

## Thermal expansion of deuterated hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{D}_2\text{O}$

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### ABSTRACT

The lattice parameters extracted from Le Bail analysis of neutron powder diffraction data collected between 2 and 300 K have been used to calculate the temperature evolution of the thermal expansion tensor for hopeite,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , *Pnma*,  $Z=4$  with  $a = 10.6065(4)$  Å,  $b = 18.2977(4)$  Å,  $c = 5.0257(2)$  Å at 275 K. The  $a$  lattice parameter shows a negative thermal expansion, the  $b$  lattice parameter appears to saturate at 275 K while the  $c$  lattice parameter has a more typical positive thermal expansion. At 275 K, the magnitudes of the thermal expansion coefficients are  $\alpha_a = -1.1(4) \times 10^{-5} \text{ K}^{-1}$ ,  $\alpha_b = 2.4(9) \times 10^{-6} \text{ K}^{-1}$  and  $\alpha_c = 3.6(2) \times 10^{-5} \text{ K}^{-1}$ . Under the conditions of these experiments, hopeite begins to dehydrate to the dihydrate between 300 and 325 K, and between 480 and 500 K the monohydrate is formed. The thermal expansion of the dihydrate has been calculated between 335 and 480 and at 480 K the magnitudes of the thermal expansion coefficients are  $\alpha_a = 1(2) \times 10^{-5} \text{ K}^{-1}$ ,  $\alpha_b = 4(1) \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha_c = 4(2) \times 10^{-5} \text{ K}^{-1}$ ,  $\alpha_\beta = 1(1) \times 10^{-5} \text{ K}^{-1}$ , and  $\alpha_\gamma = 2(2) \times 10^{-5} \text{ K}^{-1}$ . The thermal expansion of hopeite is described in terms of its crystal structure and possible dehydration mechanisms for the  $\alpha$  and  $\beta$  modifications of hopeite are discussed.

**Keywords:** Hopeite, thermal expansion, dehydration, neutron diffraction

### INTRODUCTION

The formation of metal phosphates in metal-contaminated soil is increasingly recognized as a potentially cost effective in situ remediation technology (Cotter-Howells and Caporn 1996; Ma et al. 1993). Current methods of treating metal-contaminated soils essentially isolate the soil from the ecosystem by capping or removing the soil and dumping it elsewhere (Wood 1997). Clearly these methods are not sustainable. At present, one of the main challenges to using metal phosphate formation as a remediation technology is the identification of an affordable phosphate source of appropriate solubility and dissolution rate. Previous experiments (Basta et al. 2001; Hodson et al. 2000a, 2000b) indicated that bone meal (crushed sterilized bone) appears to be a suitable phosphorus source.

Metal phosphates are highly insoluble (Nriagu 1984) and, it has been suggested, their low solubility renders metals in metal phosphates non-bioavailable. Thus the conversion of metals in metal-contaminated soils into metal phosphates represents a potential in situ remediation technique. Laboratory and field experiments on metal-contaminated soils using bone meal as a phosphate source indicate that bone meal additions reduce both metal release from metal-contaminated soils and metal availability as determined by chemical extractions (Hodson and Valsami-Jones 1999; Hodson et al. 1999, 2001). Extensive multi-technique characterization of the treated metal-con-

taminated soils and laboratory-reacted hydroxy apatites has revealed that in addition to mixed-metal hydroxy apatites, reaction products can include hopeite,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Chen et al. 1997; Lusvardi et al. 2002; Cheung et al. 2002). The stability of these hopeite phases, and hence the non-bioavailability of Zn, is partly dependent upon formation conditions, with chemical conditions affecting the morphology of the phosphates (Rinaudo et al. 1994), and also aging/dehydration reactions (Haussühl et al. 1991) that in turn relate to the stability of the subsequent dehydration phases. In both instances, however, it is likely to be the hydrogen bonding which ultimately controls the stability of hopeite  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ .

Hopeite has received considerable study with respect to its use in the formation of corrosion resistant coatings on steel and its biomineralized appearance associated with surgical implants (Rolland et al. 1989). Three modifications of hopeite have been postulated (Goloshchapov and Filatova 1969; Nikonenko et al. 1985; Al-Maydama et al. 1992) with  $\alpha$ -hopeite the most commonly studied (Pawlig and Trettin 1999). The three modifications are indistinguishable using X-ray powder diffraction and seemingly differ primarily in their thermal behavior and the frequencies of the stretching modes of the water molecule in the mid-infrared region. As a consequence, the non-hydrogen atom positions are believed to be identical in each of the modifications, but there are differences in some of the hydrogen atom positions and hydrogen bonding within the three modifications (Hill and Jones 1976; Al-Maydama et al. 1992; Pawlig and Trettin 1999). The thermal expansion of synthetic hopeite has been studied within a limited temperature range (Haussühl et al. 1991) and

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some elastic constants calculated (Haussühl and Friedrich 1993), but as yet there are no such measurements for the dihydrate.

## EXPERIMENTAL METHODS

### Synthesis

Protons have a large incoherent cross section for the scattering of thermal neutrons and so it was necessary to prepare a deuterated sample of hopeite for powder diffraction experiments to avoid large backgrounds and improve signal-to-noise. The material used for these experiments was synthesized by direct precipitation, performed just prior to the commencement of the experiment to minimize the possibility of  $H \leftrightarrow D$  exchange.

Deuterated hopeite was synthesized by direct precipitation from solution at room temperature. A 0.3 M solution of zinc nitrate  $[Zn(NO_3)_2]$  and a 0.2 M solution of potassium dihydrogen phosphate ( $KH_2PO_4$ ) were prepared by dissolving the solids in  $D_2O$ . These solutions were mixed in equal volumes so that the Zn:P molar ratio was 3:2. A white precipitate formed immediately. The white suspension was filtered through a Whatman 541 filter paper and washed with  $D_2O$  and then allowed to dry at 30 °C in a drying oven. Optical examination revealed that the white precipitate comprised needle like crystals with a maximum length of about 100  $\mu m$ .

The synthetic product was characterized using X-ray powder diffraction and scanning electron microscopy to confirm that it was single-phase hopeite, and ICP-AES to check the Zn:P ratio. There is considerable literature on the characterization of  $\alpha$ -hopeite (e.g., Pawlig and Trettin 1999). The main difference between the modifications is in their thermal response, and DTA/TG has shown that the  $\beta$ -modification releases its 4  $H_2O$  molecules in a single reaction (Goloshchapov and Filatova 1969), whereas the  $\alpha$ -modification shows two or three endothermic effects depending upon the specific hydrogen atoms positions and hydrogen bonding within the structure (Hill and Jones 1976; Pawlig and Trettin 1999). Hill and Jones (1976) have tentatively correlated the changes in the DTA curves of  $\alpha$ -hopeite to the pH conditions of synthesis. There are as yet no DTA/TG data for the  $\gamma$ -modification of Al-Maydama et al. (1992). The DTA/TG curves of our sample (Fig. 1) are similar to those described by Haussühl and Friedrich (1993), Hill and Jones (1976), and Arnaud et al. (1988) and confirm that it is the  $\alpha$ -modification.

Infrared spectroscopy (Fig. 2) confirmed the sample was deuterated  $\alpha$ -hopeite (Pawlig et al. 2001). A clear shift is evident in the  $H_2O$  stretching modes from 3000–3500  $cm^{-1}$  in protonated  $\alpha$ -hopeite to 2200–2700  $cm^{-1}$  in the deuterated form and also in the  $H_2O$  bending modes from 1580–1700  $cm^{-1}$  in protonated  $\alpha$ -hopeite to 1380–1500  $cm^{-1}$  in deuterated  $\alpha$ -hopeite. Any hint of OH is considered to be related to adsorbed hydrous species. In addition, the mainly incoherent scattering of neutrons by hydrogen can be used to qualitatively assess the degree of deuteration of the sample and in this case the absence of a large incoherent background in the powder diffraction pattern indicated that the deuteration of the hopeite was indeed very high.

