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## Neutron powder diffraction study of the fast-ion transition and specific heat anomaly in $\beta$ -lead fluoride

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**Abstract.** A powder sample of  $\beta$ -PbF<sub>2</sub> has been studied by neutron diffraction using the High Resolution Powder Diffractometer at the Rutherford-Appleton Laboratory. Rietveld profile refinements have been performed on data collected at roughly 100 temperatures from ambient to well above the transition to the fast-ion phase, which occurs at  $T_c \sim 710$  K. The lattice parameter,  $a_0(T)$ , the concentration of Frenkel defects, and thermal parameters for both the fluorine and the lead ions have been determined as a function of temperature. Precise values of  $a_0(T)$  enable the linear expansivity to be calculated, for which there is a pronounced peak centred on  $T_c$ . It is possible to calculate contributions to the specific heat,  $C_p$ , from harmonic and anharmonic lattice vibrations, Frenkel disorder and lattice dilation; a broad peak is obtained centred on  $T_c$ , which is in good agreement with the directly determined experimental data.

### 1. Introduction

The majority of compounds with the fluorite crystal structure exhibit a broad peak in their specific heat,  $C_p$ , at a temperature,  $T_c$ , well below the melting temperature  $T_m$ . In the region of  $T_c$  the ionic conductivity increases rapidly, approaching that of the molten salt [1, 2]. Owing to the relatively simple crystal structure of fluorite compounds, their 'fast-ion' phase behaviour has been widely studied using both experimental and theoretical techniques. It is now widely accepted that at high temperatures fluorite compounds such as CaF<sub>2</sub>, SrCl<sub>2</sub> and PbF<sub>2</sub> undergo a diffuse transition at  $\sim T_c$  to a state of high dynamic disorder. Dilatometer and laser interferometer measurements have shown that anomalies also occur in the thermal expansion coefficient,  $\alpha_1$ , in the vicinity of  $T_c$  [3, 4]. Detailed investigations of the disordered phase have been made using single-crystal neutron scattering techniques and the results have been interpreted in terms of a model of short-lived, fluctuating clusters of defective anions, comprising Frenkel pairs and surrounding relaxed anions [5, 6].

Lead fluoride, PbF<sub>2</sub>, is of particular interest since it has the lowest value of  $T_c$  of the halide fluorites ( $\sim 710$  K) and has a wide temperature range between  $T_c$  and the melting point ( $T_m = 1128$  K). At room temperature PbF<sub>2</sub> can exist in either the fluorite  $\beta$ -phase ( $Fm\bar{3}m$ ,  $a_0 = 5.94$  Å) or in the more closely packed  $\alpha$  modification

( $Pmnb$ ,  $a_0 = 7.64 \text{ \AA}$ ,  $b_0 = 6.43 \text{ \AA}$ ,  $c_0 = 3.89 \text{ \AA}$ ). On heating at ambient pressure the irreversible  $\alpha \rightarrow \beta$  transition occurs at  $\sim 610 \text{ K}$ , the  $\alpha$ -phase being recovered by application of pressures above  $\sim 4 \text{ kbar}$  at ambient temperature [7].

In this paper we present the results of a high resolution powder neutron diffraction study of  $\text{PbF}_2$  over the temperature range 273–1078 K. Rietveld profile refinement of the diffraction data collected at each temperature has given accurately the variation of the lattice parameter,  $a_0$ , of  $\beta\text{-PbF}_2$  in the vicinity of  $T_c$ . The variations in the Bragg intensities with  $T$  have also been used to investigate in detail the extent of anion disorder, using the Frenkel defect model of the time-averaged structure proposed in previous single-crystal diffraction studies [8]. A preliminary report has presented the results of the profile refinements [9]. These results, derived from a diffraction experiment, have enabled estimates of the contribution to the specific heat from lattice dilation and thermally induced disorder to be made, for comparison with the experimentally determined peak in  $C_p$  centred on  $T_c$  [10, 11, 12].

