Writing equation (17) as

$$R_H \propto \int_{-\infty}^{\infty} \exp\{-\tfrac{1}{2}[A'x_1^2 + B'x_1 + C']\} dx_1 \quad (19)$$

and putting

$$b_0 = a_1a_2 + a_7a_8$$
$$b_1 = a_2^2 + a_3^2 + a_8^2$$
$$b_2 = a_4^2$$
$$b_5 = a_1^2 + a_7^2 \quad (20)$$

we have

$$A' = 2b_0C + b_1C^2 + b_2E^2 + b_5 \quad (21a)$$
$$B' = 2[(b_0 + b_1C)D + b_2F] \quad (21b)$$
$$C' = b_1D^2 + b_2F^2 \quad (21c)$$

and on integration equation (19) becomes

$$R_H = R_o^h \exp\{-\tfrac{1}{2}[C' - B'^2/4A']\} . \quad (22)$$

From equations (21) it can be seen that

$$C' - B'^2/4A' = g_0D^2 + g_1F^2 + g_4DF \quad (23)$$

where

$$g_0 = b_1 - (b_0 + b_1C)^2/A'$$
$$g_1 = b_2 - (b_2E)^2/A'$$
$$g_4 = -2(b_0 + b_1C)b_2E/A' . \quad (24)$$

We can then write the resolution function in the form

$$R(\mathbf{Q}_0 + \Delta\mathbf{Q}) = R_0 \exp\{-\tfrac{1}{2} \sum_{k=1}^{3} \sum_{l=1}^{3} M_{kl}X_kX_l\}, \quad (25)$$

where $X_1 = \Delta Q_x, X_2 = \Delta Q_y, X_3 = \Delta q_z$ and we have

$$M_{kl} = \tfrac{1}{2}[2g_0d_kd_l + 2g_1f_kf_l + g_4(d_kf_l + d_lf_k)] \quad (26)$$

for $k$ and $l = 1$ or 2.

Since the vertical term in the resolution function is independent of the horizontal term we have

$$M_{k3} = M_{3l} = 0 \quad (27)$$

for $k, l \neq 3$
and the matrix element $M_{33}$ is as derived in paper I, equation (57):

$$M_{33} = \frac{a_{11}^2 a_{12}^2}{a_{11}^2 + a_{12}^2} \quad (28)$$

where

$$a_{11}^2 = \frac{1}{(4\tan^2\theta_M\eta'^2_M + \beta_0^2)k_I^2} + \frac{1}{\beta_1^2 k_I^2}$$
$$a_{12}^2 = \frac{1}{\beta_2^2 k_I^2} . \quad (29)$$

**Reference**

COOPER, M. J. & NATHANS, R. (1967). Acta Cryst. **23**, 357.

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# Neutron Diffraction Studies of Anharmonic Temperature Factors in BaF2

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Accurate integrated intensities for the Bragg reflexion of neutrons from BaF2 have been measured at various temperatures in the range 20–600°C and corrections for the effects of both thermal diffuse scattering and extinction have been applied. The experimental data show systematic deviations from the predictions of a model which assumes harmonic temperature factors for both types of atom, with observed intensities differing by up to ±60% from the calculated 'harmonic' values. Vibrational anharmonicity can be allowed for by using an effective one-particle potential of the form: $V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x^2 + y^2 + z^2) + \beta_j xyz$, where $x$, $y$ and $z$ are the coordinates defining the instantaneous displacement $\mathbf{r}$ of the nucleus of the $j$th atom and $\alpha_j$ and $\beta_j$ are the coefficients of the quadratic and cubic terms respectively in the potential expansion. The site symmetry of the atoms allows the anharmonicity parameter $\beta_j$ to be non-zero only for the fluorine atoms, and introduction of this single parameter brings the observed and calculated structure factors into very good agreement ($R \sim 1\%$) at all temperatures: the $R$ value obtained for a harmonic model increases from 1·8% at room temperature to 8·9% at 600°C. The value obtained for $\beta_F$ is $-3\cdot06 \times 10^{-12}$ erg.Å$^{-3}$ at room temperature, falling to $-2\cdot52 \times 10^{-12}$ erg.Å$^{-3}$ at 600°C. The present measurements provide no evidence for the existence of any appreciable anisotropic quartic, or higher-order, contributions to the temperature factors. The ratio of nuclear scattering lengths, $b_{Ba}/b_F$, was refined to 0·932 ($\pm 0\cdot004$), which gives a value for the nuclear scattering length of barium of $b_{Ba} = 0\cdot522$ ($\pm 0\cdot011$) × $10^{-12}$ cm, assuming $b_F = 0\cdot560$ ($\pm 0\cdot010$) × $10^{-12}$ cm.

## 1. Introduction

Anisotropy in the temperature factors of cubic crystals with atoms at sites of non-centric cubic symmetry has previously been observed by Willis and co-workers in their studies of UO2 (Willis, 1963; Rouse, Willis & Pryor, 1968) and CaF2 (Willis, 1965). In this paper we present the results of a neutron diffraction study of

similar anisotropic vibrational effects in $BaF_2$, which is isostructural with $UO_2$ and $CaF_2$, over the temperature range 20 to 600°C. The experimental results are analysed in terms of an effective one-particle potential which, in the case of the fluorine atoms, contains a cubic (third-order) anharmonic term consistent with the non-centric symmetry of the atomic site. The present measurements are more extensive than those on $UO_2$ and $CaF_2$ and, unlike the earlier work, the $BaF_2$ data have been corrected for the effects of both thermal diffuse scattering and extinction.

## 2. Theory

Anharmonic vibration in fluorite structures has been considered recently by Dawson, Hurley & Maslen (1967) using a treatment based on Dawson's generalized structure factor formulation (Dawson, 1967). These authors assume that the vibration of each atom $j$ is governed by an effective one-particle potential $V_j(\mathbf{r})$ which is of the form:

$$V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x^2 + y^2 + z^2)$$
$$+ \text{cubic and higher order terms}, \quad (1)$$

where $x$, $y$ and $z$ are the coordinates defining the instantaneous displacement $\mathbf{r}$ of the $j$th atom, the term in $x^2 + y^2 + z^2$ is the normal harmonic potential and the parameter $\alpha_j$ is related to the mean-square displacement of the atom in this potential*. The form of the cubic and higher order terms in equation (1) is dictated by the site symmetry of the atom concerned. In the case of the fluorine atoms with $\bar{4}3m$ site symmetry, the cubic term is of the form $\beta_F\, xyz$, where $\beta_F$ is a parameter related to the degree of tetrahedral distortion of the anionic smearing function, defined in equation (3). On the other hand, the $m3m$ site symmetry of the barium atoms does not allow any non-zero cubic term.

In the present study the measurements could be explained adequately without the introduction of terms of higher order than cubic and a potential was used of the form:

$$V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x^2 + y^2 + z^2) + \beta_j(xyz), \quad (2)$$

where $j$ refers either to the barium atom or the fluorine atom and $\beta_{Ba} = 0$.

