is $S/N=\exp[-E_S/kT]$ with $E_S=0.69$ eV$+4.05kT$.

heated dry nitrogen gas over the sample. The single crystal used was cylindrical with a diameter of $\frac{1}{4}$ in. and a length of $\frac{3}{8}$ in. In order to avoid distortions and saturation, the magnetic field scanning speed, the modulation frequency and amplitude, and the magnitude of the rf field were chosen at each temperature so that by decreasing their magnitudes still further no changes in the resonance line were observed. The spectrum at each temperature was scanned as many as 100 times and stored in a Varian C-1042 time averaging computer. This procedure improves the signal-to-noise ratio as the square root of the number of scans. The use of this procedure was necessary because below 300°K the line is so broad that a signal-to-noise ratio of unity was typical for a single passage through the resonance line. However, at high temperatures, the signal-to-noise ratio is greatly enhanced because of the observed narrowing. The spectra were recorded as the derivatives of the absorption curves. The derivative curve was then integrated on an IBM-7094 computer.

Below 300°K the rigid lattice NMR signal is a single line with a shape that is squarer than a Gaussian. The half-width at half intensity is measured to be 16.6 kc/sec. As the temperature is raised from 300 to 450°K, the single line simultaneously narrows and splits into a superposition of a broad and narrow line. At the 16.00 Mc/sec frequency which was used in these measurements, the two lines are chemically shifted but never enough to be resolved by the Rayleigh criterion. However, some splitting was resolved[8] at 94 Mc/sec in this temperature region. At room temperature and 94 Mc/sec the line showed enough structure to indicate it was not a single line but a group of lines which could be analyzed into four chemically shifted lines. This is consistent with the LaF_3 crystal structure. At 475°K and 16 Mc/sec the "two lines" coalesce into a single narrow line with a half-width of 0.53 kc/sec. As the temperature is raised further, the line broadens slightly. The line width in this higher temperature range is under investigation by M. Goldman and L. Shen.[10]

Figure 5 is a plot of the logarithm of the half-width as a function of $1/T$ measured parallel and perpendicular to the c axis. Within the experimental accuracy the line width is the same along the two directions. The narrowest measured half-width of 0.13 G=0.52 kc/sec is not limited by magnetic-field inhomogeneities. Whenever there appeared to be more than one line, the values of the half-widths are those of the combined lines. The data below 375°K are well fitted by a diffusion coefficient[1] D_{NMR} given by

$$D_{\mathrm{NMR}}=(4.2\pm1)\times10^{-4}\exp(-0.43\pm0.05\ \mathrm{eV}/kT)\ \mathrm{cm}^2/\mathrm{sec}. \quad (3)$$

C. The Electrical Conductivity

The electrical conductivity of several LaF_3 crystal wafers was measured from room temperature to 825°K. The wafers were 1 cm^2 in area, 0.05 cm thick, and oriented with the c axis perpendicular to the wafer's flat face. A few measurements at room temperature were made on wafers with an a axis perpendicular to the face, and no significant anisotropy was observed. The electrodes were evaporated gold and in some cases silver epoxy. Again there were no differences observed for different metallic electrode material. The conductivity measurement is complicated by the fact that LaF_3 exhibits an unusually large low frequency polarization effect.[11] Thus when a step voltage is impressed across a crystal, the current increases in less than 1 μsec to some initial value and then decays with time. Sutter and Nowick[12] have pointed out that if space charge polarization of the type first suggested by Jaffe[13] dominates, then the "true" conductivity is given by the initial current divided by the applied voltage. On the other hand, if the time variation of the polarization arises from a large dielectric relaxation time, then the "true" conductivity is equal to the residual current at infinite charging time divided by the applied voltage. Since the polarization effect in LaF_3 is extraordinarily large and not completely understood we have designed several experiments to decide between the two possibilities. The measurements were made by applying a step voltage through a mercury relay. The rise time of the switch was less than one microsecond. The results are summarized below:

(1) The initial current I_0 varies linearly with voltage over more than four decades of voltage. No such simple relationship exists with the residual current I_∞.

(2) The ratio I_0/V has been measured as a function of wafer thickness and Ohm's law is well obeyed. On the other hand, I_∞ seems to be independent of thickness.

(3) One electrode of a bar of LaF_3 has been made of an electrolyte. Under these conditions the polarization effect disappears and the sample becomes ohmic. The conductance measured in this way agrees closely with the I_0/V measurement. The electrolytes employed were 0.1 to 1 molar HF or HCl water solution. These measurements provide strong evidence that the electrical conductivity is due to ionic motion, the polarization is due to metal electrodes being blocked, and hence the "true" conductance is given by I_0/V. The NMR measurements also support these conclusions and suggest that the fluorine ions act as the carriers.

The room temperature conductivity of LaF_3 is rather large ($\sim10^{-7}$ mho cm^{-1}), particularly when one remembers its high melting point ($\sim$1760°K) and excellent optical quality.[14] The principal cation impurities are other trivalent rare earths isomorphic with La^{3+} and would not be expected to influence the con-

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[10] M. Goldman and L. Shen (private communication).

[11] R. Solomon, A. Sher and M. W. Muller, Bull. Am. Phys. Soc. **9**, 742 (1964).

[12] P. H. Sutter and A. S. Nowick, J. Appl. Phys. **34**, 734 (1963).

[13] G. Jaffe, Phys. Rev. **35**, 354 (1952).

[14] Similar crystals have shown less than one fringe distortion per cm path in a Twyman-Green interferometer.