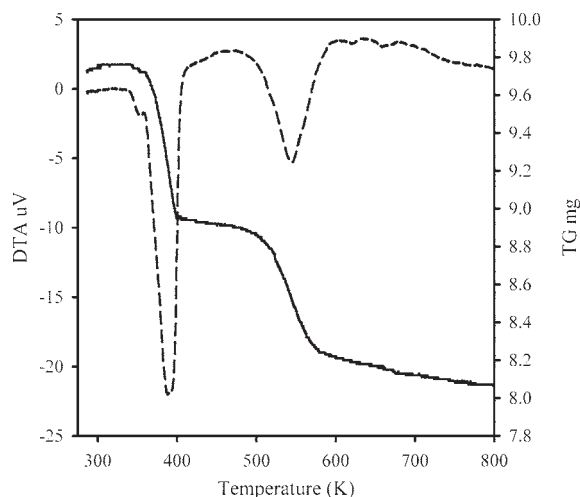


FIGURE 1. DTA and TG profile of deuterated  $\alpha$ -hopeite with a heating rate of 10 K/min.

### Neutron diffraction

Neutron time-of-flight powder diffraction data were collected on the fixed geometry, high resolution diffractometer HRPD (Ibberson et al. 1992) at the ISIS neutron spallation source, Rutherford Appleton Laboratory, U.K. (Wilson 1995). Two grams of deuterated hopeite were packed into an indium sealed cylindrical vanadium can with an external diameter of 11 mm, quenched in liquid nitrogen before being placed in a cryofurnace and cooled to 2 K. Diffraction patterns were collected for a period of 400  $\mu A$  hours (average effective circulating proton current of 35  $\mu A$ ) at 2 and 200 K and for 10  $\mu A$  hours at 50 K, 100 K, and at intervals of 25 K up to 175 K and also from 225 to 300 K. After the sample temperature had increased to the set point, and prior to the collection of the diffraction data, there was an equilibration time of 10 min and the variation of the temperature during

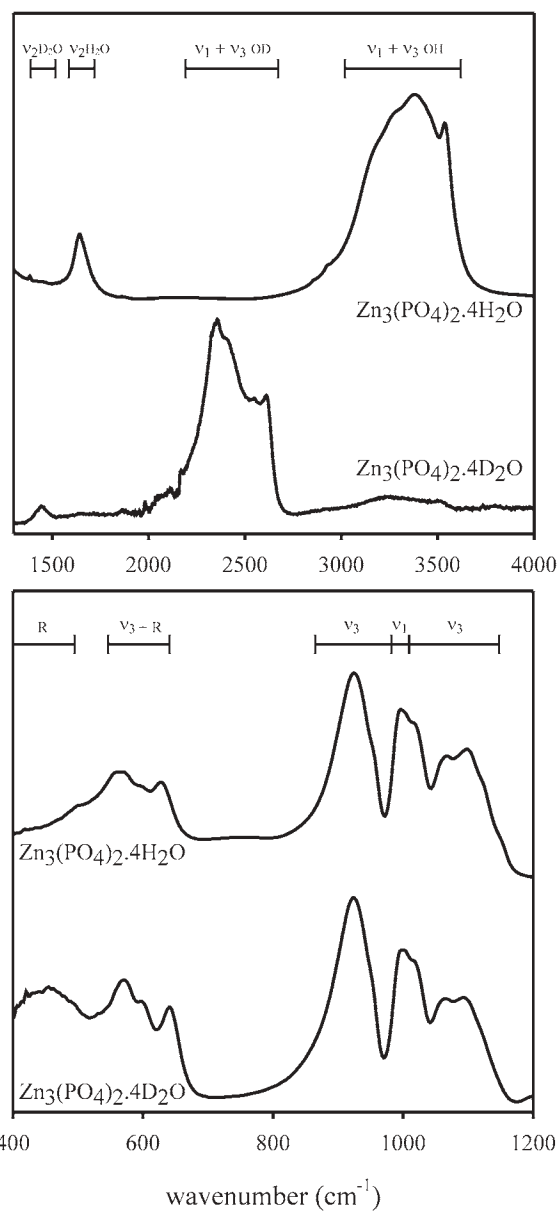


FIGURE 2. Infrared absorption spectra for deuterated and protonated  $\alpha$ -hopeite in the region 4000 to 1300  $cm^{-1}$  (top) showing the internal modes of the  $H_2O/D_2O$  molecules and in the region 1200 to 400  $cm^{-1}$  (bottom) showing the internal modes of the phosphate molecules and librational modes (R) of the  $H_2O/D_2O$  molecules.

data collection was  $\pm 0.1$  K. To ensure that no dehydration had occurred at temperatures of 300 K or below, and to monitor the onset of dehydration of hopeite, a series of isothermal diffraction patterns were collected for 10  $\mu$ A hours at 335, 345, and 355 K. The dehydration of hopeite through a series of subhydrates was monitored by collection of diffraction patterns for a minimum period of 10  $\mu$ A hours at temperature intervals of 20 K between 360 and 520 K.

Data were collected simultaneously in two separate detector banks set at mean scattering angles of  $2\theta = 90^\circ$  and  $2\theta = 168.329^\circ$  in the time-of-flight ranges 35 000–11 400  $\mu$ s and 32 000–120 000  $\mu$ s, respectively. Data were binned as  $\Delta t/t = 0.0005$  for the  $2\theta = 90^\circ$  data and  $\Delta t/t = 0.0003$  for the back-scattering data. Background from the cryofurnace was subtracted from the data, which was then normalized to the incident flux distribution using the isotropic incoherent scattering from a vanadium rod and corrected for absorption and self-scattering. These data were subsequently used in a 2-bank whole profile refinement to extract the lattice parameters.

### Data refinement

Lattice parameters for deuterated hopeite between 2 and 300 K were determined by whole pattern profile fitting of the diffraction data using the LeBail least squares procedure for intensity extraction within the General Structure Analysis System (GSAS) code of Larson and Von Dreele (1994). The first refinement was performed on the data collected at 2 K using the coherent scattering lengths from Sears (1992) (Zn 5.680 fm, P 5.13 fm, O 5.803 fm, and D 6.671 fm). The converged parameters for this refinement were then used as the initial data set for all the subsequent refinements. Data from two detector banks were refined simultaneously with a final total of 25 variables and 5016 observations per refinement. For each refinement and histogram, only the background (consisting of 10 Chebyshev polynomial terms) was initially refined before incorporating the lattice parameters and finally a sample dependent Gaussian profile parameter into the overall refinement. The lattice parameters, goodness-of-fit parameters, refinement, and experimental details are summarized in Table 1, and some representative diffraction data, their calculated fits, and residuals are presented in Figure 3.

Between 335 and 480 K, the diffraction data were consistent with those of deuterated zinc phosphate dihydrate. The lattice parameters for this phase were also determined by whole pattern profile fitting of the diffraction data using the LeBail method within GSAS. Data from the  $90^\circ$  detector bank were refined with 1478–1496 observations per refinement. After refining the background (consisting of 10 Chebyshev polynomial terms), these parameters were fixed and the monoclinic lattice parameters and a sample dependent Gaussian profile parameter were refined. The lattice parameters and refinement and experimental details for this part of the study are summarized in Table 2.

### LATTICE EXPANSION OF HOPEITE

The lattice parameters within the temperature range 2 to 300 K for deuterated hopeite, displayed in Figure 4 show that the thermal expansion of hopeite is anisotropic, with the  $a$  lattice parameter actually decreasing as the temperature is increased. This negative thermal expansion amounts to 0.13% of the 2 K value. The  $b$  lattice parameter increases as a function of increasing temperature by 0.13% of the 2 K  $b$  lattice parameter, and appears to saturate above about 275 K. The largest expansion is in the  $c$  lattice parameter (0.64% of the 2 K  $c$  lattice parameter) which exhibits typical Grüneisen behaviour throughout the temperature range of this study and dominates the increase in the unit-cell volume, representing some 0.64% of the volume at 2 K.

