Lattice Parameters, Spontaneous Strain and Phase Transitions in Pb$_3$(PO$_4$)$_2$

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Abstract

The temperature evolution of the lattice parameters of lead phosphate, Pb$_3$(PO$_4$)$_2$, indicates three lattice instabilities with anomalies near 530, 453 and *ca* 430 K. Only the phase transition at 453 K is ferroelastic with a spontaneous strain $\mathbf{e} = (e_1 \ -e_1 \ 0 \ 0 \ e_5 \ 0)$. Volume anomalies occur near 530 and *ca* 430 K that can be related to the multicomponent behaviour of the structural order parameter.

1. Introduction

Lead phosphate, Pb$_3$(PO$_4$)$_2$, is an improper ferroelastic material that became well known as a prototype for a whole class of ferroelastics (Von Hodenberg & Salje, 1977; Smirnov, Strukov, Gorelik & Dudnik, 1979; Vagin, Dudnik & Sinyakov, 1979; Dudnik & Nepochatenko, 1980; Torres, Roucau, Ayroles & Taliana, 1980; Benoit, Hennoin, & Lambert, 1981; Bismayer & Salje, 1981; Bismayer, Salje & Joffrin, 1982; Darlington, 1983; Roucau, Ayroles & Torres, 1983; Salje, Devarajan, Bismayer & Guimaraes, 1983; Salje & Wruck, 1983; Bismayer, Salje,
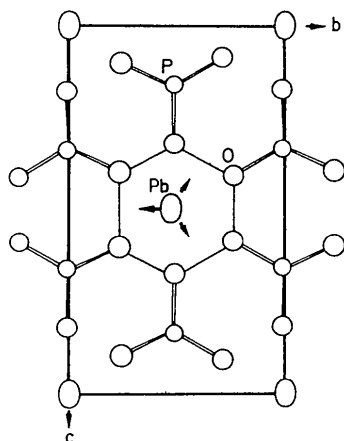

Fig. 1. Sketch of the crystal structure of lead phosphate in the ferroelastic phase. The three possible displacements of Pb are indicated by arrows.

Glazer & Cosier, 1986; Salje, 1990). It was the first material in which the ferroelastic hysteresis was measured (Salje & Hoppman, 1976). Its spontaneous strain (Guimaraes, 1979; Bismayer & Salje, 1981) and morphic birefringence (Bismayer, Salje & Joffrin, 1982) are rather large ($e_1 = e_{11} \simeq 2\%$, $2e_5 = e_{13} \simeq 0.7\%$, $\Delta n_{bc} = 1.9 \times 10^{-2}$ at room temperature) for a phase transition with second-order coupling between the strain and order parameters. The transition mechanism is related to the shift of Pb atoms from the triad and a correlated tilt of the PO$_4$ tetrahedra (Fig. 1). The global symmetry reduction is $R\bar{3}m$–$C2/c$. The transition is slightly first order and can be made tricritical or second order by appropriate chemical replacement of P by V or As (Von Hodenberg & Salje, 1977; Bismayer, Salje, Glazer & Cozier, 1986). The principal transition mechanism between the paraelastic and ferroelastic state is apparently not affected by these chemical exchanges (Salje & Wruck, 1983; Bismayer, Salje, Glazer & Cosier, 1986).

In detail, the paraelastic–ferroelastic transition mechanism of Pb$_3$(PO$_4$)$_2$ displays two distinct features. Firstly, strong short-range order exists at $T > T_c$ (Bismayer, Salje & Joffrin, 1982; Salje, Devarajan, Bismayer & Guimaraes, 1983; Salje & Wruck, 1983; Salje, Bismayer, Wruck & Hensler, 1991) leading to domains with mobile walls in crystals of high chemical purity. Impurities (such as Ba, V, As), even in small quantities, pin the walls and these only disappear with the disappearance of the short-range order itself. Due to the high wall density, self-organization could be expected and, indeed, specific heat anomalies in doped material indicate the existence of an intermediate paraelastic phase between 453 and 530 K (Salje & Wruck, 1983). Previous careful X-ray studies (Bismayer, Salje & Joffrin, 1982) have not revealed an expected incommensurate phase in clean crystals so that we must expect the wall configurations to be substantially disordered in pure lead phosphate.