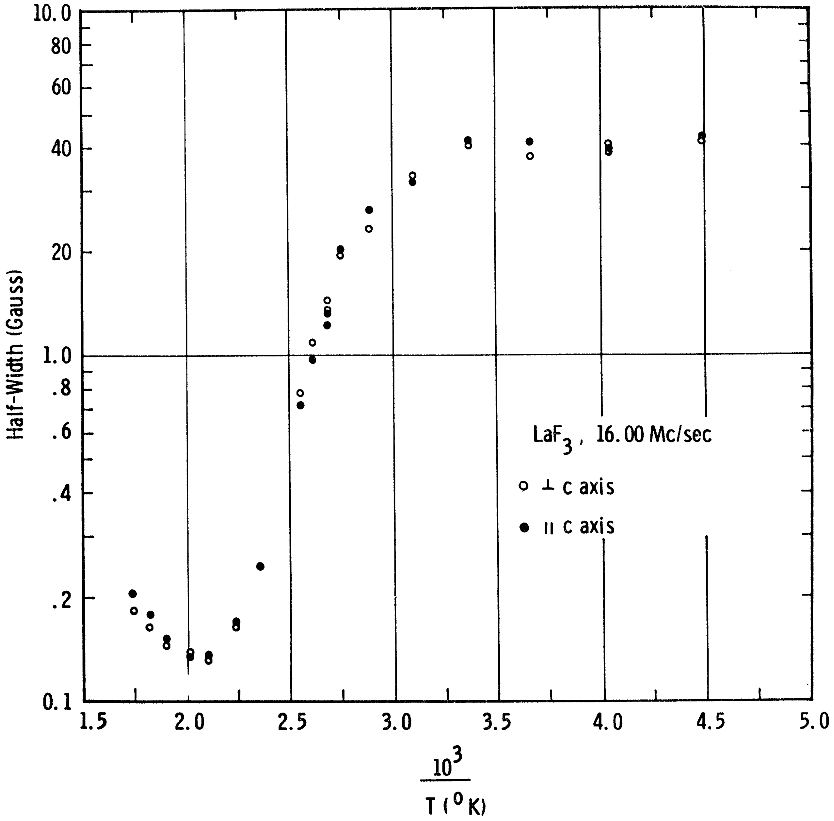

FIG. 5. F^{19} nuclear resonance half-width as a function of $1/T$. Measurements both parallel and perpendicular to the c axis.

ductivity significantly. The principal anion impurity is oxygen and because of its valence difference with fluorine might be expected to introduce significant numbers of F^- ion vacancies and hence have a strong influence on the conductivity. However, in several experiments samples with varying oxygen concentrations were investigated and no significant differences in conductivity were noted. The crystals used in the experiments reported in this paper were ones in which care was taken to eliminate oxygen contamination.

One further measurement was undertaken to verify that the conductivity is ionic. A bar of LaF_3 was carefully weighed, a metal electrode was coated on one end and the other end was submerged in an electrolyte. A known current was allowed to pass through the crystal for several days. Then the crystal was etched in nitric acid. Nitric acid normally causes no measurable weight loss. However, the acid would be expected to remove any La metal deposited on a surface. Approximate, although not exact, agreement has been found with Faraday's law. The discrepancy appears to be due to the fact that some electrolysis takes place within the bulk of the material, since lanthanum metal precipitates in the interior.

The conductance found from I_0/V has been measured as a function of temperature. The sample was heated in an oven in nitrogen and the temperature varied from room temperature to ~830°K. The sample temperature was controlled to better than a degree and measured by means of a thermocouple epoxied to the sample. No thermal hysteresis of the conductivity was detected. The conductance G can be expressed as[3]

$$G=\frac{A}{T}\exp(-E_D/kT)\,, \tag{4}$$

where E_D is the activation energy for diffusion and A is a quantity which depends on several parameters and may include some temperature dependence (see Sec. III). Figure 6 is a plot of $\ln(GT)$ versus $1/T$. The plot in Fig. 6 can be decomposed into two major straight segments, and the transition region between 350 and 430°K can also be fitted by a straight line. In the temperature range below 350°K, where the first break occurs, the data are well represented by

$$GT=2\times10^5\exp(-E/kT)\ [^\circ\mathrm{K}/\Omega]\,, \tag{5}$$

with $E=0.46$ eV$=5340$°K.

In the high temperature region, $T>430$°K, the results can be represented by an activation energy of 0.084 eV. A decrease in the activation energy for ionic conduction at high temperatures is of course extremely unusual. Although several materials, e.g., AgI, exhibit a similar decrease in the high temperature activation

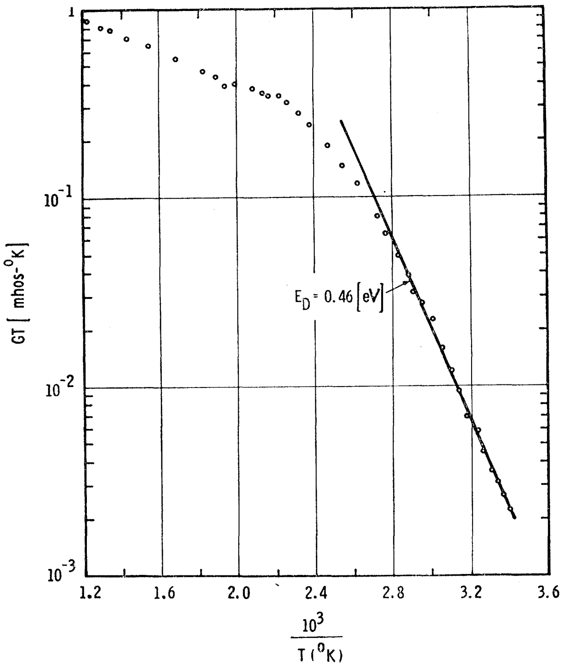

FIG. 6. Electrical conductance times temperature of a 1 cm^2 area wafer 0.05 mm thick as a function of $1/T$. The straight line is $GT \propto \exp(-E_D/kT)$ with $E_D = 0.46$ eV.