The vibration of each atom can be considered in terms of a smearing function $t_j(\mathbf{r})$ defined as the probability of finding the atom at a distance $\mathbf{r}$ from its equilibrium position. Employing classical statistics we have that the smearing function is given by

$$t_j(\mathbf{r}) = N_j \exp\left[-(V_j(\mathbf{r}) - V_{0j})/k_B T\right] \quad (3)$$

where $k_B$ is Boltzmann's constant and the normalizing constant $N_j$ is given by

$$N_j = (2\pi k_B T/\alpha_j)^{-3/2}. \quad (4)$$

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* $\alpha_j$ includes the effect of thermal expansion so that this term in the potential is in fact a quasi-harmonic term [see §4(d)].

Equation (3) is expected to apply for temperatures greater than the Debye characteristic temperature ($\sim 300$°K for $BaF_2$: Gerlich, 1964).

In calculating the structure factors for a Bragg peak, the scattering amplitude of each atom is multiplied by the relevant temperature factor $T_j(\mathbf{S})$, which is the Fourier transform of $t_j(\mathbf{r})$, where $\mathbf{S}$ is the diffraction vector. For the fluorite structure, the reflexions can be divided into three groups depending upon the sum of the indices $h$, $k$ and $l$. The calculated structure factors for $BaF_2$ for these groups, assuming a potential of the form given in equation (2), are as follows.

$$F_c(4n \pm 1) = 4b_{Ba} \exp\left[-B_{Ba}(h^2 + k^2 + l^2)/4a^2\right]$$
$$\pm 8b_F \exp\left[-B_F(h^2 + k^2 + l^2)/4a^2\right]$$
$$\times \left(\frac{B_F}{4\pi a}\right)^3 \frac{hkl}{k_B T} \beta_F \quad (5a)$$

$$F_c(4n + 2) = 4b_{Ba} \exp\left[-B_{Ba}(h^2 + k^2 + l^2)/4a^2\right]$$
$$- 8b_F \exp\left[-B_F(h^2 + k^2 + l^2)/4a^2\right] \quad (5b)$$

$$F_c(4n) = 4b_{Ba} \exp\left[-B_{Ba}(h^2 + k^2 + l^2)/4a^2\right]$$
$$+ 8b_F \exp\left[-B_F(h^2 + k^2 + l^2)/4a^2\right], \quad (5c)$$

where $a$ is the unit-cell side ($\sim 6\cdot20$ Å at 20°C), $b_{Ba}$ and $b_F$ are the nuclear scattering amplitudes of barium and fluorine and $B_{Ba}$ and $B_F$ are the isotropic (harmonic) temperature factors:

$$B_j = 8\pi^2 k_B T/\alpha_j. \quad (6)$$

In equation (5a), the coefficient of the second exponential term is $+8b_F$ for the $4n+1$ reflexions and $-8b_F$ for the $4n-1$ reflexions.

The most significant effect on the Bragg reflexions of introducing the anharmonicity parameter $\beta_F$ is, therefore, to introduce an additional term in the structure factor for reflexions with $h+k+l=4n\pm1$. This additional term is proportional to $b_F\beta_F$, to the index product $h \times k \times l$, and approximately to the square of the absolute temperature.

Equations (5) also apply in X-ray diffraction with $b_{Ba}, b_F$ replaced by the atomic scattering factors $f_{Ba}, f_F$. However, there are two reasons why anharmonic effects are detected more readily with neutrons: (i) there is no $\sin\theta/\lambda$ form-factor dependence of $b_{Ba}$ and $b_F$ so that reflexions with high index products can be examined more easily with neutrons, and (ii) the anharmonic term is associated with the lighter fluorine atom which has a more favourable scattering amplitude for neutrons ($b_F/b_{Ba} = 1\cdot1$) than for X-rays ($f_F/f_{Ba} < 0\cdot2$).

## 3. Experimental measurements

The sample was a cylindrical single crystal of $BaF_2$ of radius 1·6 mm and length 7·0 mm, with its axis parallel to a crystallographic $\langle 110 \rangle$ axis. Two-dimensional $hkk$ intensity measurements were made with a Hilger & Watts MkII automatic neutron diffractometer using an incident wavelength of 1·038 Å. Preliminary meas-

urements were made without the furnace, from which it was established (by comparing observed and calculated intensities) that the following reflexions suffered from extinction at room temperature: all $4n$ reflexions, $4n \pm 1$ reflexions with $h^2 + k^2 + l^2 \leq 67$ and $4n + 2$ reflexions with $h^2 + k^2 + l^2 \leq 44$.

The crystal was then mounted in a sealed silica tube in a small split-coil platinum resistance furnace. The temperature of the hot zone between the coils was found to be constant to within less than $\pm 5°$ over the temperature range concerned and the uncertainty associated with each temperature measurement (see Tables 1 to 8) was related to the uniformity of the hot zone. The temperature of the sample was determined by a thermocouple placed in contact with it, and this thermocouple was also used to keep the temperature of the sample constant to within very narrow limits.

In view of the extinction apparent in the preliminary measurements, the lowest-angle reflexions measured thereafter were 511 for the $4n \pm 1$ reflexions and 222 for the $4n + 2$ reflexions, although a few higher-angle reflexions were omitted at some temperatures. The value of $2\theta$ was limited geometrically to be less than about $140°$, but all 'extinction-free' reflexions with sufficient intensity were measured out to this limit and in each case all equivalent reflexions in the $\langle 110 \rangle$ zone were measured. The $4n$ reflexions were omitted from the analysis because of their severe extinction at the lower temperatures.

The reflexions were scanned in a $\theta - 2\theta$ mode using a rectangular detector aperture of width $9 \cdot 0$ mm ($9 \cdot 5$ mm at $596°C$) and height $13 \cdot 0$ mm, at a distance of $23 \cdot 0$ cm from the sample. The scan range was $\pm 1 \cdot 2°$ for all reflexions except $11,1,1$ and $5,7,7$ for which it was $\pm 1 \cdot 6°$. The background was measured by making a similar scan with the crystal misset by several degrees, thus taking into account any isotropic scattering from the furnace assembly. Wherever practicable, reflexions were measured over a sufficient period of time to provide a statistical precision for the background-corrected intensity of less than 1 to $1\frac{1}{2}\%$. No attempt was made to determine the absolute scale of the measurements although this scale remained constant over the series of measurements reported here, which were made at 20, 88, 159, 239, 317, 398 and $596°C$.

Considerable care was exercised in these measurements in order to achieve a set of data which was considered reliable to a level of accuracy determined primarily by the statistical precision. In view of the present interest in attempts to collect 'accurate' diffraction data, the techniques and precautions adopted in the present study will be discussed in detail elsewhere (Cooper & Rouse, 1968a) and we shall concentrate in this paper on the analysis of the results.

