pected to have a value between $k_{22}$ and $k_{33}$, as is indeed found to be the case experimentally (Saupe, 1960*b*).

### Application to *p*-azoxyanisole and *p*-azoxyphenetole

For a comparison of the elastic moduli of PAA and *p*-azoxyphenetole (PAP) we make the reasonable assumption that the molecular distributions in the two compounds are similar. [The difference in the density is, in any case, accounted for explicitly in equation (3)]. Using the values $B$, $D$ and $n$ of PAA and PAP (see part I), and putting $\gamma_{22}=0·300$ for both compounds, $s_1, s_2$ and $k_{22}$ have been calculated for the temperatures for which data are available. Wherever transition temperatures $T_c$ have not been specifically mentioned by the authors, the values of Chatelain & Brunet-Germain (private communication; see Chandrasekhar & Madhusudana, 1969) have been used. The results are presented below in terms of the relative temperature $T_c-T$:

| | | $s_1$ | $s_2$ | $k_{22}\times 10^7$ dyne | |
|---|---|---|---|---|---|
| | $T_c-T$ | (theor.) | (theor.) | (theor.) | (expt.) |
| PAA | 5°C | 0·422 | 0·328 | 2·95 | 2·89* |
| | | | | | 3·1† |
| PAP | 18°C | 0·632 | 0·530 | 7·03 | 7·1† |

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* Saupe (1960*b*).
† Orsay Liquid Crystal Group (1970).

The temperature variation of the elastic moduli of PAA are shown in Fig. 1 along with data of Saupe (1960*b*) for $k_{11}$ and those of Freedericks & Zwetkoff (1934; see Saupe, 1960*b*) for $k_{22}$. Here $\gamma_{11}=0·481$, and $\gamma_{22}=0·300$ as before.

The general agreement can be seen to be very good, showing that the approximations made in the calculations are justified. The results also seem to provide further confirmation of the validity of the statistical theory developed in part I.

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# Thermal Expansion of LiF by X-ray Diffraction and the Temperature Variation of its Frequency Spectrum

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The coefficients of thermal expansion of LiF are determined at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are obtained for the variation of lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The energy of formation of Schottky pairs is found to be 2·42 eV. The Grüneisen constant $\gamma$ is found to decrease with temperature. The mean frequency of the vibrational spectrum is found to decrease with temperature and the variation between 300 and 1000°K is about 13%.

## Introduction

The thermal expansion of LiF has been investigated mainly by Eucken & Dannöhl (1934), Sharma (1950) and Pathak, Pandya & Ghadiali (1963). The first two investigations are by macroscopic methods while the last one is by X-ray method.

It was shown in our previous paper (Pathak & Vasavada, 1970, to be called paper I hereafter) that values of the linear thermal expasion of NaCl, KCl and CsBr obtained by different workers agree at lower temperatures but show wide discrepancies at higher temperatures. The same feature can also be seen from Table 1 in the case of LiF.

One of the aims of the present experiment was, therefore, to determine accurate values of the thermal expansion of this salt, especially at high temperatures. The present work on LiF is a part of the general and detailed investigation of the thermal expansion of alkali halides. The thermal expansion of LiF beyond 700°C is probably determined for the first time.

## Experimental

The lattice constants were determined at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. The experimental technique has been fully described in Paper I. The accuracy of the results is estimated to be about $\frac{1}{2}$%.

## Results and discussion

The lattice constant of LiF was found to vary with temperature according to the following equations (obtained with the help of an IBM 1620 computer):

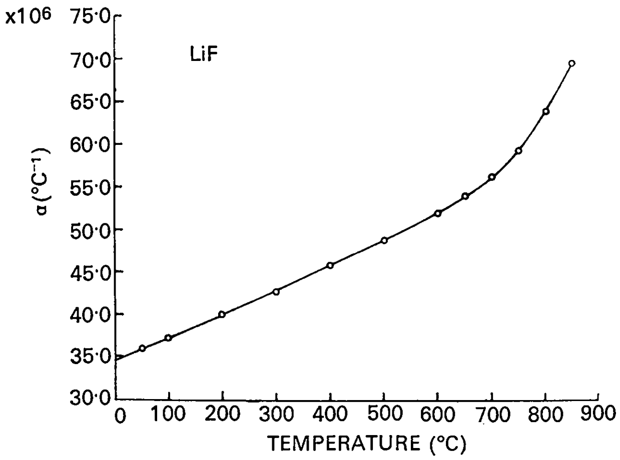

Fig. 1. Plot of coefficient of linear expansion of LiF *versus* temperature.