## 2. Experimental procedure

The  $\sim 6 \text{ cm}^3$  powder sample used in the diffraction experiment was obtained by grinding single crystals of  $\beta\text{-PbF}_2$ . The powder was encapsulated under vacuum inside a 10 mm diameter can made of Pt because of the highly reactive nature of this compound at elevated temperatures. The sample was mounted inside a furnace specifically designed for neutron diffraction experiments, constructed using vanadium foil for the resistive heating element and the heat shields. Temperature measurement and control was achieved by placing a type K thermocouple directly above the sample can.

The diffraction experiments were performed on the high resolution powder diffractometer (HRPD) at the ISIS spallation neutron source, Rutherford-Appleton Laboratory, UK [13]. With a pulsed source such as ISIS, diffraction data are collected at fixed scattering angles,  $2\theta$ , as a function of incident wavelength,  $\lambda$ , where  $\lambda$  is determined by the time taken for the neutron to travel the known distance from the source to the detector. The high resolution of HRPD ( $\Delta d/d \sim 8 \times 10^{-4}$ ) is achieved by situating the instrument at the end of a 95 m long neutron guide and positioning the neutron scintillator detectors at backscattering angles  $160^\circ \leq 2\theta \leq 176^\circ$ . In this experiment data were collected over the time-of-flight range 30 to 130 milliseconds, corresponding to an incident wavelength range  $1.2 \text{ \AA} \leq \lambda \leq 5.4 \text{ \AA}$  and a measured  $d$ -spacing region of  $0.6 \text{ \AA} \leq d \leq 2.7 \text{ \AA}$ . Diffraction data were collected at  $\sim 100$  temperatures in the range 373 to 1078 K, the temperature being increased in steps of 5 K in the region of  $T_c$  ( $673 \text{ K} \leq T \leq 973 \text{ K}$ ) and 10 K over the remainder of the range. Data collection was started ten minutes after reaching the required temperature, to allow the temperature of the furnace and the sample to reach equilibrium. Adequate counting statistics were obtained after approximately five minutes of counting.

The data at each temperature were analysed using the time-of-flight Rietveld profile refinement program TF12LS which uses a peak-shape function that is a convolution of a modified Ikeda-Carpenter lineshape and a Voigt function [13]. Least-squares refinement of the structure of  $\beta\text{-PbF}_2$  was performed by fitting the diffraction pattern only in those time-of-flight regions which contain Bragg peaks from this structure. Reflections which overlap with those from the  $\alpha\text{-PbF}_2$  or Pt phases were omitted from the refinement, though these are relatively few owing to the high instrumental resolution and the relatively simple structures involved. Estimates of the lattice parameter of Pt

were made by fitting a Gaussian lineshape convolved with the instrumental resolution function at each temperature.

### 3. Results and discussion

#### 3.1. Profile refinement

Calculation of the structure factors for the ideal fluorite lattice yields

$$F_{4n} = 4b_{\text{Pb}}T_{\text{Pb}} + 8b_{\text{F}}T_{\text{F}} \quad (1)$$

and

$$F_{4n+2} = 4b_{\text{Pb}}T_{\text{Pb}} - 8b_{\text{F}}T_{\text{F}} \quad (2)$$

where  $b_{\text{Pb}}$  is the coherent nuclear scattering amplitude,  $T_{\text{Pb}} = \exp(-B_{\text{Pb}}(Q/4\pi)^2)$  and  $B_{\text{Pb}}$  is the isotropic harmonic temperature factor for lead; similar definitions apply to the fluorine terms in (1) and (2). The lack of inversion symmetry on the anion site allows considerable anharmonicity of the thermal vibrations in fluorite compounds [14]. This affects the structure factors for the  $4n \pm 1$ -type reflections, which are given by

$$F_{4n+1} = 4b_{\text{Pb}}T_{\text{Pb}} + 8b_{\text{F}}T_{\text{F}} \left( \frac{B_{\text{F}}}{4\pi a_0} \right)^3 \frac{hkl}{k_{\text{B}}T} \beta_0 \quad (3)$$

and

$$F_{4n-1} = 4b_{\text{Pb}}T_{\text{Pb}} - 8b_{\text{F}}T_{\text{F}} \left( \frac{B_{\text{F}}}{4\pi a_0} \right)^3 \frac{hkl}{k_{\text{B}}T} \beta_0 \quad (4)$$

where  $a_0$  is the lattice parameter and  $\beta_0$  is the coefficient of the third-order term in the expansion of the potential  $V(\mathbf{r})$  for fluorine (see equation (9)).

