Pressure-induced ferroelastic phase transition in $Pb_3(PO_4)_2$: A neutron-diffraction study

D. L. Decker*, S. Petersen†, and D. Debray
Laboratoire Léon Brillouin and Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, 91190 Gif-sur-Yvette, France

M. Lambert‡
Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France
(Received 19 June 1978)

A ferroelastic phase change is observed in $Pb_3(PO_4)_2$ near 20 kbar at ambient temperature by neutron diffraction. The rhombohedral β phase above the transition pressure shows a domain-size broadening similar to that observed in the β phase at atmospheric pressure above 180 °C.

In 1970 Keppler[1] determined the structure, by x-ray diffraction, of $Pb_3(PO_4)_2$ in both the α and β phases, below and above the reversible phase transition near 180 °C. The α phase below 180 °C is monoclinic, space group $C2/c$, with four molecules per unit cell and the β phase is rhombohedral, space group $R\bar{3}m$, with one molecule per unit cell. Thus this transition can be characterized as pure ferroelastic[2] of the Aizu[3] species $\bar{3}mF2/m$. The transition near 180 °C has been observed as a dielectric anomaly,[2] as a thermal latent heat both by differential thermal analysis[4] and by differential scanning calorimetry,[2,5] by optical-refraction studies of the spontaneous birefringence,[6] by Brillouin scattering,[7] and by EPR measurements.[8] The crystal symmetry requires that the transition be first-order type and the experiments in general confirm this point.

Recent x-ray diffraction studies[9] have indicated that pairs of α-phase peaks, such as $(11\bar{3})$ and (020) (monoclinic indexing) which should coalesce to a single peak in the β phase, do not quite converge above the transition, or perhaps it is more accurate to say that the resulting rhombohedral peak is broader than the instrumental resolution. Also the $(\bar{1}12)$ monoclinic reflection does not completely disappear above 180 °C as it should for rhombohedral symmetry. From these measurements it was postulated that monoclinic microdomains of greater than 50 Å extent existed in the β phase more than 100 °C above the point of transition. An inelastic-neutron-scattering experiment[10] also showed some residual intensity near the 330 point in reciprocal space far above the transition, and showed a quasielastic peak characteristic of a fluctuation phenomenon which has been labeled monoclinic microdomains. The x-ray measurements[9] demonstrated that the β phase had a smaller volume than the α phase when extrapolated to ambient temperature. This would indicate a phase line with temperature decreasing with increasing pressure so that one might study the same ferroelastic phase transition at ambient temperature by applying pressure.

A single crystal of $Pb_3(PO_4)_2$, furnished by Professor J. P. Chapelle of Laboratoire de Physique Cristalline, Université Paris-Sud, Orsay, was powdered and then formed into a pellet 5-mm diameter by 10 mm long. A teflon chamber, containing the sample, a coil of manganin wire, and a liquid to insure hydrostatic pressure, was placed in a clamp-type pressure cell with Al_2O_3 windows for the passage of neutrons.[11] The cell was clamped at several different pressures and neutron-diffraction patterns at room temperature obtained at each pressure, using neutrons of wavelength $\lambda = 1.14$ Å. The pressure was measured by monitoring the resistance of the maganin coil. Fluorinert was first used as the pressure-transmitting liquid but it became nonhydrostatic in the region of the transition pressure so the final measurements were made in deuterated ethyl alcohol which remains liquid as evidenced by the linear response of the manganin gauge.

Seven diffraction peaks [(311), $(40\bar{2})$, (020), $(11\bar{3})$, (222), (004), and (600)] of the monoclinic phase were well resolved at atmospheric pressure. They were also separated from reflections originating from the surrounding material of the pressure cell. These peaks were followed as a function of pressure and analyzed in each spectrum to yield peak positions and intensities. The monoclinic pairs [(311), $(40\bar{2})$], [(020), $(11\bar{3})$], and [$(22\bar{2})$, (004)] should merge to single peaks in the rhombohedral phase. To illustrate, we show the (020) and $(11\bar{3})$ peaks at three pressures in Fig. 1. It is observed that the $(11\bar{3})$ peak position moves slowly with pressure while that