### 4. Analysis

#### (a) Correction for thermal diffuse scattering.

It is well known that the thermal diffuse scattering (TDS) which peaks around the Bragg reflexions can become quite appreciable, particularly at high scattering angles and at high temperatures. A correction for first-order TDS was therefore evaluated by the method of Cooper & Rouse (1968b). The value of $\kappa$ [Cooper & Rouse, 1968b, equation (3)] was calculated from the elastic constant data of Gerlich (1964) for temperatures between $4 \cdot 2$ and $300°K$, and values above room temperature were obtained by extrapolation (see Table 8). The volume of integration in reciprocal space was determined by the solid angle subtended by the detector aperture at the sample and by the angular range of the scan, and allowance was made for instrumental resolution. The TDS contribution to the peak scan was found to be equivalent, to a fairly good approximation over the range of $\theta$ concerned, to a negative contribution to the mean temperature factor. It is therefore only the thermal parameters which are affected to any large extent if TDS is ignored, but to confirm this the data were analysed both with and without the correction for TDS.

#### (b) Correction for extinction.

Plots of $\log |F_o|$ against $h^2 + k^2 + l^2$ at the various temperatures showed the expected systematic deviations of the $4n \pm 1$ reflexions from the linear plot which would correspond to a harmonic model. The data were then analysed in terms of the anharmonic model, equations (5), using a full-matrix least-squares computer program written by Dr B. H. Bracher. The program allows refinement of any combination of the five parameters $b_{Ba}/b_F$, $B_{Ba}$, $B_F$, $\beta_F$ and the overall scale factor.

Analyses at each temperature with all parameters free were combined to refine the value of $b_{Ba}$, assuming a value of $b_F = 0 \cdot 560 \times 10^{-12}$ cm (Donaldson, 1964), and the analyses were then repeated with $b_{Ba}$ fixed ($= 0 \cdot 522 \times 10^{-12}$ cm). In these analyses the observed structure factors were weighted according to their statistical precision although the results obtained were very insensitive to the weighting scheme used. Reflexions which were judged to be suffering from extinction, based on a comparison of calculated and observed structure factors, were given a negligible weight.

Under these circumstances, the choice of a cut-off point for extinction is necessarily somewhat subjective and may affect the values of the derived parameters because of remaining small extinction effects. It was decided, therefore, to investigate the possibility of applying a correction for extinction using the theory of Zachariasen (1967).

We can rewrite Zachariasen's equation (1) as

$$F_c'^2 = F_c^2 y, \qquad (7)$$

where $F_c'$ is the calculated extinguished structure factor, $F_c$ is the calculated (extinction-free) structure factor, and, for convenience, we shall consider $y$ to take the form:

$$y = (1 + 2x)^{-1/2} \qquad (8)$$

since the various forms given by Zachariasen's equation (47)] cannot be distinguished for small $x$.

Here $x$ is given by

$$x = \eta Q[\bar{t} + (\bar{T} - \bar{t}) / \sqrt{1 + (\eta/g)^2}], \tag{9}$$

where $\eta = 2\bar{t}_\perp / 3\lambda$, $Q$ is the well known crystallographic quantity which is proportional to $F_c^2 \operatorname{cosec} 2\theta$, $\bar{t}$ is the mean path length through a single domain, $\bar{T}$ is the mean path length through the crystal and $g$ is related to the half-width of the domain distribution $\Delta$ by the equation

$$\Delta = g^{-1}(\ln 2/2\pi)^{1/2}. \tag{10}$$

For the cylindrical crystal used, $\bar{T}$ is constant for all $hkk$ reflexions, so that $x$ is proportional to $F_c^2 \operatorname{cosec} 2\theta$.

In order to correct for extinction we must write

$$F_{\text{corr}}^2 = F_o^2 y^{-1} \tag{11}$$

and consider $y$ to be a function of the observed structure factor $F_o$. Using asterisks to represent quantities expressed in terms of $F_o$, that is, writing $x$ as $x^*$ and replacing $Q$ ($\propto F_c^2$) by $Q^*(\propto F_o^2)$, we then have

$$F_{\text{corr}}^2 = F_o^2[\sqrt{1 + x^{*2}} + x^*] \tag{12}$$

and

$$x^* = cF_o^2 \operatorname{cosec} 2\theta, \tag{13}$$

where $c$ is a constant.

The value of $c$ was estimated with the use of equations (12) and (13) for the strongest reflexions, known to be extinguished, by replacing $F_{\text{corr}}$ by the calculated structure factor $F_c$. Using this value of $c$, reflexions which had been presumed extinction-free were found to have a small amount of extinction and a recalculation of $c$ was made to take this into account. The value finally obtained for $c$ was $0 \cdot 0357 \times 10^{24}$ cm$^{-2}$. $F_{\text{corr}}$ was then determined for all reflexions by using equations

(12) and (13) and excellent agreement was obtained for all reflexions for which $x^*$ was less than about $0 \cdot 16$. Apart from the $4n$ reflexions, the only measured reflexions outside this range were the 511 reflexion at 20°C and the 222 reflexion at temperatures up to 400°C, and these were given negligible weight in the subsequent analysis.

(c) Final parameters.

The analysis was then repeated with all parameters free and the value of $b_{\text{Ba}}$ was determined to be $0 \cdot 522$ ($\pm 0 \cdot 002) \times 10^{-12}$ cm. Further analysis with $b_{\text{Ba}}$ fixed at this value showed that there was no significant variation in the scaling factors at all temperatures (Fig. 1) and a final analysis was carried out with the scaling factor fixed at a weighted mean value. In determining the appropriate values of $b_{\text{Ba}}$ and the scaling factor, the data obtained at 596 °C were not included because of the higher errors associated with them and because of the small number of $4n + 2$ reflexions which were measured at this temperature. No absorption correction was necessary, as $\mu R$ was extremely small ($\ll 0 \cdot 01$).

The various structure factors for this final analysis are listed in Tables 1 to 7. In each case, three observed structure factors are listed; the first is the uncorrected value, the second is the value corrected for TDS, and the third is the value corrected for both TDS and extinction. The next column is the estimated standard deviation of the observed structure factors, based on counting statistics, and the last two columns are the calculated structure factors for the anharmonic model and for the harmonic model having the same parameters except for $\beta_F = 0$. Further refinement with $\beta_F = 0$ gave no significant changes.

Table 8 lists the parameters obtained at the various temperatures, together with their standard deviations; it also lists the $R$ indices for both the anharmonic and
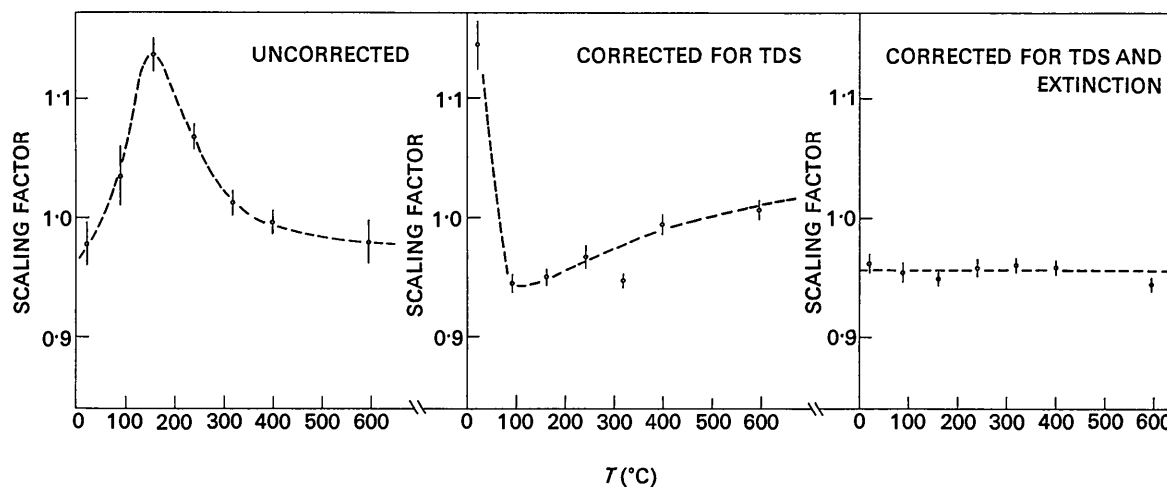