The temperature variation of the diffraction pattern obtained from the  $\text{PbF}_2$  sample is shown in figure 1. For clarity only data in the range  $1.7 \text{ \AA} \leq d \leq 2.0 \text{ \AA}$  for 15 temperatures are shown in the figure. At low temperatures additional weak reflections are observed which can be identified as a small amount of orthorhombic  $\alpha$ - $\text{PbF}_2$  present in the sample. This observation is confirmed by the disappearance of these peaks at the  $\alpha \rightarrow \beta$  transition temperature ( $\sim 610 \text{ K}$ ) where an approximately 10% increase in the intensity of the  $\beta$ - $\text{PbF}_2$  reflections is observed. It is possible that grinding the  $\beta$ - $\text{PbF}_2$  produces sufficient pressure in some of the crystallites to cause transformation to the orthorhombic phase. The values of  $b_{\text{Pb}}$  and  $b_{\text{F}}$  are such that the two terms in equation (2) almost cancel, and so at ambient temperatures the Bragg intensity is very small for  $4n + 2$ -type reflections. However, at the onset of fast-ion behaviour, where fluorine ions leave their regular sites, the structure factor changes. Thus, the appearance of the (222) peak at temperatures above  $\sim 700 \text{ K}$  gives the first indication of thermally induced anion disorder. The coherent diffuse scattering from the anion defects was too weak to detect in this experiment. However, it is known to be present since previous single-crystal studies have shown broad diffuse peaks in the fast-ion phase [5, 6].

For the case of  $\beta$ - $\text{PbF}_2$ , good fits to the data ( $R_{\text{W}} \sim 5\%$ ,  $\chi^2 \sim 1.5$  for 26 reflections and 5111 data points) were obtained using eleven fitted parameters, comprising background parameters, the scale factor, the lattice parameter  $a_0$  of  $\text{PbF}_2$ , isotropic temperature factors  $B_{\text{Pb}}$  and  $B_{\text{F}}$ , plus the width of a single Gaussian peak convolved

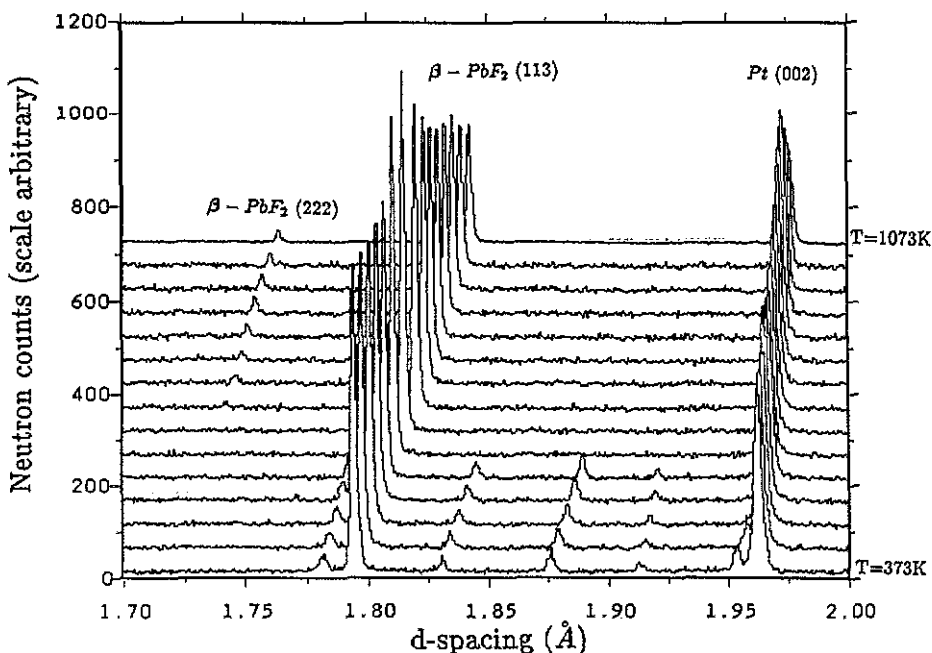


Figure 1. Evolution of the measured diffraction pattern from powdered  $\beta$ - $\text{PbF}_2$  in the region of  $d$ -spacings from 1.7 to 2.0 Å. The data shown cover the temperature range from 373 to 1073 K in 25 K steps. The additional weak reflections observed up to  $T \sim 600$  K are due to a small quantity of orthorhombic  $\alpha$ - $\text{PbF}_2$  present in the sample.