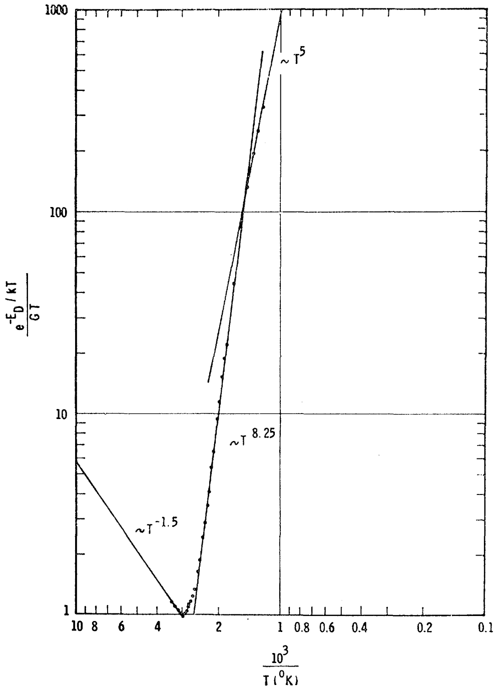

FIG. 7. The straight line function of Fig. 6 $\exp(-5340/T)$ divided by the experimental values of GT, exhibiting the power-law dependence of the conductivity.

energy, this arises because of a phase change in the material. Careful examination of x-ray and other data as a function of temperature indicate that LaF$_3$ does not undergo a high temperature phase change. We have thus far been unable to account for any other mechanism which might cause a decrease in the high temperature activation energy. Thus in attempting to interpret the results displayed in Fig. 6 we have been led to a model to be discussed below—with a constant activation energy but with an additional power law dependence on temperature. Thus we assume that the conductivity is given by an expression of the form

$$GT = B_\nu T^\nu \exp(-E/kT), \tag{6}$$

where B_ν depends only on ν.

Anticipating some of the results of the next section, we have plotted in Fig. 7 $\ln[\exp(-5340/T)/GT]$ *versus* $\ln(1/T)$, where GT are the experimental values. We see that the experimental data can then be represented by Eq. (6) if

$$\begin{aligned} \nu &\cong 1.5, & T &\lesssim 350°\text{K}, \\ \nu &\cong -8, & 400°\text{K} \lesssim T &\lesssim 650°\text{K}, \\ \nu &\cong -5, & 650°\text{K} &\lesssim T. \end{aligned} \tag{7}$$

It should be commented here that the suggestion of a $T^{3/2}$ dependence of the conductivity in the fairly narrow temperature region below ~350°K is rather arbitrary as far as the experimental data are concerned. The precision of the measurements is not sufficient to establish such a dependence. The choice of the exponent ν in this low-temperature region does have a slight influence on the value of the activation energy E. The value of 0.46 eV given above is a best fit for Eq. (6) with $\nu \cong 1.5$; the alternative assumption $\nu = 0$, $T < 350°$K as implied by Eq. (5) would lead to a best asymptotic value of $E = 0.49$ eV. The reason for our choice will become clear in the next section.

III. A MODEL OF THE LaF$_3$ CRYSTAL

In order to account for the experimental results reported above we require a model for the LaF$_3$ crystal which exhibits appropriate concentrations and motions of carriers. We shall carry out the discussion of this model in the language of chemical equilibria. The equilibrium constants are deduced from a simplified statistical treatment of the crystal.

The discussion will include a fair amount of physical detail. The inclusion of this detail is forced on us by the wealth of detail in the experimental data. We have chosen a particular combination of physical mechanisms to present in this section. This combination is by no means unique; however, it is the only one we have found which fits all the known facts.

A LaF$_3$ crystal with N formula units, i.e., N La^{3+} ions and $3N$ F$^-$ ions, is an extremely complex statistical system to investigate. Although the work of Andersson and Proctor[8] indicates the existence of six magnetically nonequivalent La^{3+} sites and four nonequivalent F$^-$

sites, for the purpose of the statistical mechanics which follows, all La^{3+} and F^- sites will be assumed to be equivalent. However, the lattice will contain a significant number M of molecular holes $[LaF_3]$. In addition, the model includes the possibility that a $[LaF_3]$ hole can interact with a formula unit LaF_3 according to the reaction

$$[LaF_3]+LaF_3 \rightleftarrows LaF_2^+ + F^- \qquad (8)$$

to form a LaF_2^+ ion and a F^- ion each occupying volumes of a formula unit.[15] The number of either the LaF_2^+ ions or the F^- ions will be called n.

We assume that the physical mechanism both for conduction and for the narrowing of the fluorine NMR line is the motion of a fluorine ion from a LaF_3 to neighboring LaF_2^+. Thus we must calculate the number n, i.e., the equilibrium of Eq. (8), and the mobility of the F^- [but note that the F^- occupying molecular vacancies, that is to say the F^- on the right-hand side of Eq. (8) are not directly involved in this process since this requires that LaF_2^+ ions move].