Fig. 1. Temperature dependence of the scaling factor derived from a least-squares analysis with four adjustable parameters. Vertical lines give the estimated standard deviations from the analysis. Introducing both a TDS and an extinction correction leads to a scaling factor which is invariant with temperature.

the harmonic models for the different types of reflexions, where $R = \Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$. The introduction of the single anharmonicity parameter reduces $R$ to a value consistent with the experimental accuracy at all temperatures and no further systematic effects were apparent.

Table 1. *Neutron structure factors for* BaF$_2$ *at* 20°C ($\pm$2°)

| | | | $F_o$ | | | | $F_c$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F_o)$ | Anharmonic model | Harmonic model |
| 5 | 1 | 1 | 1·674 | 1·660 | 1·778 | 0·006† | 1·819 | 1·822 |
| 3 | 3 | 3 | * | * | * | * | * | * |
| 7 | 1 | 1 | 1·592 | 1·563 | 1·643 | 0·006 | 1·644 | 1·640 |
| 1 | 5 | 5 | * | * | * | * | * | * |
| 3 | 5 | 5 | * | * | * | * | * | * |
| 7 | 3 | 3 | 1·505 | 1·474 | 1·537 | 0·006 | 1·560 | 1·528 |
| 5 | 5 | 5 | 1·417 | 1·377 | 1·428 | 0·006 | 1·414 | 1·475 |
| 9 | 1 | 1 | 1·415 | 1·369 | 1·420 | 0·006 | 1·420 | 1·424 |
| 9 | 3 | 3 | 1·284 | 1·242 | 1·283 | 0·006 | 1·294 | 1·327 |
| 1 | 7 | 7 | 1·328 | 1·279 | 1·324 | 0·006 | 1·307 | 1·327 |
| 7 | 5 | 5 | 1·371 | 1·325 | 1·374 | 0·006 | 1·399 | 1·327 |
| 3 | 7 | 7 | 1·349 | 1·295 | 1·346 | 0·006 | 1·338 | 1·281 |
| 11 | 1 | 1 | 1·220 | 1·165 | 1·210 | 0·003 | 1·198 | 1·194 |
| 5 | 7 | 7 | 1·116 | 1·066 | 1·100 | 0·003 | 1·108 | 1·194 |
| 2 | 2 | 2 | * | * | * | * | * | * |
| 6 | 0 | 0 | 1·606 | 1·586 | 1·678 | 0·005 | 1·691 | 1·691 |
| 2 | 4 | 4 | 1·619 | 1·599 | 1·693 | 0·005 | 1·691 | 1·691 |
| 6 | 2 | 2 | 1·525 | 1·501 | 1·575 | 0·006 | 1·568 | 1·568 |
| 6 | 4 | 4 | 1·234 | 1·204 | 1·238 | 0·005 | 1·246 | 1·246 |
| 2 | 6 | 6 | 1·158 | 1·130 | 1·159 | 0·005 | 1·152 | 1·152 |
| 10 | 0 | 0 | 0·919 | 0·883 | 0·898 | 0·003 | 0·904 | 0·904 |
| 6 | 6 | 6 | 0·865 | 0·831 | 0·844 | 0·003 | 0·831 | 0·831 |
| 10 | 2 | 2 | 0·847 | 0·814 | 0·826 | 0·003 | 0·831 | 0·831 |

\* Not measured at this temperature.
† Given negligible weight in analysis.

Table 2. *Neutron structure factors for* BaF$_2$ *at* 88°C ($\pm$3°)

| | | | $F_o$ | | | | $F_c$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F_o)$ | Anharmonic model | Harmonic model |
| 5 | 1 | 1 | 1·686 | 1·669 | 1·789 | 0·005 | 1·783 | 1·788 |
| 3 | 3 | 3 | * | * | * | * | * | * |
| 7 | 1 | 1 | 1·551 | 1·516 | 1·589 | 0·006 | 1·586 | 1·581 |
| 1 | 5 | 5 | 1·543 | 1·507 | 1·578 | 0·006 | 1·561 | 1·581 |
| 3 | 5 | 5 | 1·560 | 1·518 | 1·588 | 0·006 | 1·574 | 1·517 |
| 7 | 3 | 3 | 1·464 | 1·427 | 1·486 | 0·006 | 1·501 | 1·456 |
| 5 | 5 | 5 | 1·319 | 1·273 | 1·314 | 0·007 | 1·315 | 1·398 |
| 9 | 1 | 1 | 1·353 | 1·299 | 1·342 | 0·006 | 1·336 | 1·342 |
| 9 | 3 | 3 | 1·190 | 1·142 | 1·173 | 0·007 | 1·192 | 1·236 |
| 1 | 7 | 7 | 1·239 | 1·183 | 1·218 | 0·006 | 1·209 | 1·236 |
| 7 | 5 | 5 | 1·325 | 1·269 | 1·313 | 0·006 | 1·331 | 1·236 |
| 3 | 7 | 7 | 1·286 | 1·222 | 1·265 | 0·008 | 1·262 | 1·186 |
| 11 | 1 | 1 | 1·144 | 1·081 | 1·117 | 0·008 | 1·098 | 1·093 |
| 5 | 7 | 7 | 1·002 | 0·947 | 0·971 | 0·006 | 0·983 | 1·093 |
| 2 | 2 | 2 | * | * | * | * | * | * |
| 6 | 0 | 0 | 1·554 | 1·530 | 1·613 | 0·005 | 1·589 | 1·589 |
| 2 | 4 | 4 | 1·518 | 1·495 | 1·573 | 0·005 | 1·589 | 1·589 |
| 6 | 2 | 2 | 1·436 | 1·408 | 1·469 | 0·006 | 1·452 | 1·452 |
| 6 | 4 | 4 | 1·095 | 1·063 | 1·086 | 0·007 | 1·100 | 1·100 |
| 2 | 6 | 6 | 1·029 | 0·999 | 1·018 | 0·007 | 1·000 | 1·000 |
| 10 | 0 | 0 | 0·752 | 0·716 | 0·724 | 0·008 | 0·742 | 0·742 |
| 6 | 6 | 6 | 0·689 | 0·657 | 0·663 | 0·008 | 0·669 | 0·669 |
| 10 | 2 | 2 | 0·681 | 0·649 | 0·655 | 0·008 | 0·669 | 0·669 |

\* Not measured at this temperature.

