Renormalization of the phase transition in lead phosphate, Pb$_3$(PO$_4$)$_2$, by high pressure: lattice parameters and spontaneous strain

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Abstract

The unit-cell parameters of lead phosphate, Pb$_3$(PO$_4$)$_2$, have been measured by single-crystal X-ray diffraction in a diamond–anvil cell under hydrostatic conditions to a maximum pressure of 6 GPa. The compound undergoes an improper ferroelastic phase transition at 1.81 ± 0.01 GPa at 298 ± 1 K from a low-pressure monoclinic phase (space group $C2/c$) to a high-pressure trigonal phase. The space group of the high-pressure phase is $R\bar{3}m$ or $R3m$ and the phase boundary is the same as that crossed at *ca* 450 K at room pressure. The evolution of the spontaneous strain components arising from the phase transition is linear with pressure, indicating an effective critical exponent for the phase transition of $\beta = 0.50 \pm 0.03$. Thus, the application of pressure strongly renormalizes the effective critical exponent of the order parameter from the value of 0.236 found in high-temperature experiments.

1. Introduction

Lead phosphate, Pb$_3$(PO$_4$)$_2$, is an improper ferroelastic material that is a prototype for a large class of ferroelastics. It undergoes a phase transition from a high-temperature structure with trigonal $R\bar{3}m$ symmetry to a low-temperature phase with monoclinic $C2/c$ symmetry. In the monoclinic phase the trigonal symmetry is broken by displacements of Pb atoms from the triads, together with concomitant rotations of the PO$_4$ tetrahedra. In addition, the pure Pb$_3$(PO$_4$)$_2$ material exhibits an intermediate phase with global $R\bar{3}m$ symmetry in which the Pb atoms are locally displaced from the triads, and flip between the three alternative displacement directions on a timescale of $\sim 10^{-10}$ s (Benoit *et al.*, 1981; Salje *et al.*, 1983). The ferroelastic phase transition at high temperature therefore takes place between the monoclinic phase and this intermediate 'flip-mode' phase.

The spontaneous strain arising from the transition becomes $\sim$2% by room temperature, which is unusually large for a phase transition with quadratic coupling between the strain and the order parameter. This spontaneous strain includes a positive excess volume for the monoclinic phase at room temperature (*e.g.* Salje *et al.*, 1993). Therefore, the $C2/c = R\bar{3}m$ phase boundary

has a negative slope, dT/dP, in P-T space (Tolédano *et al.*, 1975; Midorikawa *et al.*, 1981) and the phase transition can also be studied at room temperature and elevated pressures. Decker *et al.* (1979) reported neutron powder diffraction results which indicated that lead phosphate becomes trigonal at *ca* 2 GPa under hydrostatic conditions. Raman spectra collected at high pressures (Benoit & Chapelle, 1974; Kagawa *et al.*, 1987) support this interpretation. The existing data, however, do not allow either the space group of the trigonal phase to be confirmed as $R\bar{3}m$ nor the details of the pressure evolution of the spontaneous strain, and hence the character of the phase transition, to be determined. We have therefore performed single-crystal X-ray diffraction measurements of lead phosphate at high pressures to address these questions.

2. Experimental

A single-domain (100) plate approximately 5 micron thick and 80 × 140 micron in extent was cut from a larger single crystal of the material that was synthesized by Bismayer & Salje (1981) and studied previously at high-temperatures (*e.g.* Salje *et al.*, 1993). This crystal plate and a quartz crystal were loaded into a BGI design of diamond–anvil cell (Allan *et al.*, 1996) with a 4:1 methanol:ethanol mixture as the hydrostatic pressure medium. Setting angles of diffracted beams from both crystals were determined at high pressure on a Huber four-circle diffractometer by the method of eight-position diffracted-beam centring (King & Finger, 1979), which eliminates the effects of diffractometer abberations and zero errors. Full details of the diffractometer and the peak centring algorithms are given in Angel *et al.* (1997). Unit-cell parameters (Table 1) were determined by vector-least-squares refinement (Ralph & Finger, 1982) to the setting angles of typically 20–26 reflections for the lead phosphate crystal and 10–12 reflections of the quartz crystal. Pressures were determined from the unit-cell volumes of the quartz crystal by using the calibration of Angel *et al.* (1997). All diffraction measurements were performed at 298 ± 1 K. Intensity data were also collected at each pressure by omega scans across a small number of superlattice and