When treating solids it is improper to express the total energy of the solid as a sum of individual particle energies because of the strong interactions among particles. The accepted procedure is to use collective coordinates and express the total energy of the solid as a sum of normal mode energies, i.e., phonon energies. If there is more than one particle per primitive cell, the phonon spectrum is quite complicated with three times as many branches as there are particles per primitive cell. The exact treatment of this problem lies well beyond the scope of this paper. Instead, we shall try to explain the data on the basis of physical arguments. The solid will be treated as though the interactions between the LaF_3 molecules, the principal constituent, and the $[LaF_3]$, LaF_2^+, and F^-, the minority species, are weak.[16]

In Appendix B it is shown that the number of molecular holes is given by

$$M/N = z_M\,, \qquad (9)$$

and the usual law of mass action applies to the reaction in Eq. (8).

$$n^2/MN = z_I z_n / z_M z_N\,. \qquad (10)$$

The partition functions per particle for the species LaF_3, $[LaF_3]$, LaF_2^+, and F^- are denoted, respectively, by z_N, z_M, z_I and z_n. An estimate of the partition functions must now be undertaken.

The zero of energy for the evaluation of all the partition functions will be chosen as the zero point energy of the perfect solid where there are N formula units on N lattice sites and no defects. For temperatures low compared to an effective Debye temperature T_D, z_N is of the form

$$\begin{aligned} z_N &= \exp[-u(T)/3kT] \\ &\cong 1; \quad T \ll T_D\,, \end{aligned} \qquad (11)$$

where the vibration energy per particle[17] $u(T)$ will be small compared to other energies (e.g. the energy to create a Schottky defect and the energy to dissociate a molecular hole) which appear in similar exponents; and also $u(T)/kT \ll 1$, for $T \ll T_D$. Hence, in the low temperature range z_N is approximately unity. However, as the temperature approaches the Debye temperature T_D and the Dulong and Petit limit is reached, then all the degrees of freedom are excited and z_N becomes[18]

$$\begin{aligned} z_N &= 1; & T &\ll T_D \\ &= (T/T_D)^9; & T &\gtrsim T_D\,. \end{aligned} \qquad (12)$$

The $(T/T_D)^9$ arises because a molecule which has four atoms has six vibrational degrees of freedom, and in a solid three torsional (or hindered rotational) degrees of freedom. There is a $(T/T_D)^{1/2}$ contribution to the partition function from potential energy and a $(T/T_D)^{1/2}$ contribution from kinetic energy per degree of freedom.

The molecular hole partition function z_M is

$$z_M = \exp(-E_S/kT)\,, \qquad (13)$$

where E_S is the energy to create a Schottky defect, i.e., the work required to move a lanthanum and three flourine ions from the interior of the crystal to the surface. It is simplest and most reasonable to assume that there are no internal degrees of freedom associated with a molecular hole.

The partition function z_I of the LaF_2^+ ion conceivably can be subdivided in a number of ways. For example, if this were really a molecular crystal the LaF_2^+ might have its torsional motion excited at a far lower temperature than its vibrational motion. Also, the LaF_2^+ is equivalent to a $[F^-]$ hole, and if the activation energy for hopping of the $[F^-]$ hole is low enough one should treat this hole like a particle in a box whose volume is that of the crystal. The choice for z_I which best fits the data is

$$\begin{aligned} z_I &= \exp[-(E_S+E_d)/2kT]; & & T < T_{ID} \\ &= (T/T_{ID})^6 \exp[-(E_S+E_d)/2kT]; & & \\ & & & T \gtrsim T_{ID} > T_D\,, \end{aligned} \qquad (14)$$

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[15] If the number of molecular holes M is small ($M \ll N$), the reaction Eq. (8) can be shown to be equivalent to a reaction in which a neutral molecular hole dissociates to form two ionized holes, i.e., $[LaF_3] \rightleftarrows [LaF_2^+]+[F^-]$. Here the crystal lattice which is the "space" in which the reaction takes place is implicit instead of explicit as in Eq. (8).

[16] Any treatment based on thermodynamic arguments, i.e., requiring the Gibbs free energy be a minimum for constant temperature and pressure processes, implicitly makes this weak interaction assumption in order to express the internal energy as a simple sum of energies of the various species, and to write the entropy of internal motion of the system. We prefer to display this approximation explicitly.

[17] For a simple monatomic solid $u(T) = (3\pi^4/5)kT_D(T/T_D)^4$; for a complicated solid the expression for $u(T)$ involves sums over contributions from all acoustical and optical branches.

[18] See for example, N. Davidson, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1962), Chaps. 11 and 16.

where E_d (the [LaF_3] dissociation energy) is the energy required to go from the left to the right side of the reaction in Eq. (8), and T_{ID} is the "effective Debye temperature" for the $LaF_2{}^+$ ion. The factor $(T/T_{ID})^6$ enters because the $LaF_2{}^+$ has three particles and hence three degrees of vibrational freedom and three degrees of torsional freedom. It is reasonable to take $T_{ID}>T_D$ since the $LaF_2{}^+$ ion is certainly more tightly bound than a LaF_3 molecule. It requires an energy E_S+E_d to produce a $LaF_2{}^+$ and F^- pair. To keep the bookkeeping straight the Boltzmann factors which enter into z_I and z_n are each written as $\exp[-(E_S+Er)/2kT]$. Since z_I and z_n always enter as the product $z_I z_n$ the somewhat artificial simplified procedure yields the correct answer.[19]

