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# Apparently continuous isosymmetric transition in ammonium hexafluorophosphate $NH_4PF_6$

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$NH_4PF_6$ undergoes two transitions at ambient pressure on cooling: $Fm\overline{3}m$-$C2/c$ and an isosymmetric $C2/c$-$C2/c$ transition. Isosymmetric transitions must be discontinuous. However, while this transition displays a latent heat, there is little sign of a discontinuity in neutron powder diffraction or nuclear magnetic resonance, consistent with being close to a Landau critical point. The practical implications of slightly discontinuous isosymmetric transitions are discussed.

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$NH_4PF_6$ exists in three phases, I–III, from room temperature down to 5 K. The structure at room temperature has been known for some time,[1] and is of NaCl-type, with $a = 7.92$ Å where both $NH_4^+$ and $PF_6^-$ groups are disordered. Ammonium compounds in which polyatomic anions are present frequently possess disordered $NH_4^+$ orientations, as the anionic charge is distributed over several atoms, which weakens the attraction between any of the anionic atoms and the H of $NH_4^+$, resulting in low barriers to rotation. $NH_4PF_6$ has one of the lowest known barriers of 0.8 $\mathrm{kJ\,mol^{-1}}$; c.f. $NH_4ClO_4$ and $ND_4ClO_4$ with $<4$ and 4 $\mathrm{kJ\,mol^{-1}}$, respectively.[2]

A calorimetric study of $ND_4PF_6$ put the transition temperatures at $(194.4 \pm 0.05)$ K and $(137.5 \pm 1.0)$ K, with transition entropies of $(1.013 \pm 0.016)R$, and $(0.562 \pm 0.011)R$, respectively. This thermodynamic study showed that the II-III transition has a latent heat, but that it is more gradual than the I-II transition.[3]

The existing spectroscopic evidence has suggested there is very little structural change on cooling. One nuclear magnetic resonance (NMR) study suggested that the II-III transition was an order-disorder transition similar to that of $NH_4Cl$.[4] A more detailed study showed evidence of changes in the activation energy for reorientation of $PF_6$ and $ND_4$ groups through the I-II transition and suggested there may be "little structural change" associated with the II-III transition but no discontinuity.[5] Analysis of infrared (IR) and Raman spectra showed that rotational disorder exists in all phases.[6] A later study reaffirmed that the I-II and II-III transitions "do not involve perceptible structural alterations."[7]

Samples of powdered $NH_4PF_6$ purchased from Aldrich Chemical Company were deuterated via exchange with $D_2O$ and recrystallized. The samples were loaded into a closed-cycle refrigerator and cycled through the two phase transitions in the refrigerator three times prior to diffraction measurements. The measurements were performed using the C2 neutron powder diffractometer at Chalk River, Ontario.

The diffraction patterns at low temperature were fitted using XFIT.[8] When fitting more than one peak in a clump of overlapping peaks, all peaks were constrained to have the same full width at half maximum. The resulting list of $2\theta$ was fed into the CRYSFIRE suite of indexing programs,[9] the most successful of which were LZON and ITO.

This suggested a monoclinic cell of around 9.8 Å, 5.2 Å, 9.5 Å, and 106°, agreeing with the inelastic neutron spectroscopy study[10] that suggested the symmetry of phase III is monoclinic. Profile refinements were performed using both rigid body and free-atom refinements in a general strtucture analysis system.[11] Lower-symmetry refinements of the structure were also performed to check for extra degrees of freedom, and the resulting refinements analyzed for missing symmetry using the ADDSYM (Ref. 12) routine in PLATON,[13] which consistently suggested $C2/c$ as the space group of phase III. This agrees with the first structural studies of this phase.[14] The structure in phase III at 20 K is given in Table I.

The matrix relating the axes of the $F$ cell of phase I to the $C$ cell of phase III is

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{C2/c} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \overline{1} \\ \frac{\overline{1}}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{F} . \tag{1}$$

The $C2/c$ structure refinements were extended into the phase II and phase I data sets. Figure 1(a) shows the variation in the refined value of $\Delta y$ of the N atom as a function of temperature. The quantity $\Delta y$ is defined as the displacement in $y$ relative to the position mapped from phase I, and corresponds to a displacement along $[1\overline{1}0]_F$. The undistorted cubic phase would map the $ND_4^+$ ion to $y = 0.25$. The lattice of phase II shows a pseudorhombohedral character, but the nonzero $\Delta y$ coordinate of the ammonium ion breaks the hypothetical three-fold axis. A similar value of $y$ was reported at 160 K in phase II,[14] on the basis of a symmetry-adapted spherical harmonic fit to this phase. Upon extending the fit of this subgroup into phase I, $\Delta y$ jumps immediately to zero, as