Thermal expansion of a material is a response to anharmonic terms in the expansion of the interaction energy about its equilibrium value and a rigorously harmonic crystal does not expand (Ashcroft and Mermin 1976). As far as was possible, the analysis presented here takes the same approach to that of Knight (1996) and Knight et al. (1999). Accepting the validity of Grüneisen's rule these studies used an Einstein oscillator specific heat capacity to determine the temperature dependence of the unit-cell volume in a quasi-harmonic approximation. In the Einstein model of specific heat capacity in solids, all atoms vibrate with the same angular frequency and there exists a delta function in the phonon density of states at the Einstein frequency,  $\omega_E$

$$C_v = \frac{3Nk(\vartheta_E/T)^2 \exp(\vartheta_E/T)}{[\exp(\vartheta_E/T) - 1]^2} \quad (1)$$

with  $\hbar\omega_E = k\vartheta_E$ ,  $N$  is the number of oscillators,  $k$  is Boltzmann constant,  $\vartheta_E$  is the Einstein temperature and  $2\pi\hbar$  is Planck's constant. Integrating with respect to temperature gives the expression

$$V(T) = V_0 + \frac{K}{[\exp(\vartheta_E/T) - 1]} \quad (2)$$

**TABLE 1.** Experimental and refinement details with lattice parameters of deuterated hopeite from 2 to 300 K

| $T$ (K) | Count time ( $\mu$ Ah) | Number of observations | $R_p$ (%) | $R_{wp}$ (%) | $a$ (Å)     | $b$ (Å)     | $c$ (Å)    | Volume (Å <sup>3</sup> ) |
|---------|------------------------|------------------------|-----------|--------------|-------------|-------------|------------|--------------------------|
| 2       | 400                    | 5016                   | 1.66      | 1.57         | 10.61781(9) | 18.2752(1)  | 4.99868(5) | 969.956(9)               |
| 50      | 10                     | 5016                   | 6.82      | 6.60         | 10.6182(4)  | 18.2746(4)  | 5.0000(2)  | 970.15(4)                |
| 100     | 10                     | 5016                   | 6.76      | 6.46         | 10.6172(4)  | 18.2744(4)  | 5.0022(2)  | 970.54(4)                |
| 125     | 10                     | 5016                   | 6.62      | 6.52         | 10.6160(4)  | 18.2744(4)  | 5.0045(2)  | 970.89(4)                |
| 150     | 10                     | 5016                   | 6.62      | 6.16         | 10.6159(4)  | 18.2763(4)  | 5.0062(2)  | 971.29(4)                |
| 175     | 10                     | 5016                   | 6.64      | 6.67         | 10.6145(4)  | 18.2787(2)  | 5.0102(2)  | 972.07(4)                |
| 200     | 400                    | 5016                   | 1.50      | 1.49         | 10.61356(8) | 18.28295(9) | 5.01260(4) | 972.681(8)               |
| 225     | 10                     | 5016                   | 6.96      | 6.95         | 10.6120(4)  | 18.2885(4)  | 5.0161(2)  | 973.52(4)                |
| 250     | 10                     | 5016                   | 6.93      | 6.94         | 10.6076(4)  | 18.2950(4)  | 5.0211(2)  | 974.42(4)                |
| 275     | 10                     | 5016                   | 6.62      | 6.66         | 10.6065(4)  | 18.2977(4)  | 5.0257(2)  | 975.36(4)                |
| 300     | 10                     | 5016                   | 6.90      | 6.52         | 10.6044(4)  | 18.2976(4)  | 5.0306(2)  | 976.12(4)                |

Note: The numerical agreement factors  $R_p$  and  $R_{wp}$  are defined in Young (1993).

**TABLE 2.** Experimental and refinement details with lattice parameters of the first subhydrate of deuterated hopeite, zinc phosphate dihydrate from 335 to 480 K

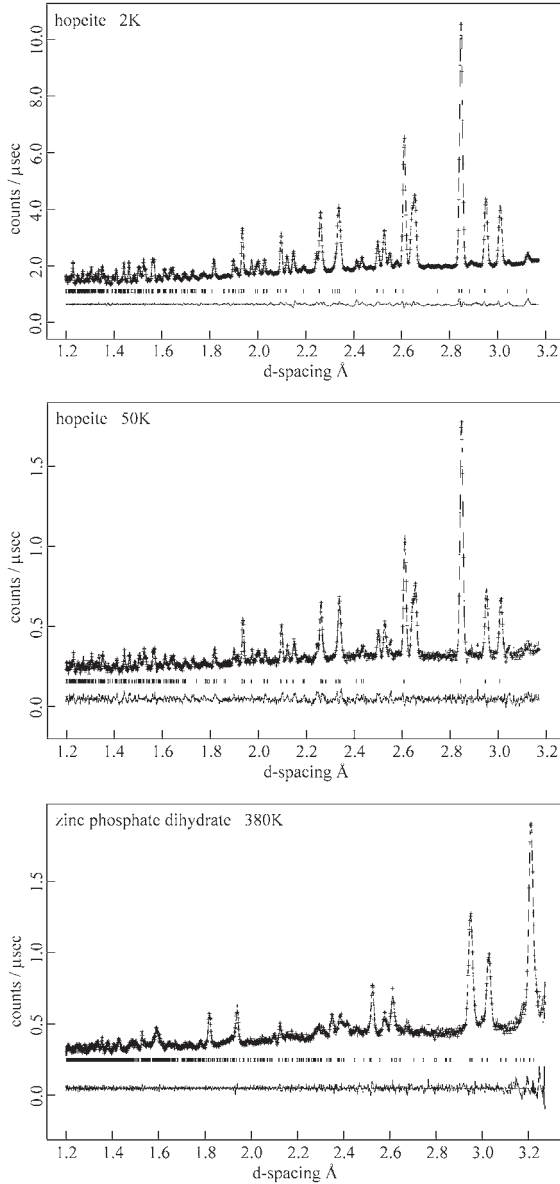
| $T$ (K) | Count time ( $\mu$ Ah) | No. of observations | $R_p$ (%) | $R_{wp}$ (%) | $a$ (Å)    | $b$ (Å)   | $c$ (Å)   | $\beta$ (°) | Volume (Å <sup>3</sup> ) |
|---------|------------------------|---------------------|-----------|--------------|------------|-----------|-----------|-------------|--------------------------|
| 335     | 10                     | 1480                | 4.47      | 4.98         | 10.475(2)  | 5.0433(7) | 31.455(5) | 92.408(9)   | 1660.3(2)                |
| 345     | 10                     | 1485                | 4.65      | 5.19         | 10.481(3)  | 5.0447(9) | 31.447(6) | 92.432(9)   | 1661.3(3)                |
| 355     | 10                     | 1488                | 4.23      | 4.77         | 10.467(2)  | 5.0456(6) | 31.489(4) | 92.385(8)   | 1661.5(2)                |
| 360     | 100                    | 1496                | 1.74      | 2.11         | 10.4628(7) | 5.0467(2) | 31.501(1) | 92.387(3)   | 1661.9(1)                |
| 380     | 20                     | 1479                | 3.17      | 3.86         | 10.459(2)  | 5.0468(4) | 31.533(3) | 92.364(6)   | 1663.0(2)                |
| 400     | 20                     | 1479                | 3.36      | 3.74         | 10.447(1)  | 5.0485(7) | 31.572(3) | 92.364(7)   | 1663.8(2)                |
| 420     | 170                    | 1478                | 3.41      | 3.79         | 10.445(1)  | 5.0490(8) | 31.573(3) | 92.373(7)   | 1663.6(2)                |
| 440     | 10                     | 1478                | 4.07      | 4.78         | 10.435(1)  | 5.0519(6) | 31.653(4) | 92.331(9)   | 1667.2(2)                |
| 460     | 25                     | 1495                | 2.76      | 2.98         | 10.4375(8) | 5.0483(6) | 31.624(2) | 92.406(6)   | 1664.8(2)                |
| 480     | 10                     | 1486                | 4.29      | 4.83         | 10.437(2)  | 5.051(1)  | 31.656(5) | 92.38(1)    | 1667.5(3)                |

Note: The numerical agreement factors  $R_p$  and  $R_{wp}$  are defined in Young (1993).

where  $K = 3\chi\gamma Nk\vartheta_E$  and  $\gamma$  is a Gruneisen parameter and  $\chi$  is the compressibility.