Table 1. *Unit-cell data for lead phosphate at high pressure*

P (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
10^{-5}	13.8064 (5)	5.6946 (2)	9.4270 (3)	102.366 (3)	723.98 (4)
0.146 (5)	13.8033 (17)	5.6759 (6)	9.4287 (8)	102.437 (10)	721.36 (13)
0.482 (4)	13.7917 (7)	5.6303 (3)	9.4332 (4)	102.646 (4)	714.73 (6)
0.819 (5)	13.7838 (5)	5.5881 (2)	9.4418 (3)	102.820 (3)	709.12 (4)
1.031 (4)	13.7761 (8)	5.5609 (3)	9.4465 (4)	102.916 (5)	705.37 (7)
1.154 (4)	13.7722 (10)	5.5466 (4)	9.4488 (5)	102.960 (6)	703.40 (8)
1.249 (5)	13.7701 (10)	5.5362 (4)	9.4512 (4)	103.003 (5)	702.03 (7)
1.543 (4)	13.7678 (20)	5.4996 (6)	9.4664 (8)	103.165 (11)	697.93 (14)
1.816 (4)	5.4676 (2)		20.0940 (8)		520.22 (5)
3.021 (6)	5.4322 (2)		20.0080 (6)		511.31 (4)
4.086 (5)	5.4071 (2)		19.9418 (7)		504.91 (4)
4.710 (7)	5.3936 (3)		19.9082 (9)		501.57 (5)
5.981 (7)	5.3684 (3)		19.8455 (8)		495.33 (5)

sublattice reflection positions. A second set of experiments with a larger crystal of lead phosphate, approximately 50 microns thick and 200 microns square, yielded the same results within experimental errors, but are not reported here because the larger crystal size restricted the maximum pressure achieved to ~3.8 GPa.

A full set of intensity data consisting of all reflections corresponding to a primitive trigonal unit-cell was collected from the first crystal at 1.816 (4) GPa with an Enraf–Nonius CAD-4 diffractometer, operated in 'fixed-phi' mode (Finger & King, 1978) to maximize access to reflection positions. Data was collected with ω-scans of width $1.0 + 0.35\tan\theta°$ in a constant precision mode, which resulted in individual scan times ranging from 60 to 300 s. Integrated intensities were corrected for Lorentz and polarization effects and for absorption by the crystal and the pressure-cell components using a modified version of the *ABSORB* program (Burnham, 1966). Refinements were performed with the *RFINE*90 program, a development of *RFINE*4 (Finger & Prince, 1975).

3. Results

3.1. High-pressure phase transition

The intensities of strong superlattice reflections with $h + l =$ odd and $k + l =$ odd of the monoclinic phase decreased with increasing pressure (*e.g.* Fig. 1) and were undetectable at 1.816 (4) GPa. The unit-cell parameters of lead phosphate at pressures of 1.816 (4) GPa and greater conformed to trigonal symmetry, and the (0001) crystal plate exhibited no optical birefringence. The intensity dataset collected at this pressure contained no reflections violating the absence rule $-h + k + l = 3n$. The diffraction symbol was determined to be $R{--}$, and averaging of intensities confirmed that the Laue class was $\bar{3}m$. These results are consistent with the space group being $R3m$ or $R\bar{3}m$. Attempts to refine the structure were only partially successful. Although Pb1,

Pb2 and P were located at the same positions as in the $R\bar{3}m$ structure of Ba-doped $Pb_3(PO_4)_2$ (Hensler *et al.*, 1993), of the two symmetrically distinct oxygen positions only O2 was located.