TABLE I. The structure of $ND_4PF_6$ at 20 K from a free-atom refinement with atomic temperature factors. The space group is $C2/c$ (number 15), the unique axis is $b$, and the origin choice is 1.

| Atom | $x$ | $y$ | $z$ | $U$(Å$^2$) |
|---|---|---|---|---|
| N | 0.0000 | 0.1542(17) | 0.2500 | 0.003(4) |
| D | −0.0597(14) | 0.0498(19) | 0.3000(14) | 0.016(3) |
| D | −0.0606(13) | 0.2704(21) | 0.17802(14) | 0.016(3) |
| P | 0.2500 | 0.2500 | 0.0000 | 0.003(4) |
| F | 0.4003(10) | 0.1388(19) | 0.0921(12) | 0.001(2) |
| F | 0.1688(11) | −0.0090(18) | 0.0441(12) | 0.001(2) |
| F | 0.2797(11) | 0.0983(20) | −0.1401(12) | 0.001(2) |
| $a$ | $b$ | $c$ | $\beta$ | Volume (Å$^3$) |
| 9.656(1) | 5.0386(7) | 9.681(1) | 103.134(7) | 458.7(1) |
| $R_{wp}$ | | $R_p$ | | $R_E$ |
| 0.0351 | | 0.025 | | 0.015 |

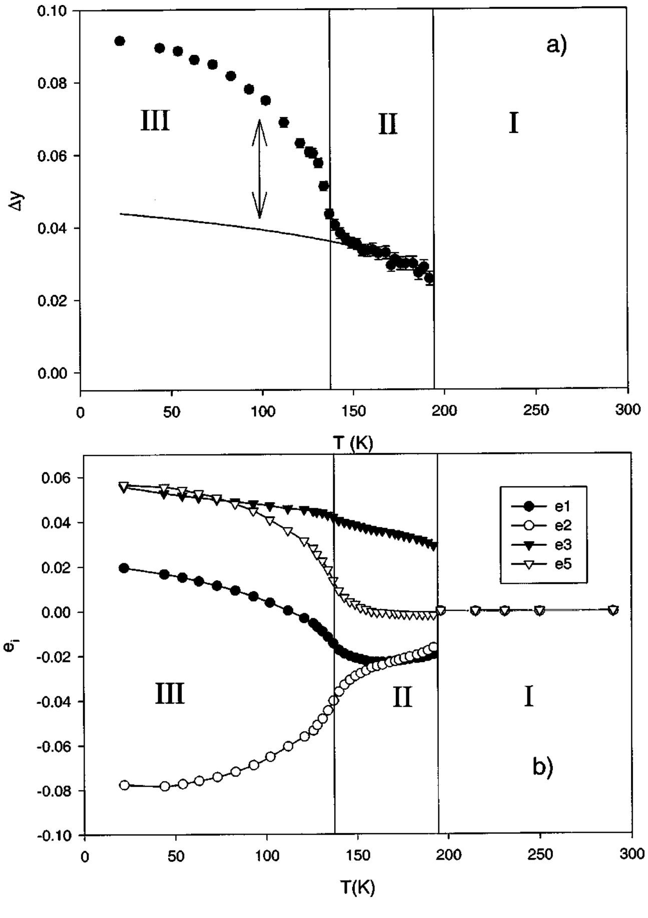

FIG. 1. (a) $\Delta y$, defined as the $y$ displacement of $NH_4^+$ in the monoclinic cell, from the position mapped from the cubic phase. Roman numerals indicate the phase. The curve is an extrapolation of $\eta$ for the I-II phase transition. $\Delta y_{\text{excess}}$, $\eta$, for the II-III transition is shown by $\updownarrow$. (b) The components of spontaneous strain, $e_i$, as a function of temperature. Reference lines are for $T_{\text{tr}}$ of transitions defined from calorimetric data (Ref. 3).

expected. Symmetry analysis in phase II shows that it is still in $C2/c$; i.e., II-III is an isosymmetric transition. Hence, the I-II transition is from $Fm\bar{3}m$ to $C2/c$, and the pseudorhombohedral nature comes from a soft $L$-point Brillouin-zone boundary optic mode.[15] This limits the active representation for the I-II transition to either $L_3^+$ or $L_3^-$.[16]

Here we demonstrate that (i) large distortions are involved in both these transitions, in strong contrast to the interpretations from spectroscopy, (ii) the II-III transition is apparently continuous by diffraction [and NMR (Ref, 5)], and (iii) isosymmetric transitions may be more common than thought and that phase-sensitive techniques may have particular difficulty in revealing the discontinuous nature of weakly first-order isosymmetric transitions.