with the instrumental peak shape. In the profile refinements the background contribution to the measured diffraction pattern was fitted by a fourth order polynomial in time-of-flight. Owing to the high instrumental resolution the background coefficients were uncorrelated with the structural parameters. Equations (3) and (4) show that anharmonic lattice vibrations lead to an increase in the intensity for  $4n + 1$ -type reflections and a decrease for  $4n - 1$ . However, these reflections are superimposed in powder studies of compounds with cubic symmetry. The refinements are, therefore, not sensitive to anharmonicity and so no attempts have been made to examine its temperature dependence in this experiment.

At all temperatures the possibility of disorder of the anion sublattice was included by allowing the occupancy of the fluorine site to vary from unity. Refinements were initially performed without constraints on the time-averaged positions of the disordered anions, which is equivalent to assuming a random distribution throughout the unit cell. A more physically realistic model has been derived previously from single-crystal diffraction studies of  $\beta$ - $\text{PbF}_2$  at elevated temperatures [8]. The time-averaged structure which best fits the data has fluorine interstitial ions at  $(\frac{1}{4} - y, \frac{1}{4} + y, 0)$ , with  $y = 0.07$ , resulting in relaxations of the two nearest neighbour anions into  $(x, x, x)$  sites with  $x = 0.32$  (see figure 2). Constraining the disordered anions to occupy these two sites in the ratio 1:2 resulted in slightly improved fits to the powder diffraction data at high temperatures, although attempts to vary the positional parameters proved unsuccessful. As a result, all refinements to the powder data were performed with these site positions fixed and, furthermore, the thermal parameters of the disordered

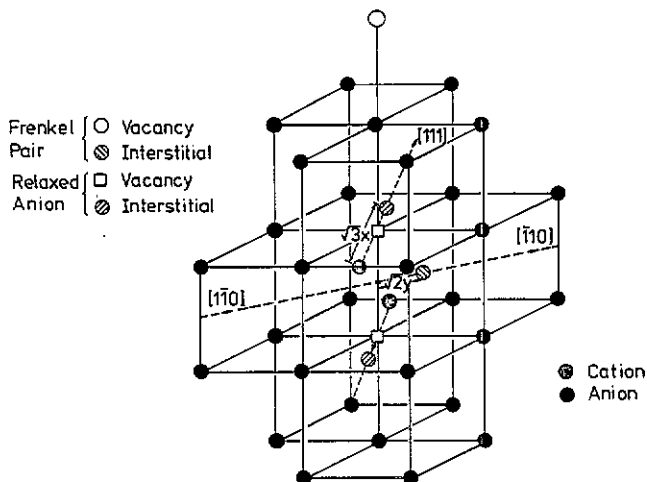


Figure 2. The disordered fluorite structure derived from single-crystal diffraction [9]. The Frenkel pair comprises an interstitial anion situated  $(y, y, 0)$  from the centre of a cube edge and an associated anion vacancy. This causes relaxation of the two nearest neighbour anions towards empty cube centres by  $(x, x, x)$  from the cation site.

anions were held equal to those on the lattice sites.

The temperature variation of the lattice parameter of  $\beta$ -PbF<sub>2</sub> is shown in figure 3(a); the estimated standard deviation of the  $a_0$  values is around  $3 \times 10^{-5}$  Å at all temperatures. The anomalous behaviour of the lattice parameter, suggested previously by macroscopic techniques [3, 4], is confirmed in this experiment. Refinements of the lattice parameter of the Pt can were also performed and are shown in figure 3(b) for comparison. Figure 4 indicates that a corresponding anomaly is also observed in the isotropic temperature factors of PbF<sub>2</sub>, particularly that of the fluorine ions. The extent of thermally induced disorder of the anion sublattice is characterized by the fraction of anions,  $n_v$ , which leave their regular sites [8] and is simply determined from the refined values of the anion site occupancy. The temperature variation of  $n_v$ , shown in figure 5, indicates the onset of disorder at  $T \sim 630$  K. Although the previously reported single-crystal diffraction studies were performed at relatively few temperatures the values of  $n_v$  obtained [8] are in excellent agreement with those determined in this experiment.