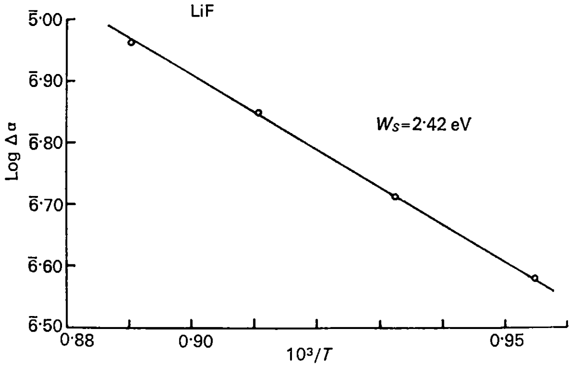

Fig. 2. Plot of logarithm of excess expansion *versus* reciprocal of temperature

From 0 to 625°C

$$a_t = 4{\cdot}0104 + 1{\cdot}3928 \times 10^{-4} t + 5{\cdot}023 \times 10^{-8} t^2 + 1{\cdot}287 \times 10^{-11} t^3. \quad (1)$$

From 575 to 850°C

$$a_t = 4{\cdot}1096 + 2{\cdot}1595 \times 10^{-4}(t-575) + 3{\cdot}400 \times 10^{-9}(t-575)^2 + 3{\cdot}204 \times 10^{-10}(t-575)^3. \quad (2)$$

The coefficient of linear expansion, defined by $\alpha = (1/a_t)\,(\mathrm{d}a_t/\mathrm{d}t)$ is given in Table 1 along with those determined by other workers.

Table 1. *Coefficient of linear expansion* $\alpha$ *of* LiF

| Temperature (°C) | $\alpha$(°C⁻¹) × 10⁶ | | | |
|---|---|---|---|---|
| | *a* | *b* | *c* | *d* |
| 0 | – | 33·8 | 32·7 | 34·7 |
| 50 | – | 34·9 | 34·9 | 36·0 |
| 100 | 36·5 | 36·3 | 37·2 | 37·3 |
| 200 | 40·3 | 39·8 | 41·5 | 40·0 |
| 300 | 44·6 | 44·3 | 45·7 | 42·7 |
| 400 | 49·3 | 49·8 | – | 45·8 |
| 500 | 54·6 | 56·2 | – | 48·8 |
| 600 | 60·3 | 63·7 | – | 52·0 |
| 650 | – | – | – | 54·0 |
| 700 | 66·5 | 72·1 | – | 56·2 |
| 750 | – | – | – | 59·4 |
| 800 | – | – | – | 63·9 |
| 850 | – | – | – | 69·6 |

(*a*) Eucken & Dannöhl (1934); (*b*) Sharma (1950); (*c*) Pathak & Pandya (1963); (*d*) Present result.

According to Grüneisen's theory the thermal expansion of alkali halides should be a slowly varying function of temperature, especially above the Debye temperature, and can be represented by

$$\alpha(T) = \alpha(T_0) + (\mathrm{d}\alpha/\mathrm{d}T)_{T=T_0}(T-T_0) + \Delta\alpha\,. \quad (3)$$

Here $\alpha(T)$ is the linear coefficient of thermal expansion at any temperature $T$ between $T_0$ and the melting point and $\Delta\alpha$ is the 'anomalous' part of the expansion which may be due to the thermally generated defects at high temperatures. In paper I it was shown that the energy of vacancy formation can be deduced from the slope of log $\Delta\alpha$ *versus* $1/T$.

It is assumed in this paper that the defects do not play any significant role below the temperature approximately corresponding to the 'knee' of the electrical conductivity *versus* $1/T$ plot. The 'knee' temperature for LiF is approximately 650°C. Thus it is assumed that equation (1) holds up to the melting point and that any deviation $\Delta\alpha$ from it is due to defects (Fig. 1). The plot of log $\Delta\alpha$ *versus* $1/T$ for LiF is shown in Fig. 2. The energy of formation, $W_s$, of the Schottky defects, determined from the slope, is 2·42 eV. The experimentally determined values obtained by different workers range from 2·34 to 2·68 eV (Haven, 1950; Barsis, Lilley & Taylor, 1967; Stoebe & Praat, 1967).

It was shown in paper I that the plot of the reduced expansion $[\alpha/(\alpha)_{m/2}]$ *versus* the reduced temperature $T/T_m$ gives a common curve for the three alkali halides

NaCl, KCl and CsBr. Here $T_m$ is the melting point and $(\alpha)_{m/2}$ is the coefficient of thermal expansion at $T=\frac{1}{2}T_m$. The common curve is given in Fig. 3 and points for LiF are shown on it. It can be seen that LiF also follows the 'law of corresponding states'.