Nonetheless, these observations confirm the earlier reports of a monoclinic to trigonal transition in lead
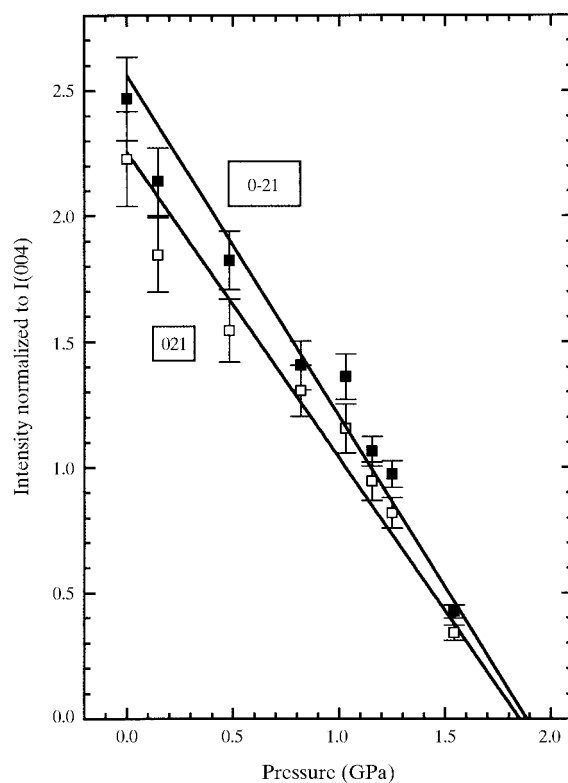

Fig. 1. The variation with pressure of the intensities of two superlattice reflections of the monoclinic phase of lead phosphate, normalized to the measured intensity of the sublattice reflection 004. Intensities have not been corrected for absorption by either the crystal or the diamond–anvil cell, but the diffraction geometry did not vary by more than 2° for either reflection at any pressure.

phosphate at pressures below 2 GPa (Decker *et al.*, 1979; Kagawa *et al.*, 1987) at room temperature. Measurements of the slope of the transition boundary at low pressures and high temperatures vary from −85 (Tolédano *et al.*, 1975) to −98 K GPa^{-1} (Midorikawa *et al.*, 1981). Linear extrapolation of these results to 298 K yields estimated transition pressures ranging from ∼1.58 to ∼1.82 GPa. The agreement of these estimates with a transition pressure of ∼1.8 GPa obtained from our direct observations confirms that the phase transition boundary crossed in our experiments is the same as that observed at *ca.* 450 K and atmospheric pressure.

3.2. *Lattice parameters and spontaneous strains*

The general pattern of evolution of the lattice parameters of the monoclinic phase with increasing pressure (Fig. 2) is very similar to that observed with increasing temperature (Salje *et al.*, 1993). This reflects the dominance of the ferroelastic strains in determining the unit-cell parameters of the ferroelastic phase, to the extent that they result in negative compressibility for directions near the *c* axis at high pressures and negative thermal expansion for this same direction at high temperatures.
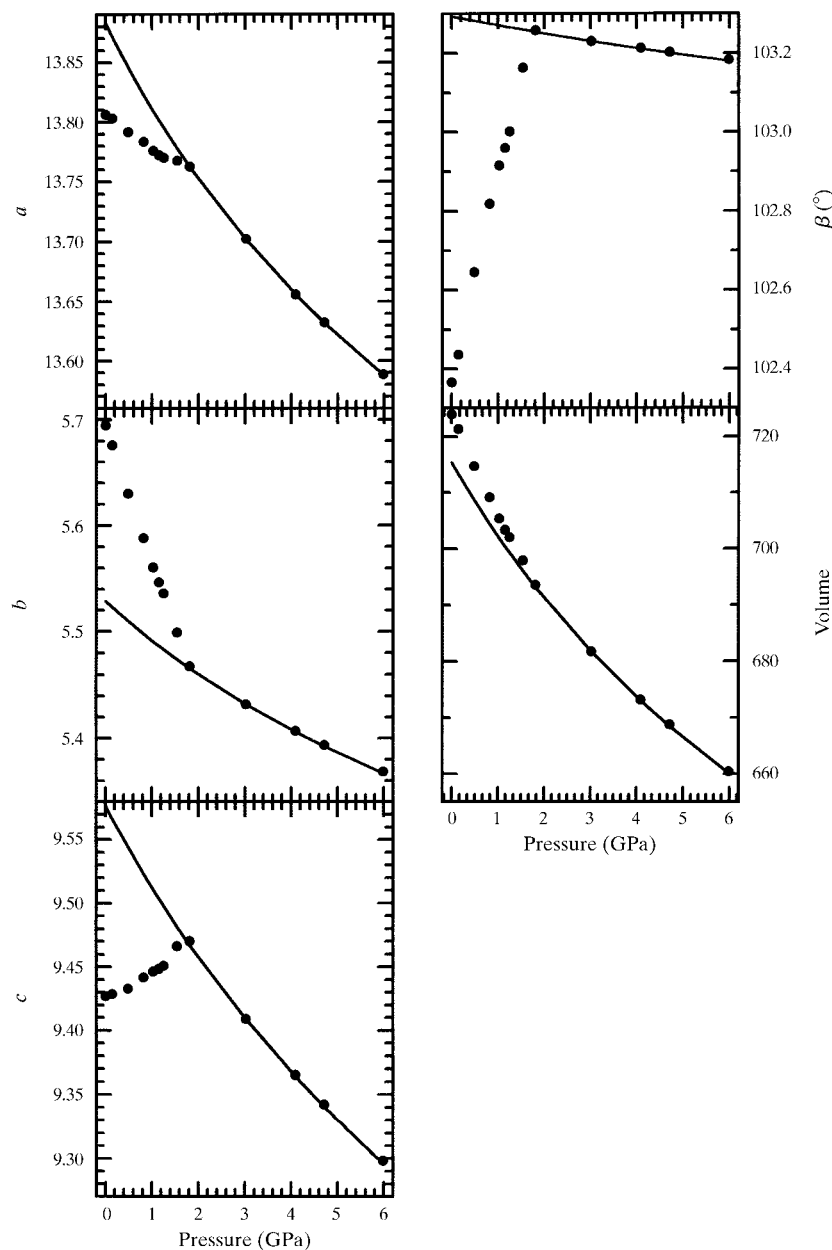