Finally, we estimate the factor before the exponential in z_n. The simplest picture for a fluorine ion in a formula unit volume is that of a particle in a potential well. The form of the potential is of course quite complicated because the ion will tend to be fairly strongly bound to the "walls" of the vacancy. We are here primarily interested in the number of degrees of freedom available to the ion, and in the characteristic temperature for their excitation. The number of degrees of freedom is of course 3; and it is probably safe to say that the characteristic temperature T_n is lower than the Debye temperature. Thus we write

$$z_n=(T/T_n)^3\exp[-(E_S+E_d)/2kT]. \tag{15}$$

Substituting Eqs. (9), (12), (14), and (15) into Eq. (10) yields

$$\frac{n}{N}=\exp[-(E_S+E_d)/2kT]$$
$$\times\begin{cases}(T/T_n)^{3/2}; & T_n<T<T_D\\ (T/T_n)^3(T_D/T)^{9/2}; & T_D<T<T_{ID}\\ (T/T_n)^{3/2}(T_D/T)^{9/2}(T/T_{ID})^3; & T_{ID}<T.\end{cases} \tag{16}$$

We now proceed to an estimate of the electrical conductivity

$$\sigma=e\frac{n}{V}\mu, \tag{17}$$

where e is charge on an electron, V is the volume of the crystal, n is the number of carriers in the crystal, and μ, the mobility, is related to the diffusion coefficient through the Einstein relation

$$kT\mu=eD. \tag{18}$$

The relevant diffusion process, as we have mentioned earlier, is the motion of a fluorine ion from a LaF_3 to a neighboring $LaF_2{}^+$. For a physical picture of this process it is useful to visualize the missing fluorine ion of the $LaF_2{}^+$ as a vacancy; we need to determine the conditions for a neighboring F^- to jump into this vacancy. The diffusion coefficient can be expressed in terms of the average fluorine-fluorine spacing a and the correlation time τ_c as

$$D=a^2/6\tau_c. \tag{19}$$

The correlation time, in turn, can be expressed as

$$1/\tau_c=(kT_D/h)W, \tag{20}$$

where $kT_D/h=\omega_D$, the Debye frequency, is taken as the presentation frequency of a fluorine ion at the boundary of a vacancy, and W is the probability that on any given presentation the fluorine ion hops into the vacancy. The transition probability W is generally written as a Boltzmann factor. Physically it is the probability that a sufficiently large thermal fluctuation of the lattice occurs so that there is enough room for the ion in question to move to the vacancy. No rigorous theory of this process exists even for simple lattices. The method commonly applied to this problem has only one virtue, namely that it works.[20] The method uses equilibrium thermodynamics to calculate the number of complexes in which the lattice has expanded and a fluorine ion (in our case) is in an interstitial position, half-way between its lattice site and the adjoining site. The transition probability W is then set equal to

$$W=\frac{\xi}{N}, \tag{21}$$

the number of such complexes ξ divided by the number of formula units. The major objection to this calculation is that these complexes form and disappear in times short compared to the time for the lattice to adjust to them, hence the use of equilibrium thermodynamics is incorrect rigorously. The formation of the complexes can be thought of as a chemical reaction of the form

$$LaF_3+[F'^-]\rightleftarrows(LaF_2{}^+)+F'^-, \tag{22}$$

where F'^- stands for a fluorine ion in an interstitial position, [F'^-] the absence of a fluorine ion in an interstitial position, and ($LaF_2{}^+$) a $LaF_2{}^+$ adjacent to a flourine ion complex. The law of mass action for this reaction is then

$$\frac{\xi^2}{NN'}=\frac{z_{(LaF_2{}^+)}z_{F'^-}}{z_N z_{N'}}\simeq\frac{\exp(-E_h/kT)}{z_N}$$
$$=\exp(-E_h/kT)\begin{cases}\times 1; & T<T_D\\ \times(T_D/T)^9; & T>T_D.\end{cases} \tag{23}$$

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[19] The problem of the artificial division of the energy to produce a pair of ions between their partition functions does not arise if the zero of energy corresponds to the energy of the system with all the particles infinitely separated. However, then it is necessary to keep account of the binding energies of the various species. The final answer is unaffected by this bookkeeping choice.

[20] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill Book Company, Inc., New York, 1963), p. 57.

The partition function $z_{N'}$ for interstitial vacancies is $z_{N'}=1$. Also $z_{(\mathrm{LaF}_2{}^+)}z_{F^-}=e^{-E_h/kT}$ is the correct expression since the complex certainly has no internal degrees of freedom excited and E_h, the hop activation energy, is the energy relative to the perfect lattice required to form the complex. The partition function z_N is the same as before, Eq. (12). Equations (17) to (23) can now be combined to yield an expression for σ which can be compared with the experimental data.

$$\sigma T \cong \frac{e^2a^2}{6\hbar}\left(\frac{N}{V}\right)T_D\left(\frac{N'}{N}\right)^{1/2}\exp[-(E_S+E_d+E_h)/2kT]$$

$$\times\begin{cases}(T/T_n)^{3/2}; & T_n<T<T_D\\ (T/T_n)^{3/2}(T_D/T)^9; & T_D<T<T_{ID}\\ (T/T_n)^{3/2}(T_D/T)^9(T/T_{ID})^3; & T_{ID}<T\end{cases}\qquad(24)$$

Equation (24) is consistent with the form of the experimentally determined temperature dependence of the conductivity and with the reported value of the Debye temperature of 360°K if we let $E_d+E_h=0.87$ eV, using the value of $E_S=0.069$ eV$+4.05kT$ from Eq. (2) as determined by thermal expansion measurements. The change in power law dependence at $T\sim650$°K may be identified with the predicted change at T_{ID}.