Below the ferroelastic transition point at 453 K, a second anomaly exists at 433 K (Smirnov, Strukov,

Gorelik & Dudnik, 1979; Torres, Roucau, Ayroles & Taliana, 1980; Bismayer & Salje, 1981; Salje & Wruck, 1983). This anomaly was correlated with small changes of the spontaneous strain (Guimaraes, 1979), but has never been measured with sufficient accuracy to compare the experimental observations with the results of spectroscopic and theoretical stud-

ies. It is, in fact, not clear whether the 433 and 533 K anomalies exist in thermal expansion. It is the aim of this paper to present such evidence.

2. Experimental

Pb$_3$(PO$_4$)$_2$, synthesized as described earlier by Bismayer & Salje (1981), was annealed at 1280 K in a platinum crucible and then heated to 1315 K. A single crystal was subsequently pulled using the Czochralski technique utilizing the growth parameters as published by Bismayer & Salje (1981). The final crystal was analysed using an electron microprobe. No impurities were found within the experimental resolution (*e.g.* 10 p.p.m. for Ba). No attempt was made to determine the total oxygen content of the sample, although it might be expected that small oxygen substoichiometries constitute the main source of point defects. Repeated heating and cooling of parts of the sample showed only little memory effect of the domain boundaries so that we may be satisfied that the defect-pinning volume of the sample was sufficiently small that it did not influence the macroscopic lattice parameters.
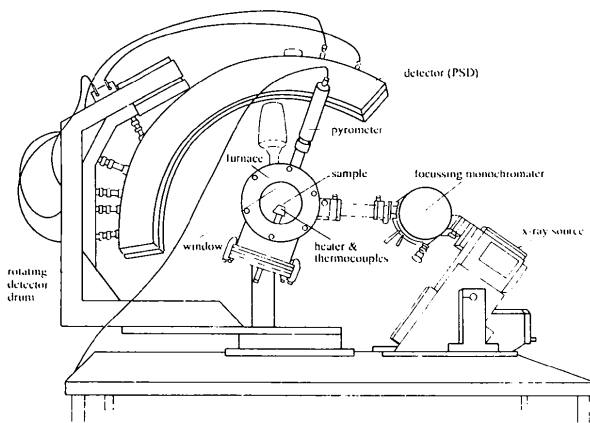