of (020) shifts rapidly merging into the $(11\bar{3})$ peak, such that at 23 kbar a single symmetric Gaussian peak remains. The solid lines in this figure represent the least-squares fitting of the data by Gaussian functions. This peak at 23 kbar has a width 14(3)% greater than the instrumental resolution of 0.28° (2θ) full width at half maximum (FWHM). This instrumental resolution, measured from the peak width at low pressure is shown by the horizontal line segment centered in the 23-kbar peak. Since the (020) and $(11\bar{3})$ peaks should have a relative intensity of 1:2 as they approach, one would think that the symmetry of the observed peak is an indication that this line is no longer made of two peaks as at 17 kbar but a single peak possibly broadened by domain size.[9] If we calculate[12] the required domain size to cause this much broadening we obtain 360 Å. Since in fact the data can also be well represented by two peaks of natural line width with intensity ratio 1:2 and with separation shown by the vertical arrows, we must resort to other evidence to decide whether the 23-kbar pattern is in the rhombohedral phase.

In Fig. 2 we plot the separation of the two peaks (020) and $(11\bar{3})$ as a function of hydrostatic pressure. It is observed that the separation is approaching zero near 20 kbar. The point at 23 kbar is the separation required to give the broadened peak as discussed above. This plot is very similar to that shown by Joffrin *et al.*[9] for the separation of these lines versus temperature, and is a strong indication that the α-β phase transition takes place near 20 kbar.

From the positions of the seven peaks at each pressure, we calculated the lattice parameters a, b, c, and β for a monoclinic lattice. The results are shown in Fig. 3 where they are plotted as c, $3^{1/2}b$, and $-3a\cos\beta$ versus pressure. These three quantities must all coincide when the lattice becomes rhombohedral. Again the points above 20 kbar were ob-

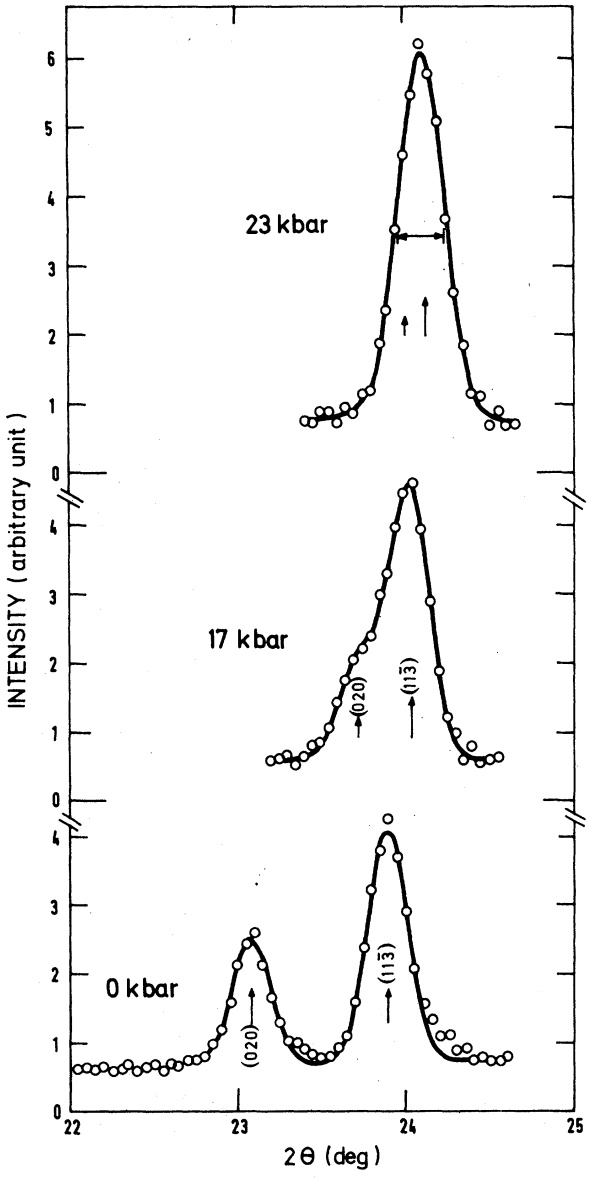

FIG. 1. Neutron-diffraction data in the neighborhood of the (020) and $(11\bar{3})$ monoclinic reflections in $Pb_3(PO_4)_2$ at 0, 17, and 23 kbar. The solid lines represent least-squares Gaussian fits.