The trends for the lattice parameters  $a$  and  $c$ , and the unit-cell volume are indeed well fitted to an Einstein expression of the form  $X = X_0 + K/[e^{(\vartheta/T)} - 1]$ , where  $X_0$  is the parameter  $X$  at 0 K,  $K$  is the Einstein constant,  $\vartheta$  is the effective Einstein temperature and  $T$  is the temperature in Kelvin between 2 and 300 K. These fits are displayed with the raw data graphically in Figure 4, and are tabulated with the associated errors derived from the fitting process in Table 3.

The instantaneous (isobaric) thermal expansion, which is



**FIGURE 3.** Diffraction data (crosses) from the 90° detector bank of HRPD, their calculated fits (solid lines) difference curve and calculated reflection positions (vertical tick marks) for hopeite at 2 K collected for 400  $\mu$ Ah (top), hopeite at 50 K collected for 10  $\mu$ Ah (middle) and zinc phosphate dihydrate at 380 K collected for 20  $\mu$ Ah (bottom).

related to the unit-cell parameter  $x$ , where  $\alpha_x = (1/x_0)(\delta x/\delta T)$  and  $x_0$  is the magnitude of parameter  $x$  at 0 K, is displayed graphically in Figure 5. At 275 K, this gives values for the thermal expansion coefficients  $\alpha_a$ ,  $\alpha_c$ , and  $\alpha_V$  of  $-1.1(4) \times 10^{-5}$ ,  $3.6(2) \times 10^{-5}$ , and  $3.8(2) \times 10^{-5} \text{ K}^{-1}$ , respectively and the associated representation quadric is a hyperboloid of one sheet. At very high temperatures  $e^{(\vartheta/T)} \approx 1 + (\vartheta/T)$  and consequently  $(1/x_0)(\delta x/\delta T) \approx K/(x_0\vartheta) \cdot [1 + (\vartheta/T)]$ . Thus for very high temperatures, the thermal expansion coefficients for  $a$ ,  $c$ , and  $V$  can be represented by

$$\alpha_a = (1/a_0)(\delta a/\delta T) \approx K/(a_0\vartheta) \cdot [1 + (\vartheta/T)] = -1.59 \times 10^{-5} [1 + (\vartheta/T)] \quad (3)$$

$$\alpha_c = (1/c_0)(\delta c/\delta T) \approx K/(c_0\vartheta) \cdot [1 + (\vartheta/T)] = 4.04 \times 10^{-5} [1 + (\vartheta/T)] \quad (4)$$

$$\alpha_V = (1/V_0)(\delta V/\delta T) \approx K/(V_0\vartheta) \cdot [1 + (\vartheta/T)] = 4.38 \times 10^{-5} [1 + (\vartheta/T)] \quad (5)$$

leading to theoretical high-temperature limits of  $-5.4(4) \times 10^{-5}$ ,  $9.5(2) \times 10^{-5}$ , and  $1.06(2) \times 10^{-4} \text{ K}^{-1}$  for  $a$ ,  $c$ , and  $V$ , respectively.

Unlike the  $a$ ,  $c$ , and  $V$  parameters, the temperature dependent trend of the  $b$  lattice parameter is not well fitted to an Einstein expression above 275 K. Instead, the apparent saturation of  $b$  above 275 K causes the trend to be better represented by an asymmetric logistic expression of the form  $X = X_0 + (X_{300} - X_0)/[1 + (T/f)^d]^g$ , where  $X_0$  and  $X_{300}$  are the  $b$  parameter at 0 and 300 K respectively,  $d$  is a slope parameter,  $f$  is the temperature at the inflection point,  $g$  is an asymmetry parameter, and  $T$  is the temperature in Kelvin between 2 and 300 K. This fit is displayed with the raw data for  $b$  in Figure 4, and tabulated in Table 3. From this the thermal expansion coefficient for  $b$  at 275 K is

$$\alpha_b = (1/b_0)(\delta b/\delta T) = 2.4(9) \times 10^{-6} \text{ K}^{-1} \quad (6)$$

As noted previously, above 275 K the  $b$  lattice parameter no longer increases as a function of increasing temperature. Thus, it would be expected that  $\alpha_b$  will reach a maximum at the temperature of the inflection point of the logistic and then decrease as the temperature continues to increase above this and approach zero above about 275 K. With the parameterization we have used for the  $b$  lattice parameter, this is indeed the case (Fig. 5).

Haussühl and Friedrich (1993) state that the linear thermal expansion coefficients for hopeite are  $\alpha_{11} = -3.3(5) \times 10^{-6}$ ,  $\alpha_{22}$

**TABLE 3.** Tabulated results and errors from the lattice parameter fitting procedures for the data in the range  $2 \leq T \leq 300 \text{ K}$

|     | $X_0$                     | $K$        | $\vartheta$ |        |         |
|-----|---------------------------|------------|-------------|--------|---------|
| $a$ | 10.6178(1) Å              | -0.11(1)   | 652(22) K   |        |         |
| $c$ | 4.9988(1) Å               | 0.075(2)   | 371(5) K    |        |         |
| $V$ | 969.978(9) Å <sup>3</sup> | 16.6(4)    | 391(4) K    |        |         |
|     | $X_0$                     | $X_{300}$  | $d$         | $f$    | $g$     |
| $b$ | 18.2951(1)                | 18.2980(5) | -16(2)      | 240(3) | 0.36(8) |

Notes: Lattice parameters  $a$  and  $c$  and the unit-cell volume  $V$  were fitted by Einstein functions. Lattice parameter  $b$  was fitted by an empirical logistic function.  $X_0$ ,  $K$ , and  $\vartheta$  represent the 0 K cell parameter value, the Einstein constant and the effective Einstein temperatures, respectively.  $X_0$ ,  $X_{300}$  represent the cell parameter at 0 and 300 K, respectively,  $d$  is the slope parameter,  $f$  is the temperature at the inflection point, and  $g$ , the exponent of the denominator, is an asymmetry parameter.