(*d*) *Temperature dependence of the potential parameters.*
The temperature dependence of the parameters $\alpha_{Ba}$, $\alpha_F$ and $\beta_F$ is illustrated in Figs. 2 and 3. All three parameters decrease with rising temperature. Expressing this variation as a linear dependence on temperature, the observed values can be expressed approx-

Table 3. *Neutron structure factors for* $BaF_2$ *at* 159 °C ($\pm 3°$)

| | | | $F_o$ | | | | $F_c$ | |
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F_o)$ | Anharmonic model | Harmonic model |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 1 | 1·649 | 1·628 | 1·740 | 0·006 | 1·723 | 1·729 |
| 3 | 3 | 3 | 1·660 | 1·639 | 1·752 | 0·006 | 1·764 | 1·729 |
| 7 | 1 | 1 | 1·482 | 1·441 | 1·503 | 0·006 | 1·492 | 1·484 |
| 1 | 5 | 5 | 1·455 | 1·414 | 1·472 | 0·006 | 1·459 | 1·484 |
| 3 | 5 | 5 | 1·475 | 1·426 | 1·486 | 0·006 | 1·482 | 1·411 |
| 7 | 3 | 3 | 1·387 | 1·343 | 1·391 | 0·006 | 1·396 | 1·341 |
| 5 | 5 | 5 | 1·182 | 1·132 | 1·161 | 0·007 | 1·174 | 1·274 |
| 9 | 1 | 1 | 1·243 | 1·184 | 1·217 | 0·006 | 1·205 | 1·211 |
| 9 | 3 | 3 | 1·064 | 1·010 | 1·032 | 0·007 | 1·043 | 1·094 |
| 1 | 7 | 7 | 1·096 | 1·037 | 1·060 | 0·007 | 1·063 | 1·094 |
| 7 | 5 | 5 | 1·220 | 1·158 | 1·192 | 0·005 | 1·205 | 1·094 |
| 3 | 7 | 7 | 1·166 | 1·096 | 1·126 | 0·006 | 1·126 | 1·040 |
| 11 | 1 | 1 | 1·002 | 0·936 | 0·959 | 0·006 | 0·945 | 0·939 |
| 5 | 7 | 7 | 0·842 | 0·787 | 0·801 | 0·007 | 0·817 | 0·939 |
| 2 | 2 | 2 | 1·778 | 1·771 | 1·976 | 0·006† | 2·004 | 2·004 |
| 6 | 0 | 0 | 1·435 | 1·408 | 1·473 | 0·006 | 1·445 | 1·445 |
| 2 | 4 | 4 | 1·405 | 1·379 | 1·440 | 0·006 | 1·445 | 1·445 |
| 6 | 2 | 2 | 1·276 | 1·246 | 1·288 | 0·006 | 1·291 | 1·291 |
| 6 | 4 | 4 | 0·913 | 0·882 | 0·895 | 0·008 | 0·908 | 0·908 |
| 2 | 6 | 6 | 0·818 | 0·793 | 0·803 | 0·008 | 0·803 | 0·803 |
| 10 | 0 | 0 | 0·556 | 0·524 | 0·527 | 0·010 | 0·543 | 0·543 |
| 6 | 6 | 6 | 0·493 | 0·466 | 0·468 | 0·011 | 0·473 | 0·473 |
| 10 | 2 | 2 | 0·496 | 0·471 | 0·473 | 0·011 | 0·473 | 0·473 |

† Given negligible weight in analysis.

Table 4. *Neutron structure factors for* $BaF_2$ *at* 239 °C ($\pm 4°$)

| | | | $F_o$ | | | | $F_c$ | |
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F_o)$ | Anharmonic model | Harmonic model |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 1 | 1·564 | 1·540 | 1·634 | 0·005 | 1·647 | 1·656 |
| 3 | 3 | 3 | * | * | * | * | * | * |
| 7 | 1 | 1 | 1·384 | 1·339 | 1·390 | 0·006 | 1·378 | 1·368 |
| 1 | 5 | 5 | 1·327 | 1·282 | 1·326 | 0·006 | 1·334 | 1·368 |
| 3 | 5 | 5 | 1·387 | 1·332 | 1·379 | 0·006 | 1·376 | 1·284 |
| 7 | 3 | 3 | 1·279 | 1·230 | 1·266 | 0·006 | 1·275 | 1·204 |
| 5 | 5 | 5 | 1·041 | 0·989 | 1·008 | 0·006 | 1·004 | 1·130 |
| 9 | 1 | 1 | 1·105 | 1·042 | 1·064 | 0·006 | 1·052 | 1·060 |
| 9 | 3 | 3 | 0·895 | 0·843 | 0·855 | 0·005 | 0·873 | 0·934 |
| 1 | 7 | 7 | 0·950 | 0·889 | 0·904 | 0·005 | 0·897 | 0·934 |
| 7 | 5 | 5 | 1·095 | 1·029 | 1·052 | 0·004 | 1·065 | 0·934 |
| 3 | 7 | 7 | 1·041 | 0·967 | 0·987 | 0·006 | 0·976 | 0·876 |
| 11 | 1 | 1 | 0·849 | 0·782 | 0·795 | 0·004 | 0·778 | 0·771 |
| 5 | 7 | 7 | 0·669 | 0·617 | 0·624 | 0·005 | 0·634 | 0·771 |
| 2 | 2 | 2 | 1·704 | 1·696 | 1·878 | 0·006† | 1·927 | 1·927 |
| 6 | 0 | 0 | 1·273 | 1·245 | 1·290 | 0·006 | 1·276 | 1·276 |
| 2 | 4 | 4 | 1·258 | 1·230 | 1·272 | 0·006 | 1·276 | 1·276 |
| 6 | 2 | 2 | 1·121 | 1·090 | 1·118 | 0·006 | 1·105 | 1·105 |
| 6 | 4 | 4 | 0·725 | 0·698 | 0·705 | 0·006 | 0·701 | 0·701 |
| 2 | 6 | 6 | 0·607 | 0·592 | 0·596 | 0·005 | 0·596 | 0·596 |
| 10 | 0 | 0 | 0·349 | 0·325 | 0·326 | 0·006 | 0·349 | 0·349 |
| 6 | 6 | 6 | * | * | * | * | * | * |
| 10 | 2 | 2 | * | * | * | * | * | * |

\* Not measured at this temperature.
† Given negligible weight in analysis.

imately as

$$\alpha_{Ba}=\alpha_{Ba}^0(1-3\cdot6\times10^{-4}T) \tag{14a}$$

$$\alpha_{F}=\alpha_{F}^0(1-3\cdot7\times10^{-4}T) \tag{14b}$$

$$\beta_{F}=\beta_{F}^0(1-3\cdot8\times10^{-4}T)\,, \tag{14c}$$

where the zero superscripts indicate the values at $0\,^\circ$C

and $T$ is the temperature in $^\circ$C. Equations (14) are represented by the broken lines in Figs. 2 and 3.