### 3.2. Linear expansivity

The linear expansivity of the lattice,  $\alpha_1$ , is defined as

$$\alpha_1 = \frac{da_0}{dT} \frac{1}{a_0(293 \text{ K})}. \quad (5)$$

In order to determine  $\alpha_1(T)$  it is necessary to calculate the gradient of the  $a_0(T)$  curve. The lattice parameter has been measured to high precision in this experiment. A cubic function was fitted to eleven successive data points using the method of least squares and the gradient evaluated at the average temperature. By repeating the process one data point higher it was possible to smooth the data.

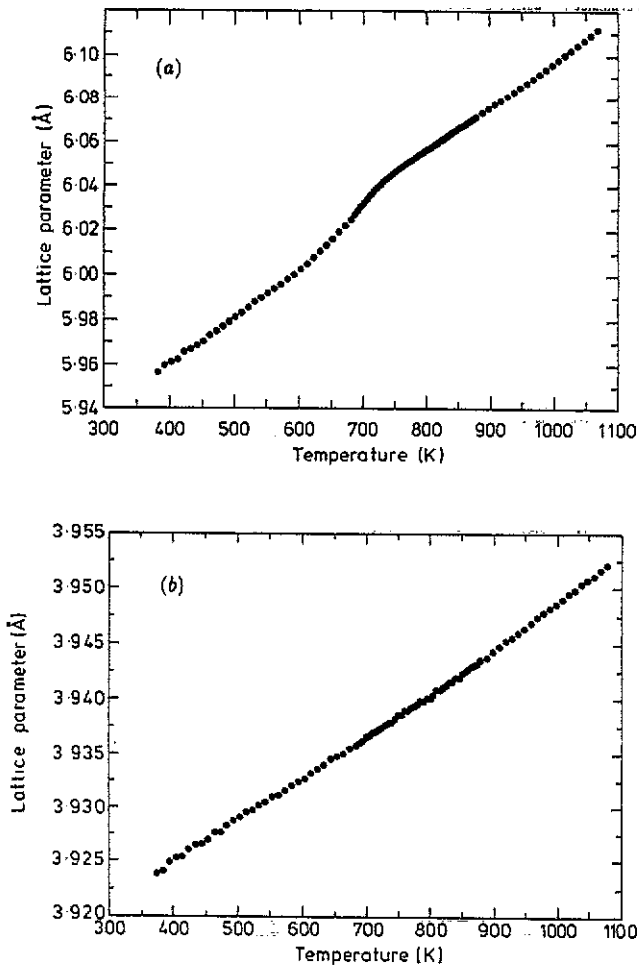


Figure 3. Temperature variation of the cubic lattice parameter (a) for  $\beta$ -PbF<sub>2</sub> and (b) for Pt, showing the anomalous behaviour of  $\beta$ -PbF<sub>2</sub> in the vicinity of  $T_c$ .

The curve of  $\alpha_1(T)$  is presented in figure 6, where comparison is made with the (macroscopic) dilatometer measurements of Roberts and White [3]. If Schottky defects are produced ions are transferred to the surface, whereas Frenkel defects occupy interstitial positions. The bulk expansivity therefore differs from the lattice expansivity if the defects are of the Schottky type, but not if they are of the Frenkel type [16]. The two data sets agree within experimental uncertainty, directly confirming the Frenkel nature of the defects.

### 3.3. Specific heat anomaly

There has been considerable interest recently in the specific heat anomaly in fluorite compounds, due largely to the use of UO<sub>2</sub> as a fuel in nuclear fission reactors [17]. The present neutron diffraction data make it possible to calculate all of the contributions to the specific heat,  $C_p$ , for PbF<sub>2</sub>. The calculation extends from 450 to 800 K, the range studied by direct measurements of  $C_p$  [10, 11, 12].