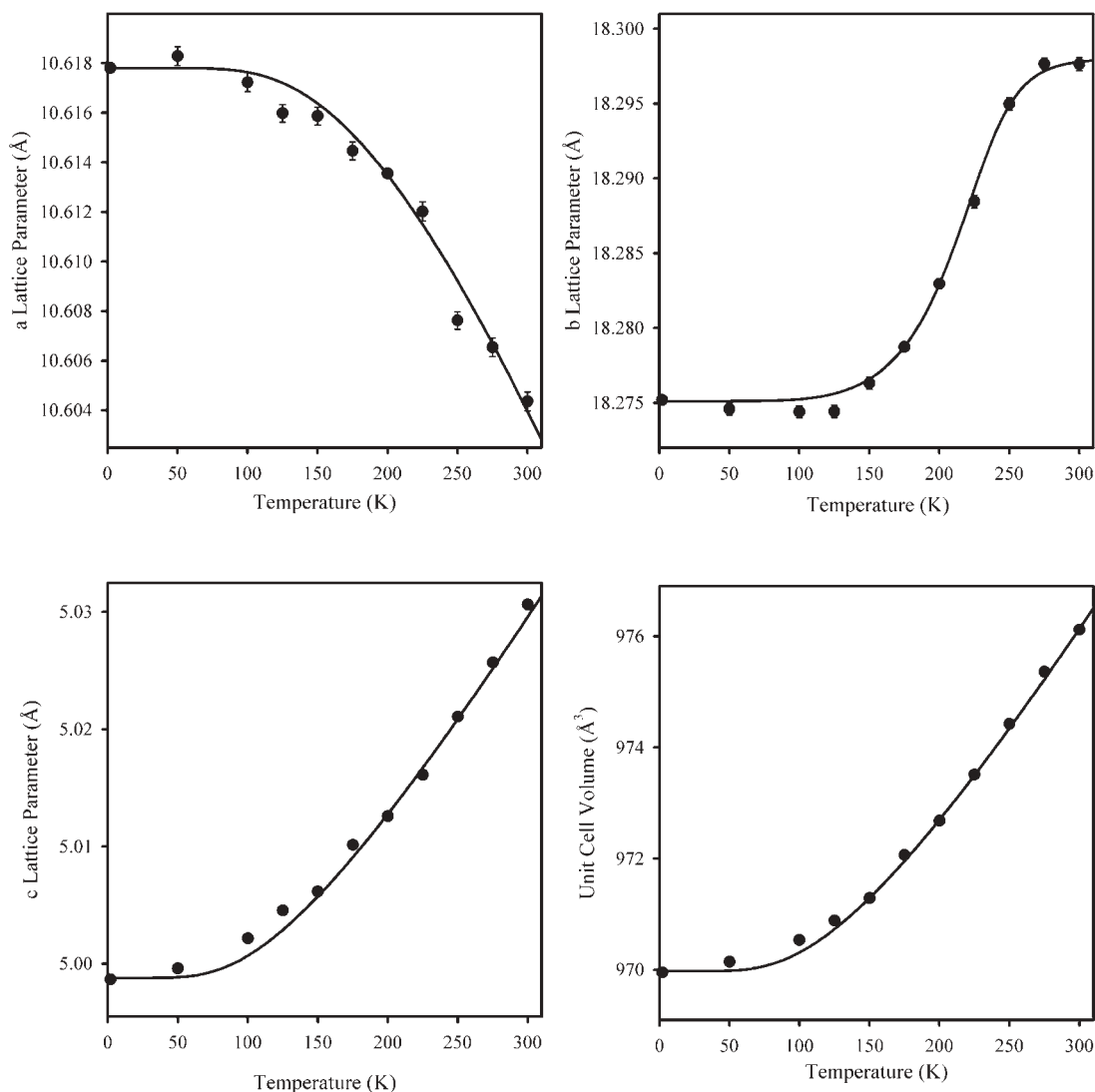


FIGURE 4. Variation of the lattice parameters of hopeite within the temperature range  $2 \leq T \leq 300$  K. The calculated fits (solid lines) are represented by Einstein functions for  $a$ ,  $c$ , and  $V$ , and by an empirical logistic function for  $b$ .

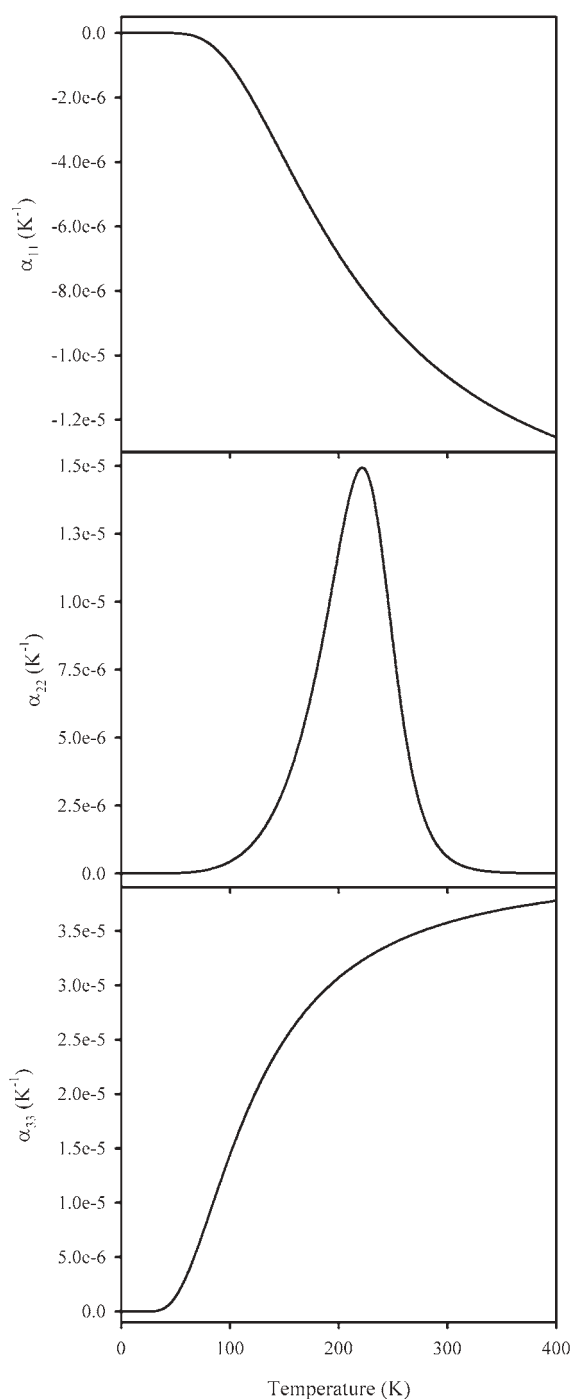
$= 3.4(5) \times 10^{-6}$ , and  $\alpha_{33} = 3.3(2) \times 10^{-5}$ . While these values are fairly close to the 275 K values from this study, the lack of data presented by Haussühl and Friedrich (1993) make it difficult to provide a more insightful comparison. It is worth noting, however, that in the study of Haussühl and Friedrich (1993) the thermal expansion of hopeite was measured between 240 and 300 K. As can be seen from Figure 4 in this manuscript, any linear treatment of data within this temperature range, particularly for the  $b$  lattice parameter, may not reflect the true temperature-dependent behavior of hopeite.

The crystal structure of hopeite (Kawahara et al. 1973; Whitaker 1975; Hill and Jones 1976) comprises layers perpendicular to  $b$  with tetrahedral sheets of corner sharing  $\text{PO}_4$  and  $\text{ZnO}_4$  tetrahedra separated by sheets of face-sharing octahedra, which are one quarter occupied by Zn atoms. Within the tetrahedral sheets are zigzag chains of corner sharing  $\text{ZnO}_4$  tetrahedra running parallel to  $c$  and the  $\text{PO}_4$  tetrahedra, share corners with two different

$\text{ZnO}_4$  tetrahedra and also form a corner sharing link to the  $\text{ZnO}_6$  octahedra. Difference analysis (Whitaker 1975) and bond valence analysis (Hill and Jones 1976) have predicted the hydrogen atom positions, with the water molecules all associated with the  $\text{ZnO}_6$  octahedra. With four of the O atoms of the  $\text{ZnO}_6$  octahedra associated with water molecules, the remaining two O atoms are in a *cis* configuration and link the tetrahedral and octahedral layers by forming bridges between  $\text{PO}_4$  and  $\text{ZnO}_6$  polyhedra.