The temperature dependence of $\alpha_{Ba}, \alpha_{F}, \beta_{F}$ can be explained by using the 'quasi-harmonic approximation', which assumes that the change in volume arising from

Table 5. *Neutron structure factors for* $BaF_2$ *at* $317\,^\circ$C $(\pm4^\circ)$

| | | | $F_o$ | | | | $F_c$ | |
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F)$ | Anharmonic model | Harmonic model |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 1 | 1·542 | 1·515 | 1·600 | 0·006 | 1·588 | 1·600 |
| 3 | 3 | 3 | 1·574 | 1·546 | 1·642 | 0·005 | 1·666 | 1·600 |
| 7 | 1 | 1 | 1·318 | 1·267 | 1·309 | 0·005 | 1·294 | 1·282 |
| 1 | 5 | 5 | 1·254 | 1·205 | 1·241 | 0·006 | 1·239 | 1·282 |
| 3 | 5 | 5 | 1·326 | 1·265 | 1·307 | 0·006 | 1·306 | 1·191 |
| 7 | 3 | 3 | 1·224 | 1·168 | 1·200 | 0·006 | 1·192 | 1·106 |
| 5 | 5 | 5 | 0·907 | 0·854 | 0·866 | 0·007 | 0·874 | 1·027 |
| 9 | 1 | 1 | 0·992 | 0·927 | 0·943 | 0·006 | 0·944 | 0·954 |
| 9 | 3 | 3 | 0·780 | 0·730 | 0·738 | 0·007 | 0·753 | 0·823 |
| 1 | 7 | 7 | 0·832 | 0·770 | 0·780 | 0·007 | 0·781 | 0·823 |
| 7 | 5 | 5 | 1·021 | 0·948 | 0·966 | 0·006 | 0·974 | 0·823 |
| 3 | 7 | 7 | 0·944 | 0·866 | 0·881 | 0·006 | 0·878 | 0·764 |
| 11 | 1 | 1 | 0·737 | 0·670 | 0·678 | 0·006 | 0·666 | 0·659 |
| 5 | 7 | 7 | 0·548 | 0·499 | 0·502 | 0·008 | 0·510 | 0·659 |
| 2 | 2 | 2 | 1·671 | 1·661 | 1·830 | 0·006† | 1·862 | 1·862 |
| 6 | 0 | 0 | 1·144 | 1·114 | 1·146 | 0·006 | 1·142 | 1·142 |
| 2 | 4 | 4 | 1·138 | 1·108 | 1·139 | 0·006 | 1·142 | 1·142 |
| 6 | 2 | 2 | 0·970 | 0·939 | 0·957 | 0·006 | 0·962 | 0·962 |
| 6 | 4 | 4 | 0·572 | 0·551 | 0·554 | 0·008 | 0·551 | 0·551 |
| 2 | 6 | 6 | 0·457 | 0·451 | 0·453 | 0·010 | 0·449 | 0·449 |
| 10 | 0 | 0 | * | * | * | * | * | * |
| 6 | 6 | 6 | * | * | * | * | * | * |
| 10 | 2 | 2 | * | * | * | * | * | * |

\* Not measured at this temperature.
† Given negligible weight in analysis.

Table 6. *Neutron structure factors for* $BaF_2$ *at* $398\,^\circ$C $(\pm5^\circ)$

| | | | $F_o$ | | | | $F_c$ | |
| | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F)$ | Anharmonic model | Harmonic model |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 1 | 1·468 | 1·438 | 1·514 | 0·006 | 1·511 | 1·526 |
| 3 | 3 | 3 | 1·547 | 1·515 | 1·604 | 0·006 | 1·610 | 1·526 |
| 7 | 1 | 1 | 1·211 | 1·157 | 1·189 | 0·005 | 1·187 | 1·172 |
| 1 | 5 | 5 | 1·151 | 1·099 | 1·126 | 0·005 | 1·121 | 1·172 |
| 3 | 5 | 5 | 1·251 | 1·184 | 1·217 | 0·005 | 1·208 | 1·074 |
| 7 | 3 | 3 | 1·123 | 1·062 | 1·085 | 0·005 | 1·082 | 0·984 |
| 5 | 5 | 5 | 0·764 | 0·713 | 0·720 | 0·005 | 0·731 | 0·901 |
| 9 | 1 | 1 | 0·869 | 0·803 | 0·813 | 0·003 | 0·814 | 0·825 |
| 9 | 3 | 3 | 0·658 | 0·607 | 0·612 | 0·005 | 0·619 | 0·692 |
| 1 | 7 | 7 | 0·709 | 0·648 | 0·654 | 0·005 | 0·648 | 0·692 |
| 7 | 5 | 5 | 0·903 | 0·826 | 0·838 | 0·004 | 0·850 | 0·692 |
| 3 | 7 | 7 | 0·819 | 0·742 | 0·751 | 0·004 | 0·750 | 0·634 |
| 11 | 1 | 1 | 0·616 | 0·552 | 0·556 | 0·005 | 0·538 | 0·532 |
| 5 | 7 | 7 | 0·431 | 0·387 | 0·389 | 0·006 | 0·385 | 0·532 |
| 2 | 2 | 2 | * | * | * | * | * | * |
| 6 | 0 | 0 | 0·996 | 0·966 | 0·986 | 0·005 | 0·992 | 0·992 |
| 2 | 4 | 4 | 0·998 | 0·968 | 0·989 | 0·005 | 0·992 | 0·992 |
| 6 | 2 | 2 | 0·818 | 0·788 | 0·798 | 0·004 | 0·804 | 0·804 |
| 6 | 4 | 4 | 0·426 | 0·412 | 0·413 | 0·006 | 0·399 | 0·399 |
| 2 | 6 | 6 | 0·309 | 0·317 | 0·318 | 0·007 | 0·305 | 0·305 |
| 10 | 0 | 0 | * | * | * | * | * | * |
| 6 | 6 | 6 | * | * | * | * | * | * |
| 10 | 2 | 2 | * | * | * | * | * | * |

\* Not measured at this temperature.

thermal expansion gives rise to the same proportional change of frequency of each normal mode of vibration. The quasi-harmonic approximation leads to the equations:

$$\alpha_{Ba}/\alpha_{Ba}^0 = \alpha_F/\alpha_F^0 = \beta_F/\beta_F^0 = 1 - 2\gamma\chi T, \qquad (15)$$

where $\gamma$ is the Grüneisen constant and $\chi$ is the volume coefficient of expansion (Willis, 1968). Equation (15) applies only in the high-temperature (classical) range

above the Debye characteristic temperature, so that, if $T$ is in °C, $\alpha_{Ba}^0, \alpha_F^0, \beta_F^0$ refer to the values extrapolated from high temperatures to 0 °C. Comparing equations (15) and (16) we note that

$$\gamma\chi \simeq 1\cdot8 \times 10^{-4},$$

and inserting the average value of the expansion coefficient $\chi$ ($=87\cdot0 \times 10^{-6}/$°C) over the temperature range concerned (Sirdeshmukh & Deshpande, 1964)