Fig. 2. The evolution of the unit-cell parameters of lead phosphate with pressure. At pressures in excess of 1.8 GPa, the unit cell exhibits trigonal symmetry. For display, the trigonal unit-cell parameters at high pressures have been transformed back to the monoclinic setting. Lines represent the transformation of the trigonal unit-cell parameters obtained from the Murnaghan fits to the trigonal unit-cell data; these are the reference unit-cell parameters for calculations of the spontaneous strains.

The transformation matrix from the monoclinic unit cell to the trigonal unit cell is /0,0.5,0.5/0,−1,0/1.5,0,0.5/. For convenience, the unit-cell parameters of the trigonal phase have been transformed back to the monoclinic setting for display in Fig. 2. However, in order to determine the spontaneous strains in the monoclinic phase arising from the phase transition, the trigonal cell parameters were first fitted with a linearized Murnaghan equation of state, of the form

$$a_{\text{hex}} = a_0(1 + K'P/K_0)^{(-1/3K')} \qquad (1)$$

The unit-cell parameters of the reference trigonal unit cell at room temperature and pressure (a_0 and c_0) obtained by extrapolation from high pressure are within 0.1% of those obtained by extrapolation of the high-temperature dataset of Salje et $al.$ (1993). The agreement not only validates the extrapolations, but points to the high-pressure structure being the same phase as that which exists above the ferroelastic transition at high temperatures.

Trigonal unit-cell parameters were then calculated at each pressure for which monoclinic unit-cell data had been collected and the components of the spontaneous strain were then calculated using the Cartesian reference system of Guimaraes (1979) and Salje et $al.$ (1993)

$$i \,//\, \mathbf{c}_t \,//\, (100)_{\text{mono}}$$
$$j \,//\, \mathbf{b}_t \,//\, \mathbf{b}_{\text{mono}}$$
$$k \,//\, [210]_t \,//\, \mathbf{c}_{\text{mono}}. \qquad (2)$$

Following Carpenter et $al.$ (1998), but using this different choice of reference axes, the spontaneous strain components can be divided into 'symmetry-breaking' and 'non-symmetry-breaking' components as

$$\epsilon_{11,\text{nsb}} = 3a\sin\beta/2c_t - 1$$
$$\epsilon_{11,\text{sb}} = 0$$
$$\epsilon_{22,\text{nsb}} = \epsilon_{33,\text{nsb}} = (b + c/3^{1/2})/2a_t - 1$$
$$\epsilon_{22,\text{sb}} = -\epsilon_{33,\text{sb}} = (b - c/3^{1/2})/2a_t$$
$$\epsilon_{13,\text{nsb}} = 0$$
$$\epsilon_{13,\text{sb}} = (c + 3a\cos\beta)/4c_t$$
$$\epsilon_{12,\text{nsb}} = \epsilon_{23,\text{nsb}} = \epsilon_{12,\text{sb}} = \epsilon_{23,\text{sb}} = 0, \qquad (3)$$