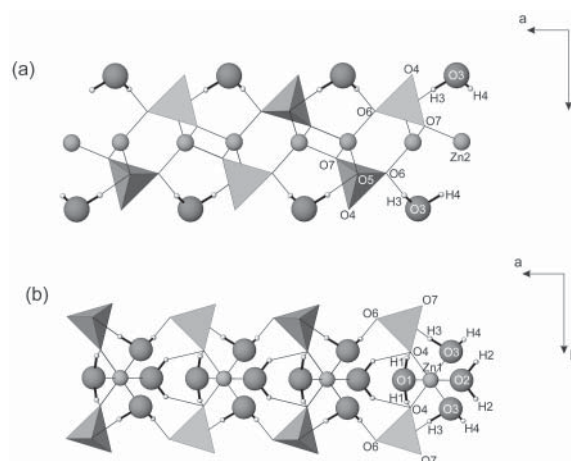
The tetrahedral sheets comprise a single layer of  $\text{ZnO}_4$  tetrahedra sandwiched between two layers of  $\text{PO}_4$  tetrahedra. These tetrahedra are all strongly distorted, and their corner sharing nature means that they form a series of 3- and 4-membered rings (Hill and Jones 1976). These 4-membered rings consist of alternating  $\text{ZnO}_4$  and  $\text{PO}_4$  tetrahedra and can be seen within the tetrahedral layer in Figure 6a. If a distortion of these 4-membered rings occurred such that the distance between the  $\text{PO}_4$  tetrahedra increased, and simultaneously the  $\text{PO}_4$  tetrahedra became





**FIGURE 5.** Temperature dependence of the thermal expansion tensor coefficients,  $\alpha_{11}$ ,  $\alpha_{22}$ , and  $\alpha_{33}$ , of hopeite as calculated from the mathematical fits of the lattice parameters.

more aligned within the **bc** plane, the overall effect would be a contraction along **a** and an expansion along **b** and **c**. Such a distortion could be related to structural or rotational modifications of tetrahedral units within the 3- and 4-membered rings. The saturation of the thermal expansion along **b** may occur due to a maximum distortion being reached within the tetrahedral layer,



**FIGURE 6.** Representation of the crystal structure of hopeite after Whitaker (1975). **(a)** The tetrahedral sheet comprising layers of  $\text{PO}_4$  tetrahedra and 1 layer of  $\text{ZnO}_4$  tetrahedra. The filled tetrahedra are  $\text{PO}_4$ , tetrahedral Zn are small shaded circles, the O atoms of the water molecules are larger, darker filled circles and the protons are white. **(b)** The layer of  $\text{ZnO}_6$  octahedra between the tetrahedral sheets with  $\text{PO}_4$  represented by filled tetrahedra, the Zn atoms are small shaded circles, the O atoms of the water molecules are larger, darker filled circles and the protons are white.

for example the cessation of tetrahedral rotation or perhaps to changes in the vibrational modes of molecular units. Additionally, reaching a maximum distortion within the  $\text{ZnO}_6$  octahedral layer (Fig. 6b), for example the  $\text{O4-Zn1-O4'}$  bond lengths and angle that effectively bind the tetrahedral layers together, may cause a saturation of the thermal expansion along **b**.

### ZINC PHOSPHATE DIHYDRATE

In these experiments, with the sample held under 30 mb He of exchange gas, deuterated hopeite began to dehydrate between 300 and 325 K. By 335 K there was no evidence of any hopeite remaining within the sample, only the subhydrate  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . Based upon evidence from thermal analysis, Nikonenko et al. (1985) suggested that the dihydrate is metastable, however, Arnaud et al. (1988) showed that the dihydrate is a stable phase formed as part of the dehydration mechanism from hopeite to the monohydrate and anhydrous  $\text{Zn}_3(\text{PO}_4)_2$ . Indeed, Arnaud et al. (1988) suggest that a further metastable phase may appear, albeit transiently, toward the end of this dehydration reaction with a composition near  $2\text{Zn}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ . As yet there has been no structural determination for the dihydrate, although Arnaud et al. (1988) show that the structure of the dihydrate is topologically similar to that of hopeite, with a space group of  $P2_1/c$  and lattice parameters  $a = 10.451 \text{ \AA}$ ,  $b = 5.036 \text{ \AA}$ ,  $c = 31.437 \text{ \AA}$ , and  $\beta = 92.46^\circ$ . The dihydrate produced by the dehydration of deuterated  $\alpha$ -hopeite in our experiment was further heated and found to dehydrate between 480 and 520 K to the monohydrate phase.

At 10 temperatures between 335 and 480 K diffraction data were collected from which the lattice parameters of zinc phosphate dihydrate could be refined and the thermal expansion calculated. These parameters are tabulated in Table 2 and displayed graphically in Figure 7, and as observed for hopeite the thermal

expansion of the dihydrate is anisotropic. The  $a$  lattice parameter decreases by 0.36% of the 335 K value, as the temperature is increased. The  $b$  and  $c$  lattice parameters increase as a function of increasing temperature by 0.15% and 0.64% of their 335 K values, respectively. The  $a$ ,  $b$ , and  $c$  lattice parameters all appear to saturate at about 440 K. The  $\beta$  angle appears to show an overall decrease of about  $0.03^\circ$ , with either a saturation occurring at about 440 K or even oscillatory behavior, with a potential increase above about 440 K. The unit-cell volume shows a steady increase of 0.4% of the volume at 335 K.

The diffraction data from this part of the study were not ideal. A combination of short data collection times and the broad peak width, in addition to the weak intensity of the Bragg peaks that is so common in subhydrate dehydration products, reduces the precision of the refined parameters. Furthermore, when coupled with the limited range of both the diffraction data and the overall temperature interval, the degree of analysis undertaken for hopeite is not justified for the dihydrate data. The temperature dependent trends of the lattice parameters of zinc phosphate dihydrate were, therefore, empirically modeled using the quadratic  $X = X_0 + dT + fT^2$  where  $X_0$  is the parameter  $X$  at 0 K and  $T$  is the temperature in Kelvin between 335 and 480 K. These fits are displayed in Figure 7 and are tabulated in Table 4. These data in turn lead to thermal expansion coefficients for the lattice parameters of

$$\alpha_a = (1/a_0)(\delta a/\delta T) = (1/a_0)(d + 2fT) = -1.8(2) \times 10^{-4} + 4.0(3) \times 10^{-7}T \quad (7)$$

$$\alpha_b = (1/b_0)(\delta b/\delta T) = (1/b_0)(d + 2fT) = 8.1(2) \times 10^{-5} - 1.6(3) \times 10^{-7}T \quad (8)$$

$$\alpha_c = (1/c_0)(\delta c/\delta T) = (1/c_0)(d + 2fT) = 2.0(2) \times 10^{-4} - 3.3(3) \times 10^{-7}T \quad (9)$$

$$\alpha_\beta = (1/\beta_0)(\delta \beta/\delta T) = (1/\beta_0)(d + 2fT) = -6(1) \times 10^{-5} + 1.5(2) \times 10^{-7}T \quad (10)$$

$$\alpha_V = (1/V_0)(\delta V/\delta T) = (1/V_0)(d + 2fT) = 8(2) \times 10^{-5} - 1.2(2) \times 10^{-7}T \quad (11)$$

At 480 K [the temperature limit of the stability of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  in this study] the coefficients were  $1(2) \times 10^{-5}$ ,  $4(1) \times 10^{-6}$ ,  $4(2) \times 10^{-5}$ ,  $1(1) \times 10^{-5}$ , and  $2(2) \times 10^{-5} \text{ K}^{-1}$ , respectively.