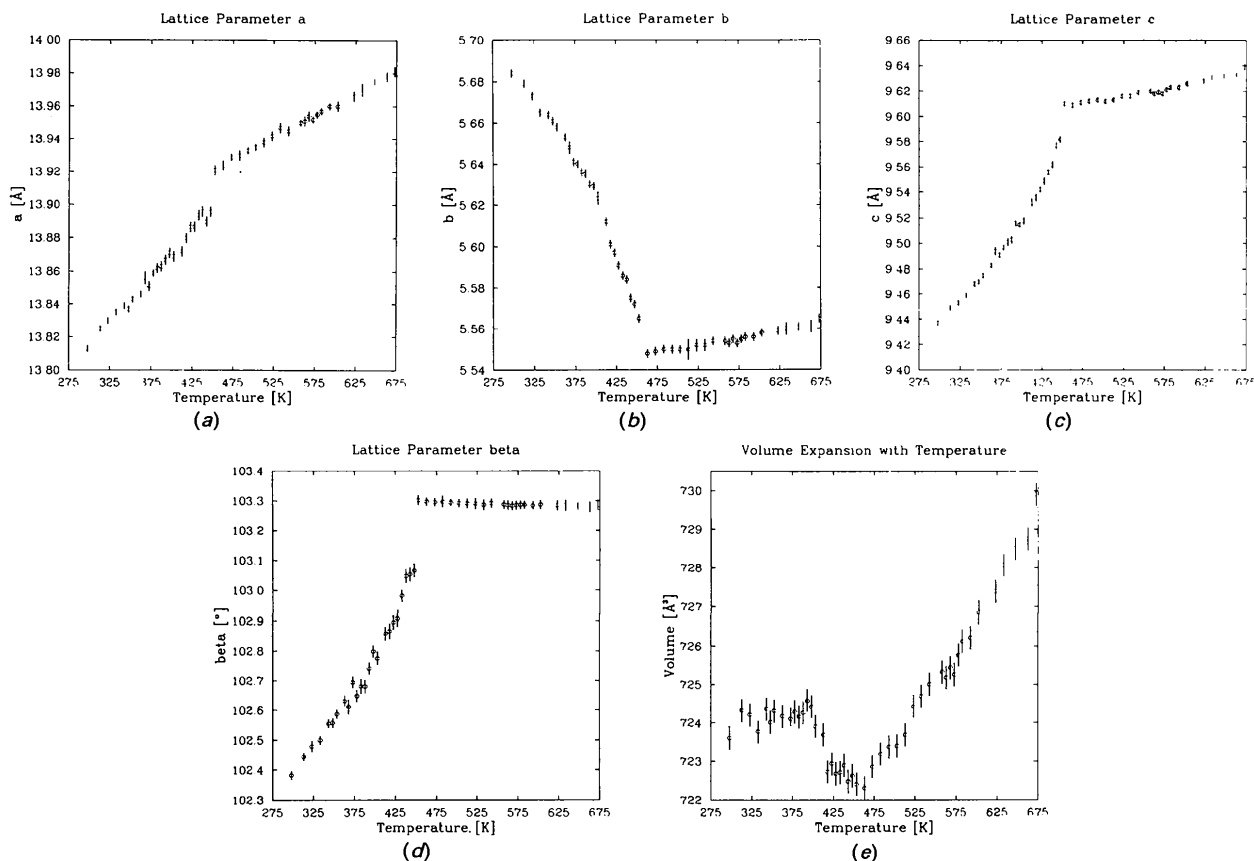Fig. 2. Experimental arrangement of the high-temperature X-ray diffractometer.

Fig. 3. Temperature dependence of the lattice parameters (*a*) *a*, (*b*) *b*, (*c*) *c* and (*d*) *β* and (*e*) the cell volume.

Part of the crystal was crushed and ground to a fine powder. The powder was then mixed with Si as an internal standard and spread over a Pt heating strip in a novel heating powder camera. Its main features are shown in Fig. 2. A strictly monochromatic (Cu $K\alpha_1$) focused X-ray beam with a diameter of 0.1×10 mm diffracts from the sample and is collected by a 4 K-PSD detector (INEL). The sample is embedded in a high-vacuum heating cell (diameter 15 cm) with Kapton windows. The heating elements consist of Pt strips pulled mechanically onto a ceramic plate. The sample thickness is 0.2 mm and the temperature is monitored with ultra-thin thermocouples (Pt/Rh–Pt) welded onto the heating strip. The temperature was calibrated using quartz and langbeinite [$Cd_2K_2(SO_4)_3$] as standards; the evolution of their lattice parameters and the transition temperatures agreed with their thermocouple read-out to within ± 2 K between room temperature and 900 K. At low temperatures, the agreement was ± 1 K. The transition temperature of $Pb_3(PO_4)_2$ of 453 K (Salje & Wruck, 1983) was reproduced in this arrangement to within ± 0.5 K.