Table 7. *Neutron structure factors for* $BaF_2$ *at* 596 °C ($\pm6$°)

| | | | | $F_o$ | | | | $F_c$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Corrected for | | | | |
| $h$ | $k$ | $l$ | Uncorrected | TDS | TDS and extinction | $\sigma(F)$ | Anharmonic model | Harmonic model |
| 5 | 1 | 1 | 1·370 | 1·330 | 1·390 | 0·005 | 1·372 | 1·397 |
| 3 | 3 | 3 | 1·506 | 1·462 | 1·542 | 0·005 | 1·532 | 1·397 |
| 7 | 1 | 1 | 1·060 | 0·994 | 1·014 | 0·004 | 1·012 | 0·992 |
| 1 | 5 | 5 | 0·982 | 0·920 | 0·936 | 0·006 | 0·920 | 0·992 |
| 3 | 5 | 5 | 1·130 | 1·047 | 1·070 | 0·006 | 1·063 | 0·885 |
| 7 | 3 | 3 | 0·971 | 0·896 | 0·910 | 0·005 | 0·913 | 0·789 |
| 5 | 5 | 5 | 0·543 | 0·493 | 0·495 | 0·006 | 0·500 | 0·704 |
| 9 | 1 | 1 | 0·671 | 0·602 | 0·606 | 0·006 | 0·616 | 0·628 |
| 9 | 3 | 3 | 0·462 | 0·412 | 0·413 | 0·007 | 0·424 | 0·500 |
| 1 | 7 | 7 | 0·500 | 0·443 | 0·445 | 0·006 | 0·454 | 0·500 |
| 7 | 5 | 5 | 0·723 | 0·638 | 0·643 | 0·007 | 0·663 | 0·500 |
| 3 | 7 | 7 | 0·632 | 0·552 | 0·556 | 0·005 | 0·560 | 0·446 |
| 11 | 1 | 1 | * | * | * | * | * | * |
| 5 | 7 | 7 | * | * | * | * | * | * |
| 2 | 2 | 2 | 1·498 | 1·483 | 1·603 | 0·004 | 1·597 | 1·597 |
| 6 | 0 | 0 | 0·687 | 0·658 | 0·664 | 0·005 | 0·673 | 0·673 |
| 2 | 4 | 4 | 0·704 | 0·675 | 0·682 | 0·005 | 0·673 | 0·673 |
| 6 | 2 | 2 | 0·498 | 0·474 | 0·476 | 0·007 | 0·482 | 0·482 |
| 6 | 4 | 4 | * | * | * | * | * | * |
| 2 | 6 | 6 | * | * | * | * | * | * |
| 10 | 0 | 0 | * | * | * | * | * | * |
| 6 | 6 | 6 | * | * | * | * | * | * |
| 10 | 2 | 2 | * | * | * | * | * | * |

* Not measured at this temperature.

Table 8. *Parameters and R indices for* $BaF_2$

$\pm \varepsilon(T)$ is the estimated maximum error in measured temperature $T$.
$\sigma(p)$ is the estimated standard deviation of the parameter $p$.

| Temperature | | 20 °C | 88 °C | 159 °C | 239 °C | 317 °C | 398 °C | 596 °C |
|---|---|---|---|---|---|---|---|---|
| $\varepsilon(T)$ | (°C) | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| $\kappa \times 10^{11}$ | (dyn$^{-1}$ cm$^2$) | 0·910 | 0·928 | 0·951 | 0·980 | 1·013 | 1·051 | 1·164 |
| $B_{Ba}$ | (Å$^2$) | 0·678 | 0·790 | 0·984 | 1·237 | 1·440 | 1·720 | 2·255 |
| $\sigma(B_{Ba})$ | (Å$^2$) | 0·005 | 0·006 | 0·006 | 0·006 | 0·007 | 0·005 | 0·011 |
| $B_F$ | (Å$^2$) | 1·048 | 1·238 | 1·537 | 1·924 | 2·255 | 2·684 | 3·684 |
| $\sigma(B_F)$ | (Å$^2$) | 0·004 | 0·007 | 0·007 | 0·008 | 0·009 | 0·008 | 0·014 |
| $\alpha_{Ba}$ } $\times 10^{12}$ | (erg Å$^{-2}$) | 4·711 | 4·977 | 4·785 | 4·511 | 4·464 | 4·251 | 4·198 |
| $\sigma(\alpha_{Ba})$ } | (erg Å$^{-2}$) | 0·035 | 0·040 | 0·027 | 0·023 | 0·020 | 0·013 | 0·020 |
| $\alpha_F$ } $\times 10^{12}$ | (erg Å$^{-2}$) | 3·045 | 3·177 | 3·063 | 2·899 | 2·851 | 2·724 | 2·570 |
| $\sigma(\alpha_F)$ } | (erg Å$^{-2}$) | 0·012 | 0·017 | 0·014 | 0·013 | 0·012 | 0·008 | 0·010 |
| $-\beta_F$ } $\times 10^{12}$ | (erg Å$^{-3}$) | 3·056 | 3·418 | 3·030 | 2·777 | 2·823 | 2·603 | 2·520 |
| $\sigma(\beta_F)$ } | (erg Å$^{-3}$) | 0·258 | 0·267 | 0·155 | 0·121 | 0·097 | 0·059 | 0·074 |
| $R$(all) | anharmonic | 0·75% | 1·01% | 0·85% | 0·99% | 0·73% | 0·78% | 1·09% |
| $R(4n+2)$ | anharmonic | 0·60% | 1·43% | 0·96% | 1·09% | 0·44% | 1·15% | 0·88% |
| $R(4n\pm1)$ | anharmonic | 0·86% | 0·81% | 0·81% | 0·95% | 0·81% | 0·68% | 1·17% |
| $R$(all) | harmonic | 1·84% | 2·65% | 3·24% | 4·50% | 5·55% | 7·03% | 8·91% |
| $R(4n\pm1)$ | harmonic | 2·74% | 3·24% | 4·00% | 5·76% | 7·04% | 8·59% | 11·64% |

we obtain $y = 2\cdot1$. There is no independent experimental value of $y$ for comparison, but the present estimate of $y$ lies well within the range, $1\cdot25$ to $2\cdot50$, which is appropriate for the common simple ionic solids (Kittel, 1966).