We have used the Institute of Radio Engineers (IRE) convention for the orthonormal tensor basis:  $\mathbf{e}_3 \parallel \mathbf{c}$ ,  $\mathbf{e}_2 \parallel \mathbf{b}^*$ ,  $\mathbf{e}_1 \parallel \mathbf{a} \times \mathbf{c}$ , and the Lagrangian thermal expansion tensor coefficients for a

monoclinic crystal with  $\mathbf{b}$  as the unique axis are given by Schlenker et al. (1975). Using these expressions we have calculated the temperature variation of the thermal expansion tensor coefficients for zinc phosphate dihydrate between 335 and 480 K by incorporating the parameters refined from the least squares fitting of the temperature dependence of the lattice parameters. The principal axes and their orientation were determined analytically (Knight et al. 1999). The temperature dependence of the principal axes magnitudes and the angle of orientation of the principal axis  $\alpha_{11}$  with respect to  $\mathbf{c}$  are shown in Figure 8. The magnitudes of the principal axes  $\alpha_{11}$  and  $\alpha_{22}$  decrease on increasing temperature, with  $\alpha_{22}$  becoming negative above about 500 K. The magnitude of  $\alpha_{33}$  is negative throughout the entire temperature range but increases toward zero as a function of increasing temperature. The angle of orientation of the principal axis  $\alpha_{11}$  with respect to  $\mathbf{c}$  appears to decrease from about  $5^\circ$  at 335 K as a function of increasing temperature, becoming zero at about 440 K where  $\alpha_{13}$  becomes negative before rising sharply. This behavior above about 440 K may be related to the parameterization of the  $\beta$  angle that shows a minimum at about 440 K (Fig. 7). At 400 K the principal axes have magnitudes and directions:  $\alpha_{11}$ ,  $4.6(7) \times 10^{-5} \text{ K}^{-1}$  ( $-0.050, 0, -0.999$ );  $\alpha_{22}$ ,  $1.6(5) \times 10^{-5} \text{ K}^{-1}$  ( $0, 1, 0$ );  $\alpha_{33}$ ,  $-2.2(7) \times 10^{-5} \text{ K}^{-1}$  ( $0.999, 0, -0.050$ ).

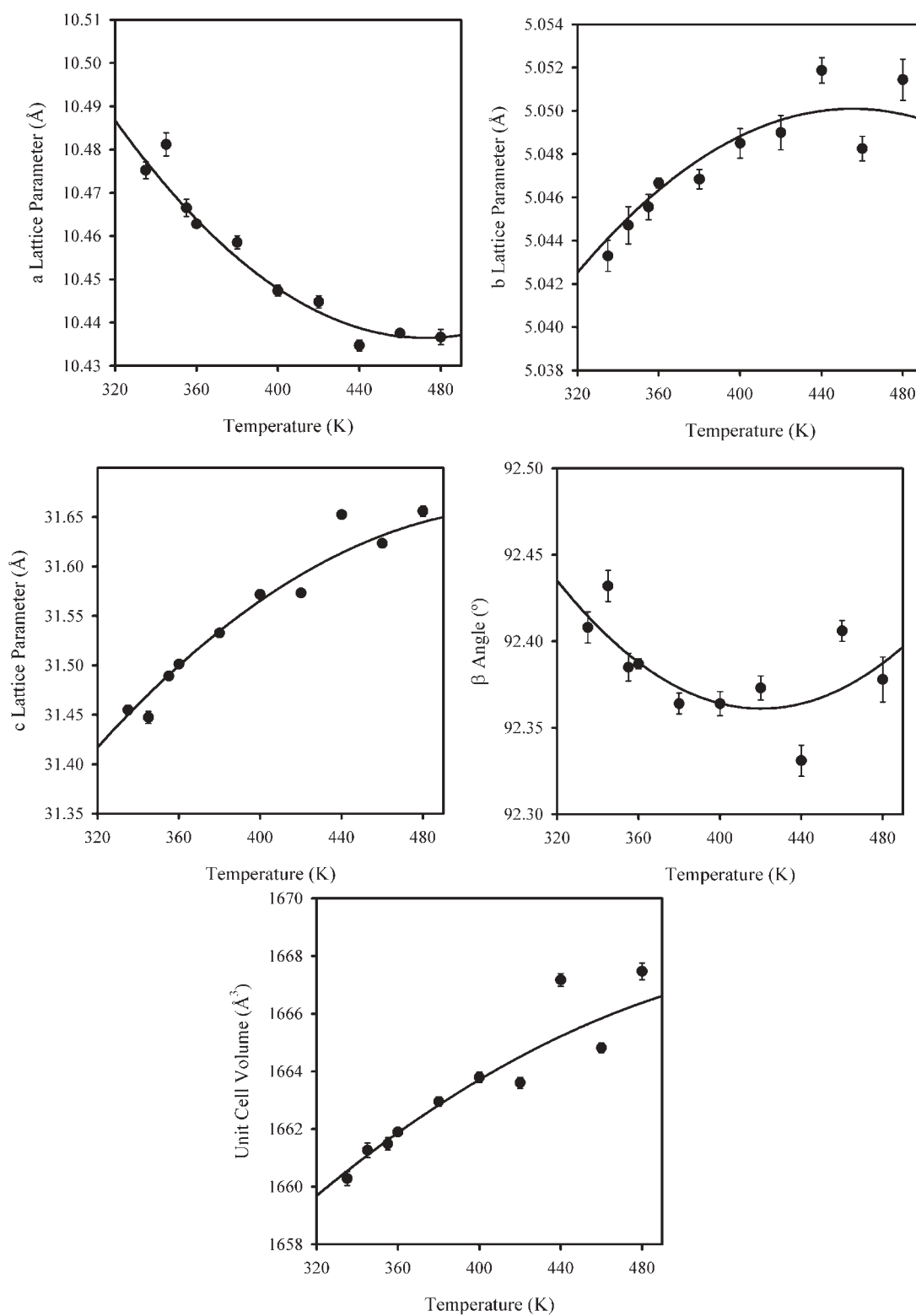
Comparison of the crystal structures of hopeite (Whitaker 1975; Hill and Jones 1976) with zinc phosphate dihydrate (Arnaud et al. 1988) and monohydrate (Riou et al. 1986) shows that the basic topology of the structures is the same. That is, the tetrahedral layers, comprising a layer of  $\text{PO}_4$  tetrahedra either side of a single layer of  $\text{ZnO}_4$  tetrahedra, are bound together by  $\text{ZnO}_6$  octahedra with a significant involvement from hydrogen bonding associated with the water molecules. The loss of water molecules from the hopeite octahedral layer transforms the  $\gamma$  angle of hopeite to the  $\beta$  angle of the dihydrate. The  $\mathbf{a}$  axis of hopeite remains the  $\mathbf{a}$  axis of the dihydrate and  $\mathbf{b}$  of hopeite becomes  $\mathbf{c}$  of the dihydrate. Subsequent transformation to the monohydrate cell defined by Riou et al. (1986) has  $\mathbf{a}$  and  $\mathbf{c}$  of the dihydrate becoming  $\mathbf{c}$  and  $\mathbf{a}$  respectively in the monohydrate. The  $\text{ZnO}_6$ , or  $\text{ZnO}_2(\text{H}_2\text{O})_4$ , octahedra are essentially isolated from each other in hopeite, but in the monohydrate the  $\text{ZnO}_6$ , or  $\text{ZnO}_5(\text{H}_2\text{O})$ , octahedra corner share with 2 other  $\text{ZnO}_5(\text{H}_2\text{O})$  octahedra to form zigzag chains along  $\mathbf{b}$ . Additionally, the  $\text{ZnO}_5(\text{H}_2\text{O})$  octahedra also form an edge sharing link with one of the two crystallographically distinct  $\text{PO}_4$  tetrahedra. The hydrogen bonding is directed into the channels between the chains of octahedra.