It has been shown by Schauer (1964) that useful information can be derived from the measurement of the volume expansion coefficient $\beta$ of a material. $\beta$ can be obtained from the relation

$$\beta=\frac{\partial^2 F}{\partial V\partial T}\,. \tag{4}$$

If the free energy $F$ is given by

$$F=U_0+\sum_{\nu} kT\log\{1-\exp(-h\nu/kT)\} \tag{5}$$

where $U_0$ is the sum of the internal energy and the zero point energy of the crystal, it can be shown that

$$\frac{\beta}{\chi_T}=\frac{1}{V}\sum\gamma_i C_i=\frac{1}{V}\frac{\sum\gamma_i C_i}{\sum C_i}\sum C_i \tag{6}$$

where $C_i$ is the specific heat of a linear harmonic oscillator of frequency $\nu$ (Einstein function). Comparing this with the usual Grüneisen relation

$$\beta=\gamma\frac{C_v\chi_T}{V} \tag{7}$$

it is possible to define $\gamma$ as

$$\gamma=\frac{\sum\gamma_i C_i}{\sum C_i}\,. \tag{8}$$

Now

$$\gamma_i=-\frac{\mathrm{d}\log\nu_i}{\mathrm{d}\log V}=-\frac{V}{\nu_i}\frac{\mathrm{d}\nu_i}{\mathrm{d}V}\,,$$

hence

$$\frac{1}{\nu_i}\frac{\mathrm{d}\nu_i}{\mathrm{d}T}=-\gamma_i\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T}=-\gamma_i\beta\,. \tag{9}$$

Multiplying equation (9) by $C_i$ and summing gives

$$\sum C_i\frac{1}{\nu_i}\frac{\mathrm{d}\nu_i}{\mathrm{d}T}=-\beta\sum\gamma_i C_i$$

or

$$\sum C_i\frac{1}{\nu_i}\frac{\mathrm{d}\nu_i}{\mathrm{d}T}\Big/\sum C_i=-\gamma\beta\,. \tag{10}$$

The type of information which is available from the above equation differs in different temperature regions. For example, if $T\simeq\theta$ ($\theta$ = Debye temperature) the solid behaves classically and we have $C_i$ = constant. From equation (8) it follows for the high-temperature limit of $\gamma$ that

$$\gamma_\infty=\frac{1}{3N}\sum_{i=1}^{3N}\gamma_i\,. \tag{11}$$

In other words, $\gamma_\infty$ is simply the arithmetic mean of the individual $\gamma_i$'s. From equation (10) we get

$$\frac{1}{3N}\sum\frac{1}{\nu_i}\frac{\mathrm{d}\nu_i}{\mathrm{d}T}=-\gamma_\infty\beta \tag{12}$$

*i.e.* $-\gamma_\infty\beta$ gives the arithmetic mean of all frequency temperature coefficients. Integration of equation (12) yields

$$\frac{1}{3N}\sum\int_{T_0}^{T}\frac{\mathrm{d}\nu_i}{\nu_i}=-\gamma_\infty\int_{T_0}^{T}\beta\mathrm{d}T \tag{13}$$

or

$$\frac{1}{3N}\sum\log\frac{\nu_i}{\nu_{i0}}=-\gamma_\infty\int_{T_0}^{T}\beta\mathrm{d}T \tag{14}$$

where $\nu_i$ is the frequency of the $i$th mode at temperature $T$ and $\nu_{i0}$ is this frequency at a certain reference temperature $T_0$. This can be rewritten as

$$\log\left(\prod_i\frac{\nu_i}{\nu_{i0}}\right)^{1/3N}=-\gamma_\infty\int_{T_0}^{T}\beta\mathrm{d}T \tag{15}$$

or

$$\left(\prod_i\frac{\nu_i}{\nu_{i0}}\right)^{1/3N}=\exp\left(-\gamma_\infty\int_{T_0}^{T}\beta\mathrm{d}T\right). \tag{16}$$