## 5. Summary

The neutron diffraction examination of $BaF_2$ has shown that systematic deviations occur between the observed structure factors and those calculated assuming har-
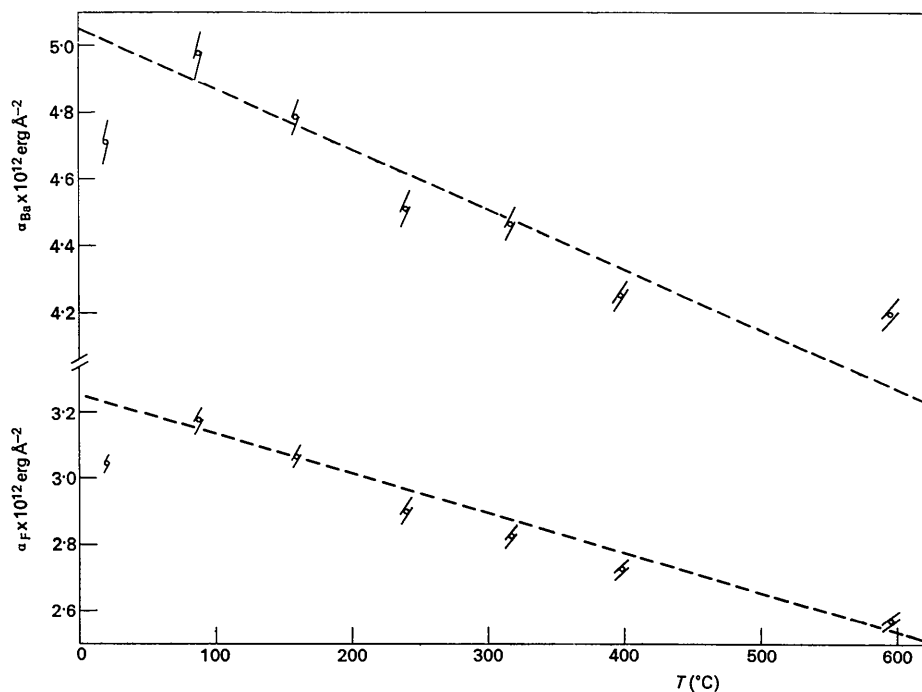
Fig. 2. Temperature dependence of the harmonic parameters $\alpha_{Ba}, \alpha_F$. The lengths of the sloping lines indicate the uncertainty arising from the error $\varepsilon(T)$ in the temperature measurement; the vertical separation of the lines gives the estimated standard deviations of the harmonic parameters.
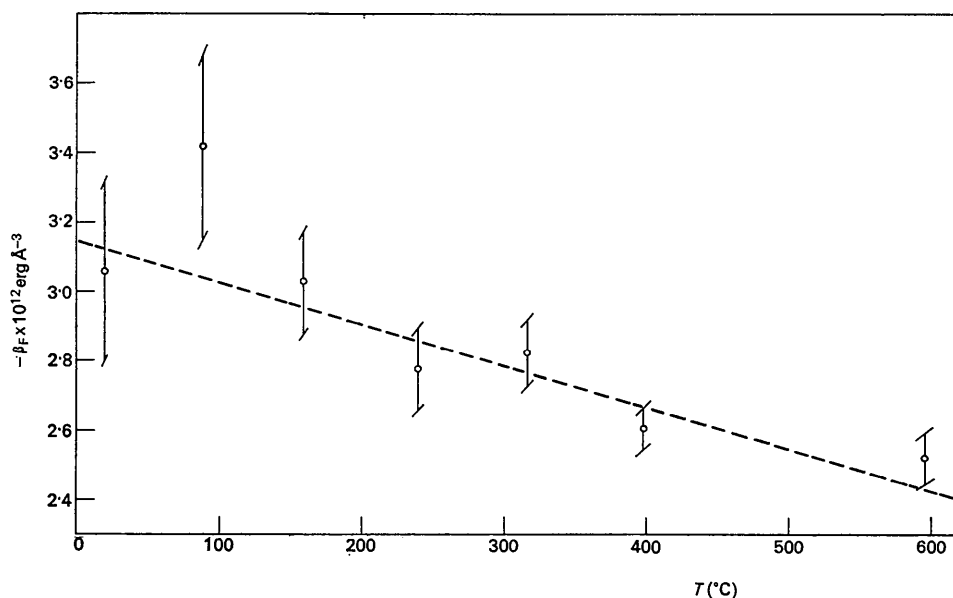
Fig. 3 Temperature dependence of the anharmonic parameter $\beta_F$. The lengths of the sloping lines indicate the uncertainty arising from the error $\varepsilon(T)$ in the temperature measurement; the vertical lines give the estimated standard deviations of the anharmonic parameter.

monic temperature factors for both kinds of atom. The deviations are restricted to the odd-index reflexions, with the observed structure factors differing by up to $\pm 30\%$ from the calculated structure factors, whereas the even-index structure factors agree to within $\sim 1\%$ at all temperatures. By introducing a single parameter, $\beta_F$, at each temperature to account for the effect of anharmonic vibrations of the fluorine atom, all the observed and calculated structure factors are brought into very good agreement ($R \sim 1\%$) at all temperatures. The deviations from the harmonic model are apparent whether or not the data are corrected for the effects of thermal diffuse scattering and extinction, but both these effects must be accounted for in a detailed treatment.

The parameter $\beta_F$ is the coefficient of the third-order term in the expression

$$V_j(\mathbf{r}) = V_{0j} + \tfrac{1}{2}\alpha_j(x^2+y^2+z^2) + \beta_j xyz$$

giving the effective one-particle potential of atom $j$ (Ba or F): see Dawson, Hurley & Maslen (1967). The corresponding parameter $\beta_{Ba}$ of the barium atom is zero, by symmetry, and the remaining parameters $\alpha_{Ba}, \alpha_F$ determine the magnitudes of the harmonic contributions to the two temperature factors. $\beta_F$ determines the degree of tetrahedral distortion of the smearing function of the fluorine atom. This distortion has been calculated at 20 °C from equations (2) and (3), using
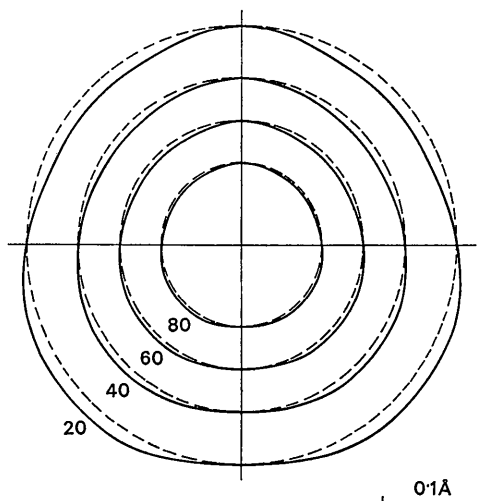
the values of $\alpha_{Ba}, \alpha_F$ and $\beta_F$ in Table 1, and is illustrated in Fig. 4.

It is difficult to make generalizations concerning the implications of the present study on the interpretation of diffraction data from other crystals. There is now no doubt that appreciable anisotropic contributions to the temperature factors of cubic crystals can arise from anharmonicity, even though some theoretical treatments (Maradudin & Flinn, 1963; Kashiwase, 1965) suggest that such contributions are negligible. However, these treatments are restricted to models in which the atoms occupy centrosymmetric sites and there is an obvious need to extend them to more general cases. Anharmonic effects will be especially important for atoms not occupying centrosymmetric sites, and, in the case of the fluorite structure, can be accounted for quantitatively by the Dawson structure-factor formalism. Further work is required to check the validity of this formalism for interpreting diffraction data from other structures.

Fig. 4. (110) section through vibrating fluorine atom at 20 °C. Full lines are contours (scaled to 100 units at centre) giving probability of displacement from centre, due to thermal motion. Broken lines are circles representing contours calculated for $\beta_F = 0$.

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