The diffraction signals were measured between $2\theta_{min} = 8$ and $2\theta_{max} = 120°$. They were subsequently corrected for acentricities of the sample position. All diffraction signals between $2\theta = 18$ and $96°$ were indexed and used for later refinement of the lattice parameters. 50 lines were used in total. The least-squares refinement led to temperature-independent uncertainties of $\pm \sim 0.002$ Å for a, b and c and $\pm \sim 0.020°$ for β. The lattice parameters at $T > 453$ K were refined under rhombohedral symmetry, which gave lower R values than the refinement under monoclinic symmetry.

3. Results

The temperature dependences of the lattice parameters of $Pb_3(PO_4)_2$ are shown in Fig. 3.* Due to the symmetry change $R\bar{3}m$–$C2/c$, the components of the spontaneous ferroelastic strain are defined (from Guimaraes, 1979) as

$$e_1 = -e_2 = e_{11} = -e_{22} = (c/3^{1/2} - b)/2b,$$

$$\tfrac{1}{2}e_5 = e_{13} = (c + 3a\cos\beta)/6a\sin\beta.$$

Their temperature evolution is shown in Fig. 4.

In all parameters, the weakly first-order phase transition at 533 K is clearly seen as a step and as a change of temperature evolution above and below the transition point. More subtle anomalies appear both in the paraelastic and the ferroelastic phase.

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* Lists of lattice parameters and strain data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55877 (1 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The lattice parameters a, b and, to a somewhat lesser extent, c, show a change of slope (da/dT, db/dT) near 530 K with a stronger temperature dependence above this temperature. The same anomaly occurs in the volume (*i.e.* small excess volume at $T \le 530$ K).

The excess volume at $T < 575$ K is now calculated by linear extrapolation (to lower temperatures) of all data at $T > 575$ K as a baseline and a plot of the difference between the actual experimental volume data and this baseline. The result is shown in Fig. 5, which shows that the excess volume increases continuously at $T < 530$ K and not stepwise at $T_c = 453$ K.

4. Discussion

The temperature evolution of the lattice parameters for $Pb_3(PO_4)_2$ confirms the notion that three anomalies are observed. The first anomaly occurs near 530 K as a small change of the thermal expansion of a, b and, in particular, V. The second anomaly is related to the ferroelastic phase transition at 453 K with the generation of components e_{11} and e_{13} of the
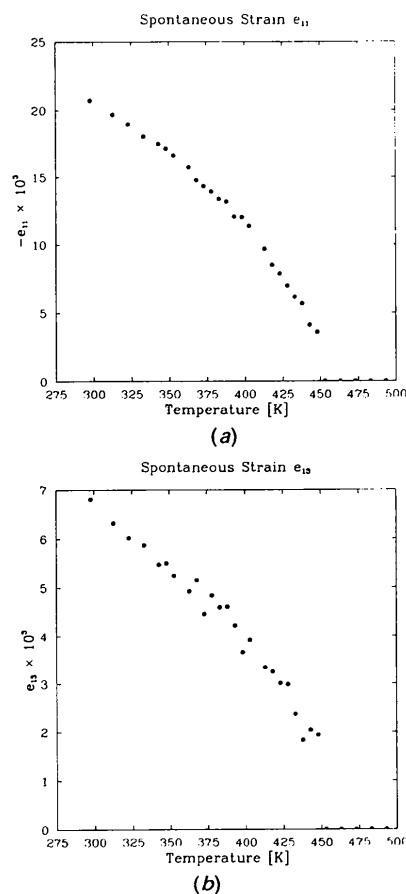

Fig. 4. Temperature evolution of the components of the spontaneous strain (*a*) e_{11} and (*b*) e_{13}.

symmetry-breaking spontaneous strain. This transition is not accompanied by a significant step in the volume although the first-order behaviour is clearly evident in the individual lattice parameters and ferroelastic strain. The steps in a and b compensate for each other ($e_{11} = -e_{22}$) and the change in β corresponds to a pure shear (e_{13}) so that there is a continuous change in the volume. The third anomaly relates to the excess volume below 430 K.