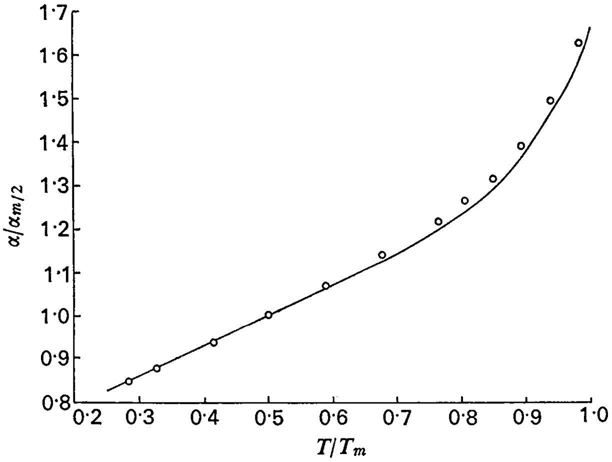

Fig. 3. Common plot of reduced expansion $\alpha/\alpha_{m/2}$ *versus* reduced temperature $T/T_m$ for all alkali halides (paper I) with points for LiF superimposed.

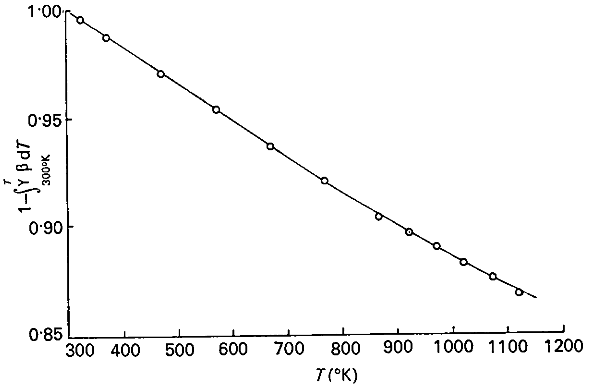

Fig. 4. Plot of geometric mean of frequency spectrum *versus* temperature.

As the exponential is small,

$$\left(\prod_i \frac{\nu_i}{\nu_{i0}}\right)^{1/3N} = 1-\gamma_\infty \int_{T_0}^{T} \beta \mathrm{d}T\,. \qquad (17)$$

Thus the integrated form yields the geometric mean of the frequency ratios $\nu_i/\nu_{i0}$.

Table 2. *Grüneisen constant* $\gamma$ *of* LiF

| Temperature (°C) | $\gamma$ |
|---|---|
| 0 | 1·63 |
| 50 | 1·59 |
| 100 | 1·50 |
| 200 | 1·42 |
| 300 | 1·34 |
| 400 | 1·26 |
| 500 | 1·14 |
| 600 | 0·98 |
| 650 | 0·91 |
| 700 | 0·83 |
| 750 | 0·77 |
| 800 | 0·73 |
| 850 | 0·71 |

Fig. 4 gives a plot of $1-\gamma_\infty \int_{T_0}^{T} \beta \mathrm{d}T$ *versus* $T$ for LiF ($\theta$=617°K). It is seen that the mean frequency decreases by about 13% between 300 and 1000°K. The values of $\gamma$ at different temperatures are given in Table 2. It is interesting to note that $\gamma$ decreases with temperature. In calculating $\gamma$ the values of $C_p$ used were those given by Douglas & Dever (1954) while the compressibility values were taken from Suss (1958). The accuracy claimed in the case of $C_p$ and compressibility is about $\frac{1}{2}$%.

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# A Simple Method for Locating Unoccupied Spaces in a Proposed Crystal Structure

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The presence of unoccupied space of sufficient cross section lying outside the van der Waals surfaces of the atoms in a crystal structure may mean that atoms have been omitted from the structure. A simple graphical method has been devised to display these voids. When such voids occur because of the omission of atoms from a trial structure, the significance of peaks in the difference map in the region of the void is enhanced. This makes it possible to detect and, within limits, to place poorly resolved atoms.

A common complication in the determination of molecular structures is the unexpected presence of molecules of solvent in the crystal. When the crystal is stable and the molecular formula of the major component is known, the presence of solvent of crystallization can be detected by density and unit-cell measurements. If the density cannot be measured or when the molecular weight of the material is high, difference Fourier maps are relied on to reveal solvent molecules. Comparison of the difference map with the structure is time-consuming for medium-sized structures, especially if the map has an irregular background. Electron density peaks due to atoms with only partial occupancy, large thermal parameters or actual positional disorder will be low and may not stand out from the background, and then may not be included in the final description of the structure. If solvent is expected, for example by analogy with a related compound, an extended space-filling model of the structure will reveal the possible sites (Powell, Watkin & Wilford, 1971) but this procedure is slow.

A graphic display has been devised to detect the omission of atoms from a structure. Scale drawings of sections through the whole unit cell are generated, with those areas falling within the van der Waals radius of each atom centre shaded in. Any voids within the cell are thus revealed, and the difference Fourier map for this region can be closely examined. A normal