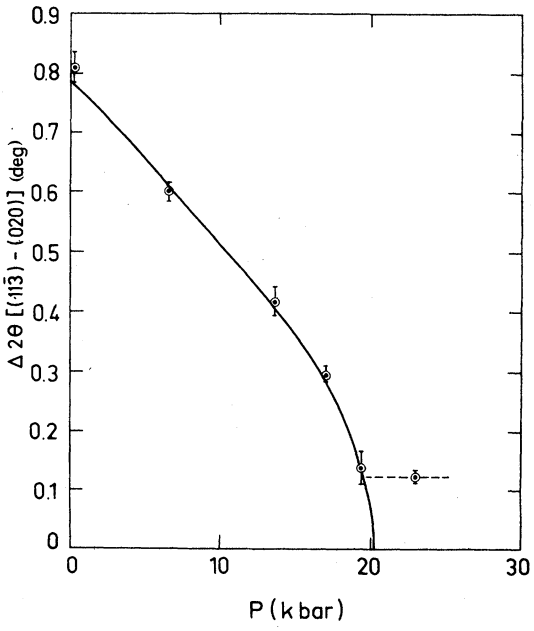

FIG. 2. Angular separation between the (020) and $(11\bar{3})$ monoclinic peaks as a function of pressure. The point at 23 kbar reflects a broadening of the $(10\bar{1})$ rhombohedral peak. The solid line is a guide to the eye.

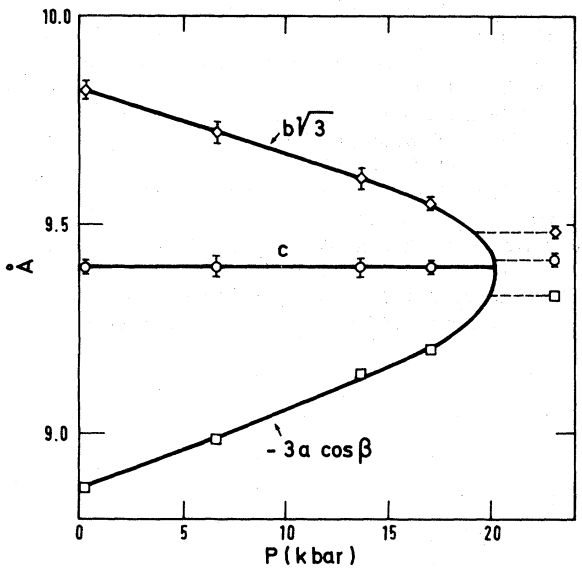

FIG. 3. c, $b3^{1/2}$, and $-3a\cos\beta$ as a function of pressure in the monoclinic phase of $Pb_3(PO_4)_2$. The points at 23 kbar reflect broadening of the (221), (10$\bar{1}$), and (200) peaks in the rhombohedral phase. The solid lines are guides to the eye.

tained by assuming the broadened peaks were composed of monoclinic pairs with natural linewidths. The solid lines in this figure are to guide the eye to the expected phase transition which is not evident from the data in this plot.

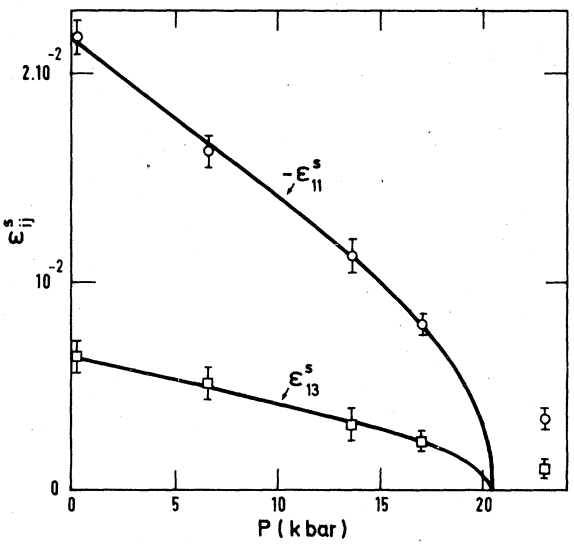

FIG. 4. Elements $-\epsilon_{11}^s$ and ϵ_{13}^s of the spontaneous elastic-strain tensor vs pressure. The points above the phase transition were calculated as described under Fig. 3. The solid lines are guides to the eye.