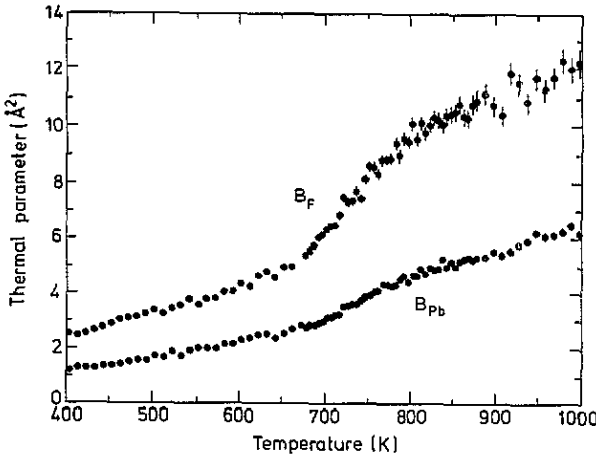


Figure 4. Temperature variation of the isotropic thermal parameters  $B_F$  and  $B_{Pb}$  of  $\beta$ -PbF<sub>2</sub>.

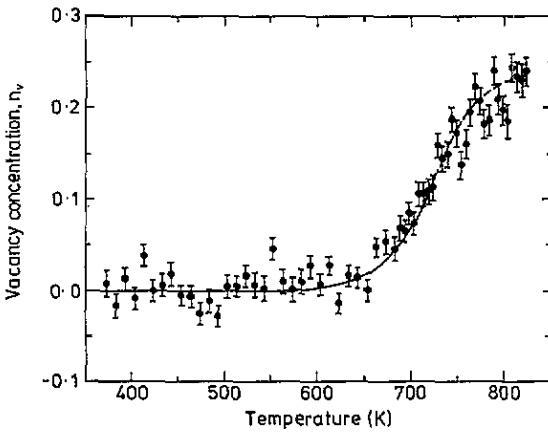


Figure 5. Temperature variation of the concentration of vacancies on the anion sublattice, indicating the onset of dynamic F<sup>-</sup> ion disorder at  $T \sim 630$  K. The full curve shows the fitted exponential function; the broken curve is the extrapolation to higher temperatures.

The specific heat at constant volume,  $C_v$ , is given by

$$C_v = C_{\text{har}} + C_{\text{anh}} + C_F \quad (6)$$

where  $C_{\text{har}}$  and  $C_{\text{anh}}$  are due to harmonic and anharmonic lattice vibrations respectively, and  $C_F$  is due to the thermal generation of Frenkel anion defects.

The harmonic contribution to equation (6) is [18]

$$C_{\text{har}} = 3nRD(T/\Theta_D) \quad (7)$$

where  $D(T/\Theta_D)$  is the Debye function and  $\Theta_D$  the Debye temperature. For PbF<sub>2</sub>  $n = 3$  and  $\Theta_D = 237$  K [19]. Over the temperature range of interest in this work  $C_{\text{har}}$  saturates at the classical value of  $9R$ .



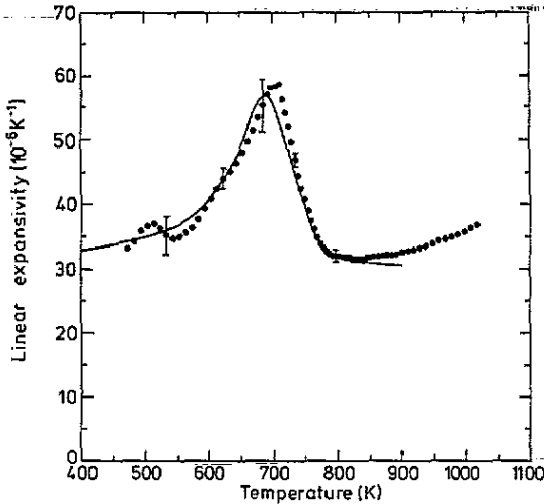


Figure 6. Temperature variation of the linear expansivity,  $\alpha = (da_0/dT)/a_0(293\text{ K})$ , of the  $\beta$ - $\text{PbF}_2$  lattice. A few representative estimated error bars are shown. The full curve shows the bulk expansivity obtained by dilatometer measurements [3].