We can now investigate the correlations between e_{11} and e_{13} on the one hand and $\Delta V/V$ on the other. The temperature evolution of e_{11} is essentially identical to e_{13}. A linear correlation is seen in Fig. 6 at $T \ll 553$ K: the square of each of the strain components e_{11} and e_{13} increases linearly with decreasing temperature, confirming the nearly tricritical behaviour of the phase transition (note, $e_{ik} \propto Q^2$). Deviations from linearity between 453 and 430 K have already been observed by several authors and are confirmed in this study. The correlation between e_{11} and e_{13} is linear (Fig. 7), although the data apparently do not give an extrapolation that passes through the origin. The offset in e_{13} at $e_{11} = 0$ is only ca 0.5×10^{-3}, however, which is at the limit of our experimental resolution. If this offset is real, it might be related to residual shear strain of the powder grains either as a result of grinding or lattice imperfections. Alternatively, it could be an indication of a further, as yet unknown, symmetry-breaking order parameter; we plan to investigate this point further with doped samples.

The excess volume shows a similar temperature evolution with $(\Delta V/V)^2 \propto \tilde{T} - T$ where $\tilde{T}$ is an empirical temperature at which $(\Delta V/V)^2$ extrapolates to zero. At temperatures above 430 K the excess volume decreases continuously with heating. No abrupt break occurs at the ferroelastic transition point at 453 K although the small excess volume in the paraelastic phase can hardly be seen when its square is plotted (Fig. 8). The tail in the raw data,

evident in Fig. 5, only disappears at temperatures above ca 530 K.

The absence of a step in $\Delta V/V$ at 453 K is not due to insufficient experimental resolution, as can be seen in a plotting of $\Delta V/V$ against e_{11} and e_{13} (Figs. 9a
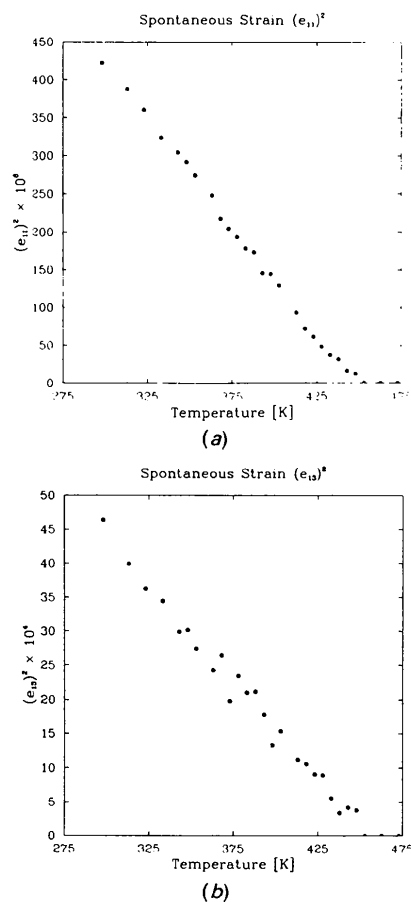

Fig. 6. Temperature dependence of (a) e_{11}^2 and (b) e_{13}^2. The linearity at $T \ll T_c = 453$ K indicates the nearly tricritical behaviour.
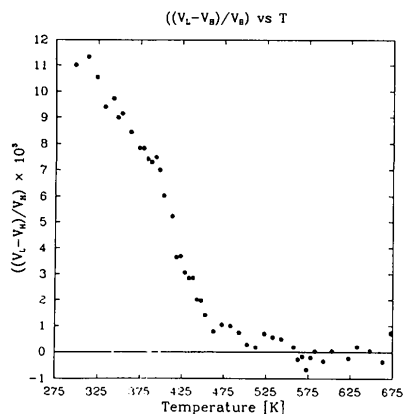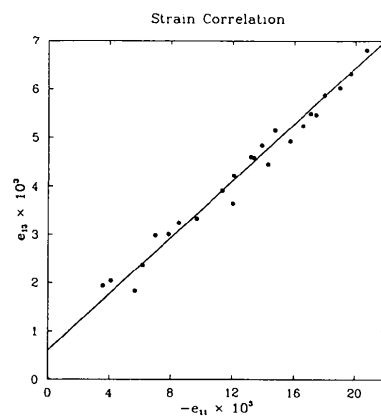

Fig. 5. Excess-volume strain *versus* temperature.