It is worth noting that only E_d+E_h can be determined from these experiments. The model requires $E_d>E_{S0}$. However, within the limits of this restriction the experiments reported here cannot distinguish between a relatively large number of carriers with low mobility ($E_d<E_h$) or relatively few carriers with high mobility ($E_d>E_h$). If the theoretical estimate[3] of $E_d=0.45$ eV is used then one finds $E_h=0.42$ eV. The near equality of E_d and E_h is curious but presumably is a coincidence.

The theory of the diffusion coefficient D_{NMR} for the fluorine nuclear magnetic resonance is almost identical with that of conductivity. In place of Eq. (19) we have,

$$D_{\mathrm{NMR}}=\frac{1}{12}\frac{a^2}{\tau_c}\frac{n}{N},\qquad(25)$$

where the factor $\frac{1}{12}$ rather than $\frac{1}{6}$ enters because the diffusion is relative to other flourine ions which may also be in motion rather than relative to the fixed coordinate system of the lattice. Thus, in the low-temperature region.

$$D_{\mathrm{NMR}}=\frac{a^2}{12}\frac{kT_D}{\hbar}\left(\frac{N'}{N}\right)\exp(-\tfrac{1}{2}\alpha_S)$$
$$\times\exp[-(E_{S0}+E_d+E_h)/2kT](T/T_n)^{3/2}.\qquad(26)$$

The observed value of the activation energy[1] as quoted in Eq. (3) and the observed transition temperature of ~375°K are consistent with the other experimental results and with our model. To compute the temperature-independent factors in Eqs. (25) and (27) we use $(N/V)=1.83\times10^{22}$ cm^{-3} obtained from the density $\rho=5.97$ g cm^{-3}, $\alpha_S=4.05$ from Eq. (2), and we need values for a and N'/N. Because of the complicated lattice structure of $\mathrm{LaF_3}$ there are a number of different near neighbor distances. There are a number of neighbors at 2.61 Å or less and then the next nearest set of neighbors start at 2.67 Å. Hence, a natural choice of the number of neighbors per formula unit (N/N') is the number of fluorine ions within 2.61 Å of another fluorine ion per fluorine ion in the unit cell. The distances separating various fluorine ions is given in Table II. There are four fluorine ions per unit cell on e sites and they have no such neighbors. There are eight F$^-$ on h sites with three neighbors each, twelve F$^-$ on j sites with four neighbors each, and twelve F$^-$ on k sites with two neighbors. Thus we take

$$N'/N=(4\times0+8\times3+12\times4+12\times2)/36=8/3\cong3.$$

This is a fairly arbitrary choice but it has little effect on the numerical answers since the square root of N'/N enters. With these values we obtain

$$\frac{e^2a^2}{6\hbar}\left(\frac{N}{V}\right)T_D\left(\frac{N'}{N}\right)^{1/2}\exp(-\alpha_S/2)$$
$$=3.8\times10^{16}\ [\text{°K/stat }\Omega\text{-cm}],\qquad(27)$$

and

$$\frac{a^2}{12}\frac{kT_D}{\hbar}\left(\frac{N'}{N}\right)^{1/2}\exp(-\alpha_S/2)=6\times10^{-4}\ [\text{cm}^2\ \text{sec}^{-1}].\qquad(28)$$

For a direct comparison with the measured values we would also require the characteristic temperature T_n, which we have made no attempt to estimate. Using the assumption (it is no better than a guess) $T_n=200$°K, the corresponding experimental values are 5×10^{15} [°K/stat Ω-cm] and 4.2×10^{-4} [cm^2 sec^{-2}]. The values predicted by the model are high in both instances, but less than an order of magnitude. In view of the crudeness of the approximations we have employed, the pre-

TABLE II. Lattice separations in $\mathrm{LaF_3}$.

Ion-neighbor	No. of neighbors at distance d	d (A)
e-e	1	2.68
e-k	3	2.70
h-h	1	2.97
h-j	3	2.67
h-k	3	2.55
j-j	4	2.61
j-h	1	2.67
j-e	2	2.93
k-k	1	3.21
k-k	2	2.55
k-e	1	2.70

dictions based on the model do not appear too unreasonable.

It is noteworthy that the factor involving α_S improves the prediction of the experimental results by this model. The usual theories[3] of ionic conductivity find that the activation energy for the generation of Schottky defects should decrease linearly as the temperature increases. Thus the constant α_S would be expected to be negative. We have no satisfactory explanation for the sign of α_S as observed in our measurements. It is clear, however, that this observed value is quite significant if the model we are proposing is to be taken seriously.

IV. OTHER MODELS

The thermal expansion measurements suggest that Schottky defects are formed and yield an activation energy for the production of these defects. The higher activation energy inferred from the low temperature conductivity and magnetic resonance measurements requires that the diffusion occur because of one of these alternatives:

(1) Schottky defects are created dissociated, i.e. $E_S > E_d$ and $E_h > E_S$, which is what usually happens.

(2) Schottky defects are initially bound, i.e. $E_S < E_d$, which is the model analyzed in Sec. III.

(3) Fraenkel defects are formed with the Schottky defects being bound, which is unlikely since it adds another degree of complication to an already complicated system.

If case (1) applies, then $M \ll n$ and the conductivity and the thermal expansion should exhibit the same thermal behavior (see Appendix A). Case (3) was eliminated both because it is unlikely and because there is no obvious mechanism which causes E_h to decrease sharply at the Debye temperature.