The anharmonic contribution to equation (6) is given by [18]

$$C_{\text{anh}} = \frac{2\beta_0^2 k_B RT}{\alpha_0^3} \quad (8)$$

where the parameters  $\alpha_0$  and  $\beta_0$  are defined by expansion of the single-ion potential,  $V(\mathbf{r})$ , for the regular anion site to third order [20]:

$$V(\mathbf{r}) = V_0 + \frac{1}{2}\alpha_0(x^2 + y^2 + z^2) + \beta_0(xyz). \quad (9)$$

The isotropic harmonic vibration (Debye-Waller) parameter,  $B^H$ , has been determined for the fluorine ion in  $\text{PbF}_2$  as a function of temperature in this experiment, and so  $\alpha_0(T)$  was calculated from the relation

$$B^H = \frac{8\pi^2 k_B T}{\alpha_0}. \quad (10)$$

An anharmonic vibration parameter given by

$$B^{\text{AN}} = \frac{B^H \beta_0}{(4\pi)^3 k_B T a_0^3} \quad (11)$$

has been obtained from single-crystal neutron diffraction [8]. Over the temperature range 450 to 800 K  $\beta_0$  is found to be constant at a value  $1.5 \times 10^{11} \text{ J m}^{-3}$ . The values of  $C_{\text{anh}}(T)$  calculated using equations (8), (10) and (11) are given in figure 7.

The thermal generation of Frenkel disorder contributes  $C_F$ , which can be written as

$$C_F(T) = (dU_F(T)/dT)_v \quad (12)$$

where

$$\Delta U_F(T) = n_F(T) \Delta H_A(T) \quad (13)$$

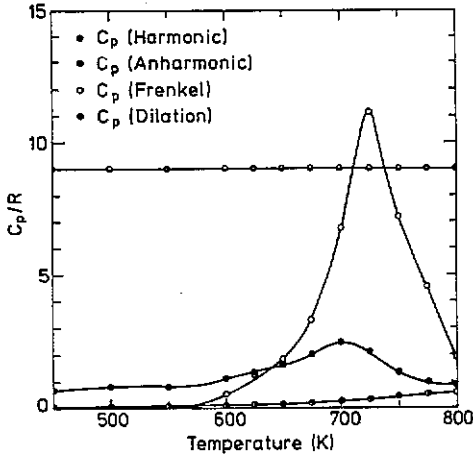


Figure 7. The contributions to  $C_p(T)$  of  $\beta$ -PbF<sub>2</sub> from harmonic lattice vibrations, anharmonic lattice vibrations, Frenkel disorder and lattice dilation.

and where  $n_F$  is the number of Frenkel defects and  $\Delta H_A$  is the activation enthalpy. Since the defect cluster model derived from single-crystal measurements [8] is assumed in this analysis,  $n_F \sim \frac{1}{3}n_v$ . For a low concentration of defects the temperature variation of  $n_F$  is given by

$$n_F(T) = A \exp(-\Delta H_F/k_B T) \quad (14)$$

where  $\Delta H_F$  is the Frenkel activation enthalpy. A least squares fit of this function to the experimentally determined  $n_v(T)$  up to  $T \sim 740$  K, as shown in figure 5, yields a Frenkel activation enthalpy  $\Delta H_F = 1.10 \pm 0.03$  eV. This agrees well with other published data, e.g. Chadwick [1] gives  $\Delta H_F = 1.09 \pm 0.05$  eV. Above  $T \sim 740$  K the concentration of defects is sufficient to make the effects of the interaction between them appreciable, giving an effective repulsive contribution to  $\Delta H_A$ , and dramatically suppressing further generation of defects. However, over the temperature range of interest, the activation enthalpy need only be increased by  $\sim 10\%$  to account for the saturation of  $n_v(T)$ . We can therefore assume that over this range of temperature the activation enthalpy is roughly constant at  $\Delta H_A(T) \sim \Delta H_F$ , and use a hand-plotted smoothed experimental curve, shown in figure 5, to give  $n_v(T)$  and  $dn_v(T)/dT$  ( $\sim 3 dn_F(T)/dT$ ). The Frenkel contribution to  $C_p$  is then given by

$$C_F(T) = \Delta H_F \frac{dn_F(T)}{dT} \quad (15)$$

and is shown in figure 7 as  $C_p$ (Frenkel).