where a_t and c_t are the values of the trigonal unit-cell parameters extrapolated to the same pressure as the monoclinic cell parameters a, b, c and β. The volume strain is simply $V_s = V/V_t - 1$, where V_t is the extrapolated unit-cell volume of the trigonal phase. Note that the expressions given above reduce to those used by Guimaraes (1979) and by Salje et $al.$ (1993) when the non-symmetry-breaking strains due to the transition are ignored.

A fit of the expression $\epsilon = \epsilon_0(P_{\text{tr}} - P)^{2\beta}$ to the data for the largest component, $\epsilon_{22,\text{sb}}$, of the spontaneous strain yielded a value of the critical exponent $\beta =$ 0.48 (3), indicating that the variation is linear with pressure (for which $\beta = 1/2$) within the estimated uncertainties. Phase transition pressures were therefore estimated from linear fits to the data for each strain component (Fig. 3). Extrapolations of the unit-cell parameters of the trigonal phase based upon other equations of state, including the Vinet (Vinet et $al.$, 1986, 1987) and the Birch–Murnaghan ($e.g.$ Birch, 1947; Stacey et $al.$, 1981) were also explored. Although the absolute values of the smaller spontaneous strain components and the pressure at which they extrapolate to zero change a little with the choice of equation used for extrapolation, their relative values and the linear variation with pressure is found for all cases.

All analyses result in $\epsilon_{13,\text{sb}}$ moving towards zero at 1.71 ± 0.03 GPa, significantly less than that of the other strain components (> 1.78 GPa). The other symmetry-breaking component, $\epsilon_{22,\text{sb}}$, moves towards zero at 1.81 (1)–1.82 (1) GPa, the precise value depending on the equation used for extrapolation. In view of the experimental measurement of a trigonal unit cell at 1.816 (4) GPa, our best estimate of the ferroelastic phase transition pressure is therefore 1.81 ± 0.01 GPa at 298 ± 1 K. The non-symmetry-breaking strains $\epsilon_{22,\text{nsb}}$ and V_s extrapolate to zero at pressures between 1.78 (3) and 2.09 (11) GPa depending on the equation of state
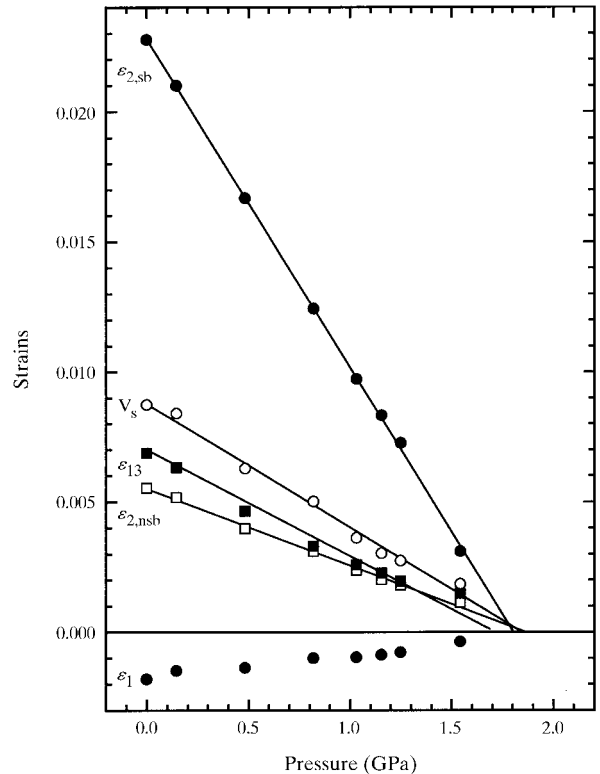

Fig. 3. The variation with pressure of the spontaneous strain components of lead phosphate, derived from the Murnaghan fits to the trigonal unit-cell data.

employed for extrapolation, while the magnitude of the component $\epsilon_{11,nsb}$ is too small for reliable conclusions to be drawn about its behaviour.