Fig. 7. Linear correlation between the components of the spontaneous strain e_{11} and e_{13}.

and 9b, respectively). We find a good proportionality with a common origin for e_{11}. Although proportionality also applies for e_{13} there may again be an offset, with slightly increased values of e_{13} near the origin. The major difference between e_{11} and e_{13} on the one hand and the excess volume on the other
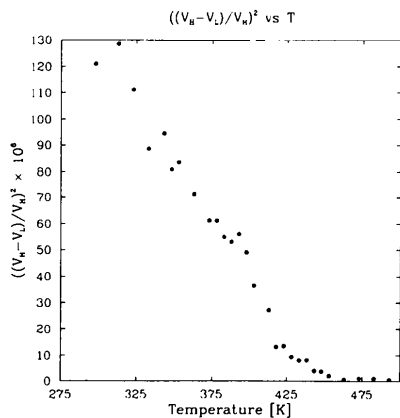

Fig. 8. Square of the excess-volume strain shown as a function of temperature. Linear behaviour at $T \ll T_c$ indicates near tricriticality.

(a)

(b)

Fig. 9. Correlation between (a) e_{11}, (b) e_{13} and the excess-volume strain.

hand is that the first-order step occurs only in the symmetry-breaking strain and not in the excess volume.

Our present results mirror earlier observations of specific heat measurements and their comparison with the temperature evolution of the morphic birefringence. The small anomaly near 530 K corresponds to the onset of the excess specific heat. This has been correlated with the generation of microdomains that have mobile walls and lifetimes on the phonon time scale (e.g. Potts flip motions due to the criticality of the order-parameter component Q_3). Below the ferroelastic transition point at 453 K, the excess entropy increased more rapidly than the macroscopic morphic birefringence (Salje & Wruck, 1983). This increase was understood as local flip rotations (Q_1, Q_2) inside the larger ferroelastic domains (Q_3). Only at lower temperatures were the proportionalities $Q_2 \propto Q_3$ for the order parameters and $\Delta n \propto \Delta S$ for the birefringence and the entropy observed.

In light of the results of the present investigations, we can elaborate on this picture. The onset of solitonic excitations and the creation of microdomains is correlated with a very weak volume increase when no macroscopic symmetry breaking occurs. At the ferroelastic transition point, the ferroelastic domains are created via a pure lattice shear without volume expansion. The coupling between the order parameter and the symmetry-breaking spontaneous strain, and between the order parameter and the volume strain, is linear quadratic. The order parameter has three degenerate components corresponding to three critical points at the surface of the Brillouin zone (Salje & Devarajan, 1981). Only identical components can couple to generate the symmetry-breaking spontaneous strain. The volume strain, on the other hand, can be generated by any squared term as its thermodynamic average $\langle Q_i Q_j \rangle$. In simple structural terms, it is the mean distance of Pb from the triad that produces the excess volume, independent of its orientation. The relevant order parameter was introduced by Salje & Devarajan (1981) as the renormalized component Q_3 of the total order parameter ($Q_1 Q_2 Q_3$). Q_3 was then directly related to the observed excess specific heat (Salje & Wruck, 1983) and the scattering intensity of optical phonons (Salje, Devarajan, Bismayer & Guimaraes, 1983). Both quantities showed the same temperature evolution as the excess volume in our present study.