Within case (2) we considered several alternatives to that of Sec. III for the decrease in the slope of the conductivity versus temperature curve. These included the possibility that E_d decreases to zero because the number of carriers becomes so high that the Debye length[18] is comparable to lattice dimensions. Even with the small activation energies and with $\epsilon = 14$, the number of carriers is not nearly large enough for temperatures ~400°K. We have also considered the possibility that chemical reactions of the form:

$$\mathrm{LaF_2^+ + [LaF_3] \rightleftarrows LaF^{++} + F^-}$$

or

$$\mathrm{LaF_2^+ + [LaF_3] \rightleftarrows LaF_2^+ + [LaF_3]}$$

occur which effectively decrease the number of carriers and hence reduce the temperature variation of the conductivity. However, all the reactions we have thought about involve an interaction between two minority species, and the concentration of these species, while enormous by ordinary standards in solids at these temperatures, still is not large enough to account for the change in slope of the conductivity curve.

V. CONCLUSIONS

It appears possible to correlate the quite unusual transport properties exhibited by lanthanum trifluoride with a model that does not violate physical intuition too flagrantly. The details of this model discussed here should probably not be taken too seriously, and certain features of it are undoubtedly too crude. The essential feature of the model is to suggest that a power-law temperature dependence of the transport properties of a crystal can arise from the excitation of lattice vibrations, and that changes in such a power-law dependence can be tentatively correlated with the distortion of the phonon spectrum by lattice irregularities. The model is likely to be useful in suggesting further measurements that should yield pertinent information. It seems, for example, that extensions of the measurements reported here to lower temperatures will prove interesting.

The experimentally measured characteristic of $\mathrm{LaF_3}$ which appears to be crucial in influencing the transport properties of the material is the strikingly low activation energy for the formation of lattice defects and the correspondingly high defect concentration. This low activation energy is the basis for the hypothesis advanced here of the formation of electrically neutral defects.[21] This hypothesis leads quite naturally to the physical and mathematical model of Sec. III.

We have made no attempt in this paper to explore the problems posed by the observation of this low activation energy. It appears likely that this feature of $\mathrm{LaF_3}$ is associated with surface effects that are also responsible for the unusually large surface polarization phenomena observed in $\mathrm{LaF_3}$.[11] We expect that the study of this group of problems will prove to be of considerable interest.

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APPENDIX A

The volume of the crystal V in terms of the volume of a formula unit v is

$$V = (N+S)v = (N+M+n)v. \qquad \text{(A1)}$$

The change of V with temperature measured by the

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[21] It may be possible to test this feature of the model using the slow motion experiments of C. P. Slichter and D. Ailion, Phys. Rev. **135**, A1099 (1964).

dilatometer is related to the change in the formula unit volume v measured by x-rays through the relation

$$\frac{\Delta V}{V}=\frac{\Delta v}{v}+\frac{\Delta S}{N}. \tag{A2}$$

The expansion of a crystal with a symmetry axis (a hexagonal crystal) can be decomposed as

$$\frac{\Delta V}{V}=\frac{\Delta L_c}{L_c}+\frac{2\Delta L_a}{L_a},$$

where the c axis is the symmetry axis and the a-axis is perpendicular to the c axis. Similarly, one can write

$$\frac{\Delta v}{v}=\frac{\Delta l_c}{l_c}+\frac{2\Delta l_a}{l_a},$$

and so

$$\frac{\Delta S}{N}=\delta_c+2\delta_a, \tag{A3}$$

where

$$\delta_c=\frac{\Delta L_c}{L_c}-\frac{\Delta l_c}{l_c},\quad \delta_a=\frac{\Delta L_a}{L_a}-\frac{\Delta l_a}{l_a}. \tag{A4}$$

Since for thermal excitation of defects we expect a temperature dependence as given by Eq. (1), we have

$$\frac{\Delta S}{N}=\exp(-E_S/kT)-\exp(-E_S/kT)_0, \tag{A5}$$

where the zero subscript refers to the reference temperature (300°K) for the expansion measurements.

Figure 4 is a plot of $\ln[\delta_c+2\delta_a+\exp(-E_S/kT)_0]$ versus $1/T$ with the reference term at 300°K chosen 1.05×10^{-3}. With this choice the measurements are well represented by a straight line in the range 300–700°K, with

$$E_S=0.069\text{ eV}+4.05kT.$$

Above 700°K there is a systematic deviation from this behavior which we make no attempt to interpret.

It is apparent from inspection of Fig. 3 that the part of the expansion to be ascribed to defect formation is strongly anisotropic, with most of the contribution coming from the a axes. This suggests that the mobility of the molecular vacancies may be larger in the transverse planes than in the c direction.

APPENDIX B

The solid will be treated as though the interactions between the LaF_3 molecules on formula unit sites, the principal constituent, and the $[LaF_3]$, LaF_2^+ and F^-, the minority species, are weak.[18] The following treatment will be devoted to the establishment of relationships among the numbers of the various species and their "single particle" partition functions.