In both crystals studied spontaneous twinning on an optical scale occurred on increasing the pressure above ~1.3 GPa, preventing the determination of accurate cell parameters in the pressure range 1.3–1.8 GPa. However, the unit-cell parameters determined at 1.543 (4) GPa fall on the trends extrapolated from lower pressures, so the spontaneous strains calculated from these data were included in the fitted linear trends shown in Fig. 3. The exclusion of data from this pressure does not significantly affect the pressures at which these trends go to zero.

4. Discussion

Despite the similarity in the evolution of the unit-cell parameters, the behaviour of the monoclinic phase below the phase transition at high pressures differs significantly from that previously observed at high temperatures, both in the detail of the evolution of the components of the spontaneous strain and in the renormalization of the critical exponent of the transition.

Careful examination of the spontaneous strains measured by Salje *et al.* (1993) below 430 K shows that they are not all co-linear (Carpenter *et al.*, 1998). The larger strains $\epsilon_{22,nsb}$ and $\epsilon_{22,sb}$ related to the Pb displacements are found to be proportional to the volume strain, V_s, and extrapolate to zero at 444 K, whereas $\epsilon_{11,nsb}$ and $\epsilon_{13,sb}$, which reflect secondary displacements, are co-linear with one another, but not with V_s, and extrapolate to zero at *ca* 455 K (Carpenter *et al.*, 1998). Within the uncertainties (at the 2σ level) all the spontaneous strains arising from the high-pressure transition except $\epsilon_{13,sb}$ are co-linear with one another, reflecting the fact that $\epsilon_{13,sb}$ extrapolates to zero at a significant interval of the order of 0.1 GPa below the remaining strains. In addition, there are small excess positive spontaneous strains $\epsilon_{22,nsb} = \epsilon_{33,nsb}$, which give rise to a small excess volume above the high-temperature transition (Salje *et al.*, 1993; Carpenter *et al.*, 1998). Similar excess quantities have been observed in the birefringence (Bismayer *et al.*, 1982) and the heat capacity (Salje & Wruck, 1983) in the temperature interval of 450 to *ca* 500 K. Diffraction from this intermediate phase also yields diffuse scattering at the reciprocal space points corresponding to the positions at which the superlattice reflections of the monoclinic phase would appear (Benoit *et al.*, 1981; Bismayer *et al.*, 1982). By contrast, there is no evidence from the high-pressure data for either excess strain in the trigonal phase above 1.8 GPa and there is no detectable diffuse scattering at the superlattice positions. The underlying structural reason for this change of behaviour at high temperature is not known in detail, but it points to a different behaviour of the Pb displacements in the high-pressure and high-temperature structures.

The high-temperature transition is weakly first-order in character, but on cooling through *ca* 430 K a cross-over occurs to a regime in which measurements of the spontaneous strain (Salje *et al.*, 1993) and optical birefringence (Wood *et al.*, 1980) show that the critical exponent is very close to the value of $\beta = 0.2365$ expected for a three-states Potts model (Burkhard *et al.*, 1976). By contrast, the linear evolution of the strains at high pressure indicates that the effective critical exponent has been renormalized to a value of $\beta = \frac{1}{2}$, corresponding to second-order behaviour of the order parameter. This is the same re-normalization that is observed under uniaxial stresses less than the coercive stress (Bismayer *et al.*, 1982). The origin of this renormalization cannot be identified from the measurements of spontaneous strain alone, but a number of factors may contribute. First, the application of pressure requires the addition of a term $Pe_{ii,nsb}$ to the excess free energy of the monoclinic phase. Second, both the elastic constants and the magnitude of the coupling coefficients between the strains and the order parameters [see equation (2) of Salje & Devarajan, 1981] will change much more rapidly with pressure than with temperature. Lastly, because the high-temperature phase is dynamic in character its thermodynamics are probably different from the high-pressure phase. For example, theoretical analysis (Salje & Devarajan, 1981) shows that, in the absence of the flip-mode phase, the transformation will approach second-order behaviour irrespective of other factors. The identification of the cause of the renormalization therefore awaits the precise determination of the nature of the high-pressure phase and the determination of the individual elastic constants at high pressures.

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