$C_p$  can be obtained from  $C_v$  by addition of a volume dilation term

$$C_p(T) = C_v(T) + \frac{\alpha_v^2(T) v(T) T}{K_T(T)} \quad (16)$$

where  $K_T$  is the isothermal compressibility and  $\alpha_v$  is the volume expansivity ( $\alpha_v = 3\alpha_1$ ). The adiabatic compressibility given by

$$K_S = 3(c_{11} + 2c_{12})^{-1} \quad (17)$$

has been measured by neutron inelastic scattering [15]. The relation between the isothermal and adiabatic compressibility is

$$K_T = K_S + \frac{\alpha_v^2 VT}{C_p} \quad (18)$$

The quantities  $\alpha_v(T)$  and  $V(T)$  were obtained from the  $a_0(T)$  values measured in this experiment. As a first approximation, the dilation term was calculated using the adiabatic compressibilities. This was added to the other three contributions to give an estimate of  $C_p(T)$ , which in turn was used to estimate  $K_T(T)$ . Iteration of this process led to convergence of the dilation term and hence  $C_p(T)$ . The contribution to  $C_p(T)$  from lattice dilation, shown in figure 7, is a significant component in the peak.

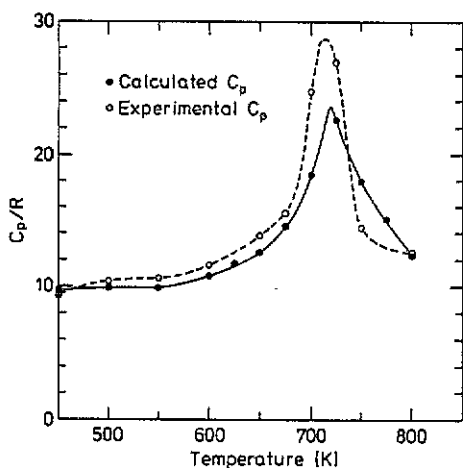


Figure 8. The total  $C_p(T)$  of  $\beta$ - $\text{PbF}_2$  calculated from neutron scattering data (see figure 7) compared with data obtained by calorimeter measurements [10].

The total  $C_p$ , shown in figure 8, has been calculated in the temperature range 450 to 800 K from the sum of the contributions:

$$C_p = 9R + \frac{2\beta_0^2 k_B RT}{\alpha_0^3} + \Delta H_F \frac{dn_F}{dT} + \frac{\alpha_v^2 VT}{K_T} \quad (19)$$

A detailed comparison of the calculated values with experimentally determined data are difficult owing to the wide variability of the latter [10,11,12]. In figure 8 our calculated values are compared with the most recent calorimetric measurements [10]. The heat content agrees to within 6%, well within experimental uncertainty.

#### 4. Conclusion

This paper presents the results of a high resolution powder diffraction study of the temperature dependence of the lattice parameter,  $a_0$ , the fraction of anions leaving their regular sites,  $n_v$ , and the isotropic harmonic temperature factors  $B_F$  and  $B_{Pb}$

for  $\beta$ -PbF<sub>2</sub>. It is found that using the HRPD instrument at ISIS it is possible to acquire data which are adequate for profile refinement from powders rapidly at elevated temperatures. The results from this experiment are in agreement with those obtained at the few temperatures studied using single-crystal diffraction. Their quality and quantity is such as to give us a more detailed understanding of the thermodynamic behaviour of  $\beta$ -PbF<sub>2</sub> during the transition to the fast-ion phase. The lattice expansivity is in agreement with bulk measurements, directly confirming the Frenkel nature of the anion disorder. Using neutron scattering data alone (the present data in conjunction with single-crystal results) it is possible to calculate the contributions to  $C_p(T)$  from harmonic and anharmonic lattice vibrations, lattice disorder and lattice dilation. The total calculated  $C_p(T)$  is in good agreement with experiment. The results of using neutron scattering data to calculate the specific heat of UO<sub>2</sub> up to its melting temperature, where crystal field and small polaron contributions must also be considered, will be presented in a future publication.

### Acknowledgments

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