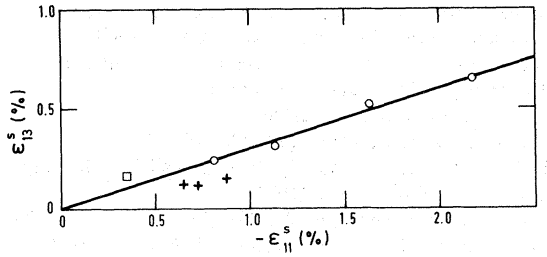

FIG. 5. Spontaneous elastic strain ϵ_{13}^s as a function of the spontaneous elastic strain $-\epsilon_{11}^2$. The solid line is a best fit to the four measurements in the α phase. ○ — α phase in a hydrostatic medium. + — measurements in a nonhydrostatic medium. (sq — the β phase in a hydrostatic medium.

From the lattice parameters one can calculate the elements of the spontaneous deformation tensor[4] which indicate the amount of monoclinic distortion from a rhombohedral structure. These are shown in Fig. 4. Gilletta *et al.*[5] point out that the spontaneous strains all depend upon the square of the order parameter and, thus, must be linearly related to each other. Thus, in Fig. 5 we plot ϵ_{13}^s vs $-\epsilon_{11}^s$ for all the data points both above and below the transition as well as some taken in Fluorinert above 20 kbar. We observe a linear relation for the points taken in the α phase but a definite deviation from the line for the measurements in a nonhydrostatic medium or at a pressure beyond the transition pressure.

We conclude that there is a phase transition at room temperature near 20 kbar in $Pb_3(PO_4)_2$, from the monoclinic $C2/c$ phase to a rhombohedral $R\bar{3}m$ phase, which shows the same characteristics as the ferroelastic phase transition near 180 °C at atmospheric pressure. That is, the β phase shows evidence of some monoclinic distortion forming possible monoclinic microdomains. With fluorinert as the pressure medium, the results between 19 and 36 kbar demonstrated almost no tendency to collapse the monoclinic reflection pairs to form single rhombohedral peaks. The final peak separation in this case at 36 kbar was more than twice that in the alcohol at 23 kbar. This indicates that the ferroelastic phase transition is very sensitive to nonhydrostatic external strain. If so, it may also be sensitive to internal local strain caused by impurities or dislocations or by a mode softening which allows the rhombohedral lattice to strain either statically or dynamically giving rise to broadened diffraction lines in the β phase.

ACKNOWLEDGMENTS

We wish to thank Mr. R. Millet for his invaluable technical assistance and Dr. P. Mériel for a critical reading of the manuscript.

*On leave from the Department of Physics and Astronomy, Brigham Young University, Provo, Utah, U.S.A.
†Graduate student from the University of Copenhagen, Copenhagen, Denmark, now returned.
‡Also of Laboratoire Léon Brillouin.

[1]U. Keppler, Z. Kristallogr. 132, 228 (1970).
[2]H. Brixner, P. E. Bierstedt, W. F. Jaep, and J. R. Barkley, Mater. Res. Bull. 8, 497 (1973).
[3]K. Aizu, J. Phys. Soc. Jpn. 27, 387 (1969).
[4]J. C. Tolédano, L. Pateau, J. Primot, J. Aubrée, and D. Morin, Mater. Res. Bull. 10, 103 (1975).
[5]F. Gilletta, M. Chabin, and C. X. An, Phys. Status Solidi 35, 545 (1976).
[6]J. Torres, J. Aubree, and J. brandon, Opt. Commun. 12, 416 (1974).
[7]C. X. An, G. Hauret, and J. P. Chapelle, C. R. Acad. Sci. Ser. B. 280, 543 (1975).
[8]H. N. Ng and C. Calvo, Can. J. Phys. 53, 42 (1975).
[9]C. Joffrin, J. P. Benoit, L. Deschamps, and M. Lambert, J. Phys. (Paris) 38, 205 (1977).
[10]C. Joffrin, M. Lambert, and G. Pepy, Solid State Commun. 21, 853 (1977).
[11]D. Debray, D. Jérome, R. Millet, and J. Malfait (unpublished).
[12]H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures,* 2nd ed. (Wiley, New York, 1974), p. 687.