For the simplified reaction  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Zn}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , the initial stage of the dehydration of hopeite is likely to be through the loss of the O3 water molecules (using the nomenclature of Hill and Jones 1976). The Zn-O3 bonds may be the longest within the octahedra, but their hydrogen bonding acts across a single tetrahedral sheet and do not contribute to binding the tetrahedral layers together, unlike the remaining hydrogen bonds. The symmetry breaking occurs at this stage as the structure reorganizes toward that of the monoclinic subhydrates, with the  $\text{ZnO}_6$  octahedra forming edge-sharing linkages with some of the phosphate tetrahedra. The loss of a third water molecule induces the formation of corner sharing  $\text{ZnO}_6$  octahedra producing the zigzag chains along  $\mathbf{b}$ , which simultaneously

**TABLE 4.** Tabulated results and errors from the lattice parameter fitting procedures for the data in the range  $335 \leq T \leq 480 \text{ K}$

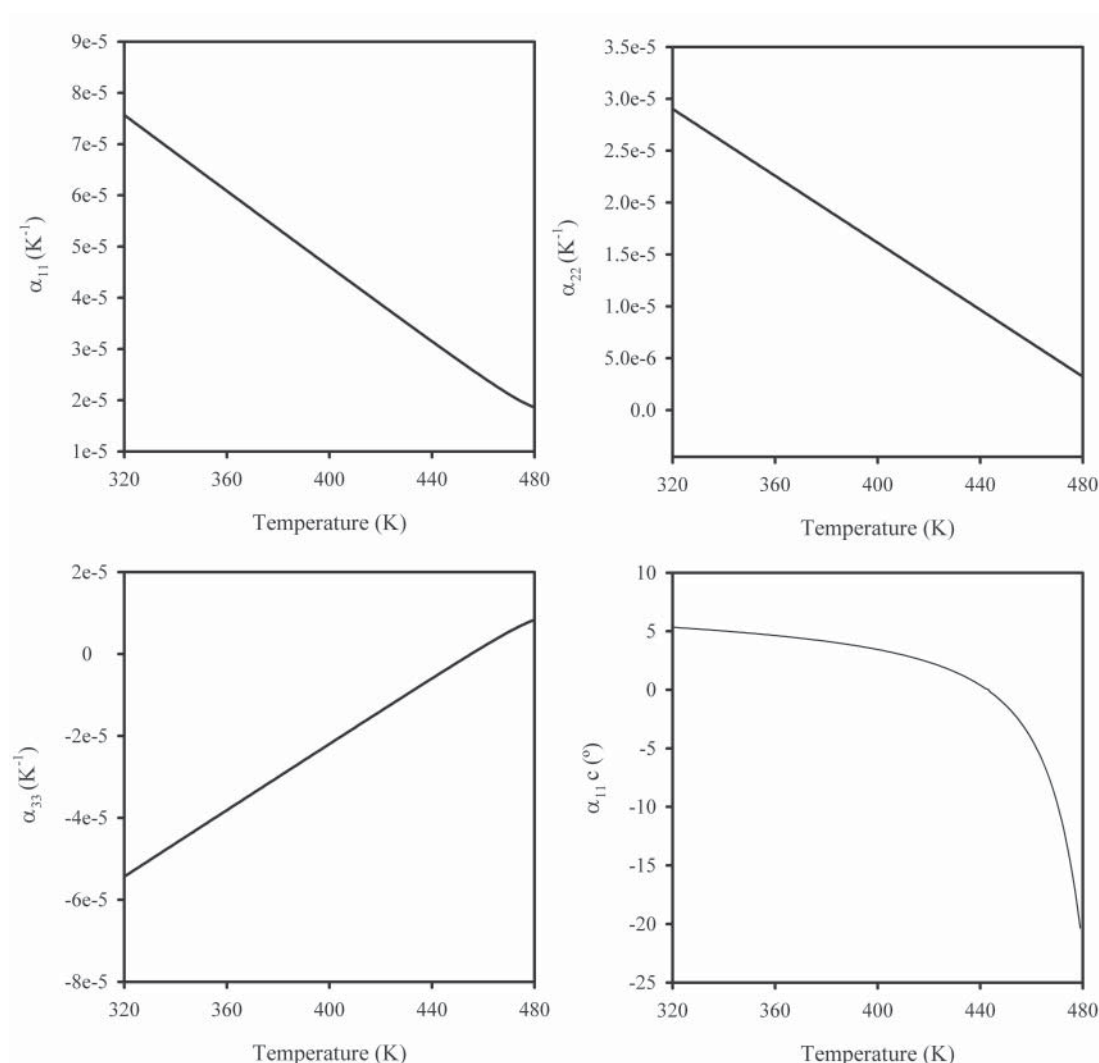
|         | $X_0$                  | $d$          | $f$                         |
|---------|------------------------|--------------|-----------------------------|
| $a$     | 10.918(46) Å           | -0.00204(22) | $2.16 \times 10^{-6}$ (27)  |
| $b$     | 4.964(21) Å            | 0.00038(10)  | $-4.1 \times 10^{-7}$ (13)  |
| $c$     | 30.14(11) Å            | 0.00572(54)  | $-5.37 \times 10^{-6}$ (66) |
| $\beta$ | 93.66(26) $^\circ$     | -0.0062(13)  | $7.4 \times 10^{-6}$ (16)   |
| $V$     | 1630(6) Å <sup>3</sup> | 0.127(32)    | $-1.06 \times 10^{-4}$ (39) |

Note: Data were empirically fitted using the quadratic  $X = X_0 + dT + fT^2$  where  $X_0$  represents the 0 K cell parameter value, and  $d$  and  $f$  are constants.



**FIGURE 7.** Variation of the lattice parameters of the hopeite subhydrate  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  within the temperature range  $335 \leq T \leq 480$  K. The calculated fits are empirically represented by a quadratic of the form  $X = X_0 + dT + fT^2$  where  $X_0$  represents the 0 K cell parameter value and  $d$  and  $f$  are constants.





**FIGURE 8.** Temperature dependence of the magnitudes of the principal thermal expansion tensors and the angle of orientation of the principal axis  $\alpha_{11}$  for  $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  as calculated from the empirical fitting of the unit-cell parameter data within the temperature range  $335 \leq T \leq 480$  K.

halves the  $c$  lattice parameter of the dihydrate into that of the monohydrate.

Without an accurate structural model of the dihydrate, it is less clear as to which of the two remaining water molecules from the original hopeite is removed to form the monohydrate of Riou et al. (1986). In hopeite the relevant Zn-O bond lengths are fairly similar with Zn-O1 = 2.098 Å and Zn-O2 = 2.103 Å (Hill and Jones 1976). Whitaker (1975) shows that the hydrogen bonding associated with O1 is clearly linked with O4, an oxygen atom from the phosphate tetrahedra, but the hydrogen bonding associated with O2 is not clear. Whitaker (1975) was unable to definitively locate the position of the fourth hydrogen atom, and suggested that the proton may be disordered on two sites, one linking to O4 and one linking to the O3 oxygen of a water molecule. Hill and Jones (1976) use bond valence arguments to suggest that the link to O4 was more likely, however, this indistinct nature for the hydrogen atoms associated with O2 may indicate that this is the water molecule that is removed in the

dehydration stage from the dihydrate to the monohydrate.

The uncertainty in the position of the hydrogen atoms associated with the O2 water molecule of hopeite may explain the existence and different thermal behavior between the  $\alpha$  and  $\beta$  modifications. If this proton is entirely in the H24 position of Whitaker (1975), that is forms a hydrogen bond between O2 and O4, then the dehydration of hopeite may occur in three stages, forming the dihydrate by loss of the O3 water molecules, then the monohydrate by loss of the O2 water molecule and finally the anhydrous form by loss of the final water molecule (associated with O1), although the stability range of the monohydrate seems to be varied, and very limited in this study. This behavior will produce the thermal properties and infrared spectrum characteristic of the  $\alpha$ -hopeite form. If however, the proton resides entirely upon the H23 position of Whitaker (1975), that is forms a hydrogen bond between O2 and O3, then the loss of O3 during the first dehydration stage of hopeite will inherently induce an instability associated with the O2 water molecule causing

it to be removed from the structure simultaneously with O3. This behavior will produce the thermal properties and infrared spectrum characteristic of the  $\beta$ -hopeite form. This proton may of course be disordered across the H24 and H23 positions of Whitaker (1975), thus producing the range of thermal properties reported in the literature, and perhaps the intergrowths described by Spencer (1908) and zonation patterns shown by Hill and Jones (1976). Such an interpretation may be idealistic as within the hopeite structure there exists the potential for non-hydrogen bonded protons, multiple hydrogen bonds per proton, and excess protons.

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