The observed excess strain between 453 and 430 K, which is over and above that due to the nearly tricritical behaviour, could mean that reorientational motion and microdomains exist not only at $T > T_c$ but also inside the ferroelastic domains at temperatures slightly below T_c. On cooling below ~430 K, these additional effects disappear and a
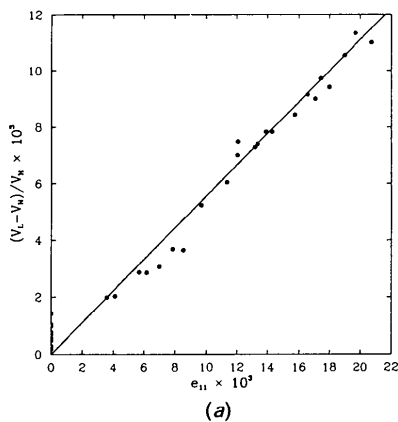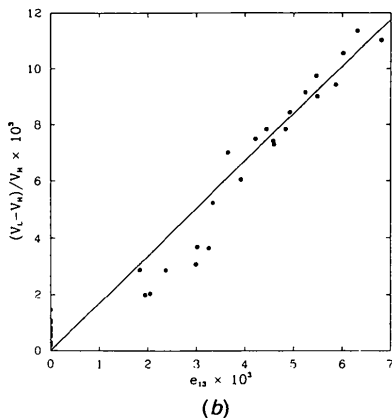
classic displacive behaviour is established. The description of the same mechanism on an increasing temperature scale leads to the following picture: a static, ferroelastic state with coarse domains exists at room temperature. Each type of domain relates to one scalar order parameter that decreases with increasing temperature. The spontaneous strain and the excess volume decrease accordingly. When the order parameter falls below a threshold at temperatures sufficiently close to T_c, flip oscillations appear and microdomains are formed. These are correlated with a relative increase of the excess volume. The excess volume then decreases continuously above T_c and merges with the classical thermal expansion at $T \gg T_c$.

This picture leads to a further question: are the local lattice relaxations near T_c replaced by a further symmetry breaking near 430 K? If so, is this additional symmetry breaking related to an offset of $e_{13} > e_{11}$ near the transition point? Further work on the symmetry change on a local scale in pure lead phosphate and Ba-doped Pb₃(PO₄)₂ is underway.

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Determination of the Incommensurately Modulated Structure of Ni₃±ₓTe₂

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Abstract

The modulated structure of nickel telluride Ni₃±ₓTe₂ (Ni₂.₇₆Te₂) is stabilized at 300 K by the substitution of a small amount of Fe (prepared as Ni₂.₅₇Fe₀.₂₉Te₂). The structure of this compound has been determined by X-ray diffraction at room temperature (1311 unique reflections). The structure is incommensurately modulated with wavevector $\mathbf{q} = 0.378\ (1)\mathbf{a}^*$. The lattice parameters of the primitive orthorhombic cell of the average structure are: $a = 3.761\ (1)$, $b = 3.796\ (1)$, $c = 6.084\ (4)$ Å with $V = 86.9$ Å³, $Z = 2$, $\mu = 317$ cm⁻¹ ($\lambda = 0.7107$ Å), $M_r = 416.4$. The symmetry of the structure is given by the superspace group $P^{Pmmn}_{\bar{1}\bar{1}s}$. Unlike the analogous Cu compound [Schutte & de Boer (1993). *Acta Cryst.* B49, 398–403]

there is no antiphase ordering along c. The final R_F factor is 0.047. Both occupational and displacive modulation functions are needed to describe the structure. The occupation of the distorted octahedral sites by Ni atoms is fully modulated ($P^{Ni^{II}}$ varying between 0 and 1). The Ni and Te atoms are slightly displaced, incommensurately with the basic lattice.

Introduction

The existence of a large number of phases in the Ni–Te system was reported by Kok, Wiegers & Jellinek (1965), Barstad, Grønvold, Røst & Vestersjø (1966) and Stevels (1969). Phases with composition Ni₃±ₓTe₂ are based on an f.c.c. arrangement of Te atoms, with Ni^I atoms in tetrahedral sites and Ni^{II}