With the assumption that the interaction energy between the majority species and each of the minority species is weak, the energy ϵ_j of the whole system in state j can be expressed as a sum of the energies of the $(N-n)$ LaF_3 strongly interacting molecules $\epsilon_{j'}(N-n)$; the molecular holes $\epsilon_{j''}(M)$; the LaF_2^+ ions $\epsilon_{j'''}(n)$; and the F^- ions $\epsilon_{j^{iv}}(n)$. Then we have:

$$\epsilon_j=E_{j'}(N-n)+\epsilon_{j''}(M)+\epsilon_{j'''}(n)+\epsilon_{j^{iv}}I(n), \tag{B1}$$

with j', j'', j''', j^{iv}, n, M specifying the state of the system. The partition function Z for the crystal is:

$$\begin{aligned}Z&=\sum_j \exp(-\epsilon_j/kT)\\ &=\sum_{M,n,j',j'',j''',j^{iv}}\{\exp-[\epsilon_{j'}(N-n)+\epsilon_{j''}(M)\\ &\qquad\qquad+\epsilon_{j'''}(n)+\epsilon_{j^{iv}}(n)]/kT\}\\ &=\sum_{M,n}\frac{(N+M+n)!}{(N-n)!M!(n!)^2}\\ &\qquad\qquad\times Z_N(N-n)Z_M(M)Z_I(n)Z_n(n),\end{aligned} \tag{B2}$$

where the partition function of the solid is

$$Z_N(N-n)=\sum_{j'}\exp[-\epsilon_{j'}(N-n)/kT];$$

the $[LaF_3]$ holes is

$$Z_M(M)=\sum_{j''}\exp[-\epsilon_{j''}(M)/kT];$$

the LaF_2^+ ions is

$$Z_I(n)=\sum_{j'''}\exp[-\epsilon_{j'''}(n)/kT];$$

the F^- ions is

$$Z_n(n)=\sum_{j^{\text{iv}}}\exp[-\epsilon_{j^{\text{iv}}}(n)/kT],$$

and the term

$$\frac{(N+M+n)!}{(N-n)!M!(n!)^2}$$

is the total number of complexions. The factorial term, the number of complexions of the system, accounts for the distinguishable ways in which the various species can be distributed on the lattice sites. There are $(N-n)+M+2n=N+M+n$ formula sites in the solid. There are $[(N+M+n)!/(N-n)!(M+2n)!]$ ways of putting $(N-n)$ indistinguishable LaF_3 molecules onto the $N+M+n$ sites. Then there are $[(M+2n)!/M!(2n)!]$ ways to put M indistinguishable molecular holes on the remaining $(M+2n)$ sites. Next there are $[(2n)!/n!n!]$ ways to put the n indistinguishable LaF_2^+ ions on $2n$ sites. And finally there is only one way to distribute the n indistinguishable F^- ions on the remaining n sites. The total number of complexions is the product of the number of ways of installing each species into the allotted space.

The partition functions for the holes and ions Z_M, Z_I, Z_n can be written in terms of the partition functions per particle z_M, z_I, z_n as

$$\begin{aligned} Z_M(M)&=z_M{}^M,\\ Z_I(n)&=z_I{}^n,\\ Z_n(n)&=z_n{}^n, \end{aligned} \tag{B3}$$

where the customary indistinguishability factors are absent because they have been incorporated into the number of complexions. The partition function for the solid $Z_N(N-n)$ has the same form

$$Z_N(N-n)=z_N{}^{N-n}; \tag{B4}$$

however, the z_N must be calculated using collective coordinates.

The probability $P(M,n;T)$ of finding M molecular holes and n dissociated holes is

$$P(M,n;T)=\frac{(N+M+n)!}{(N-n)!M!(n!)^2}z_N{}^{N-n}z_M{}^M(z_Iz_n)^n/Z. \tag{B5}$$

At fixed temperature the probability $P(M,n;T)$ is a sharply peaked function of M and n. Call M^*, n^* the point at which $P(M,n;T)$ peaks. The average number of holes is then

$$\langle M\rangle=\sum_{M,n}MP(M,n;T)\cong M^*, \tag{B6}$$

$$\langle n\rangle=\sum_{M,n}nP(M,n;T)\cong n^*. \tag{B7}$$

Hence in order to find $\langle n\rangle$ and $\langle M\rangle$ one needs only investigate the point at which $P(M,n;T)$ peaks. $P(M,n;T)$ peaks when:

$$|\nabla_{M,n}\ln P(M,n;T)|_{M^*,n^*;T}=0,$$

or

$$\left[\left(\frac{\partial\ln P(M,n;T)}{\partial M}\right)_T\right]^2+\left[\left(\frac{\partial\ln P(M,n;T)}{\partial n}\right)_T\right]^2\Bigg|_{M^*,n^*}=0,$$

which is satisfied only if

$$\left(\frac{\partial\ln P(M,n;T)}{\partial M}\right)_T\Bigg|_{M^*,n^*}=0, \tag{B8}$$

$$\left(\frac{\partial\ln P(M,n;T)}{\partial n}\right)_T\Bigg|_{M^*,n^*}=0. \tag{B9}$$

Substituting Eq. (B5) into Eqs. (B8) and (B9) and dropping the * notation, yields

$$\frac{M}{N+M+n}=z^N, \tag{B10}$$

$$\frac{n^2}{(N+M+n)(N-n)}=\frac{z_Iz_n}{z_N}. \tag{B11}$$

This calculation is only valid for $N\gg M$, n hence Eqs. (B10) and (B11) can be simplified to

$$\frac{M}{N}\cong z_M, \tag{B12}$$

$$\frac{n}{N}\cong\left(\frac{z_Iz_n}{z_N}\right)^{1/2}. \tag{B13}$$

Equations (B12) and (B13) can be combined as expected to yield the usual "law of mass action" for a four species chemical reaction.

$$\frac{n^2}{MN}=\frac{z_Iz_n}{z_Nz_M}. \tag{B14}$$