The spontaneous strains coupled to both transitions may be calculated by projecting the thermal contraction of the cubic phase into phases II and III. The strains are defined in an orthogonal frame $XYZ$, where $\mathbf{X}\|\mathbf{a}$, $\mathbf{Y}\|\mathbf{b}$, $\mathbf{Z}\|\mathbf{1/c}^*$, and $abc$ are the monoclinic axes.[17] The allowed strains, $e_i$, are shown below:

$$e_1=\frac{a\sin\gamma}{a_0\sin\gamma_0}-1,$$

$$e_2=\frac{b}{b_0}-1,$$

$$e_3=\frac{c\sin\alpha\sin\beta^*}{c_0\sin\alpha_0\sin\beta_0^*}-1,$$

$$e_5=\frac{1}{2}\left(\frac{a\sin\gamma\cos\beta_0^*}{a_0\sin\gamma_0\sin\beta_0^*}-\frac{c\sin\alpha\cos\beta^*}{c_0\sin\alpha_0\sin\beta_0^*}\right). \tag{2}$$

The spontaneous strains are shown in Fig. 1(b). The first-order nature of the I-II transition, and the more gradual nature of the II-III transitions, are quite apparent from the strains. The strains generated on entering phase III are large, and are unexpected on the basis of NMR, and Raman and IR

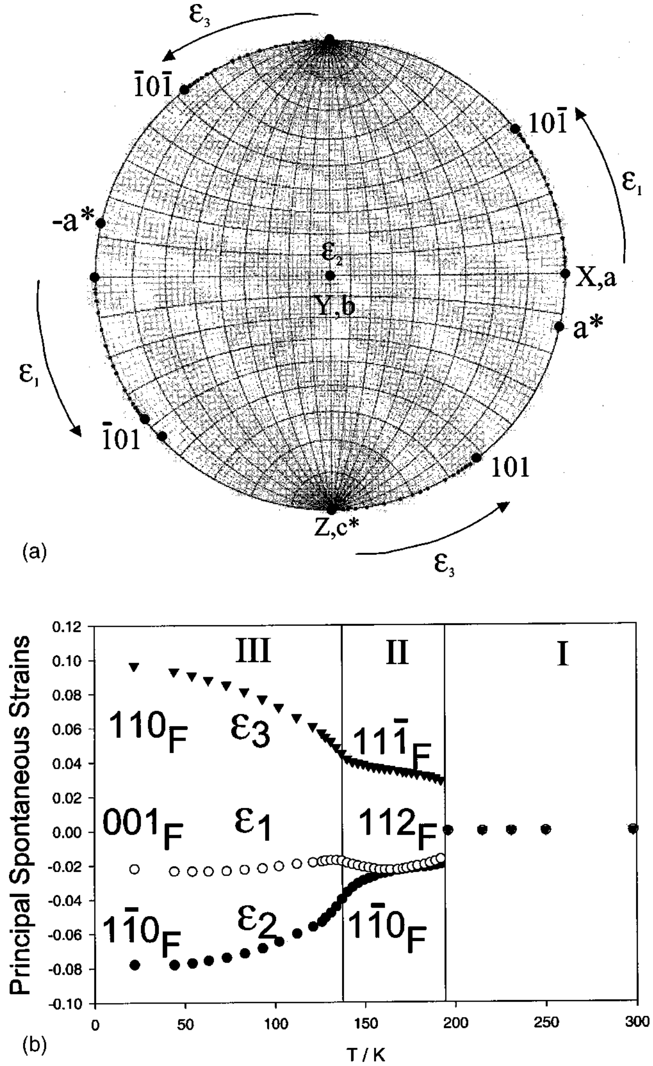

FIG. 2. (a) Eigenvectors of the spontaneous strain tensor as a function of temperature. The orthogonal basis vectors are $X\|a$, $Y\|b$, and $Z\|1/c^*$ of the monoclinic axes. One principal axis is constrained to lie along *b*. In phase II the other two principal axes lie subparallel to the face normals 001, 010 and the *a* axis of the monoclinic cell at all temperatures. On cooling to 20 K in phase III, the eigenvectors continuously rotate to ±101 and $\pm\bar{1}01$. (b) Eigenvalues of the spontaneous strain tensor. Superimposed on the graph are the directions of the eigenvectors (expressed as plane normals of phase I) of phase III at 20 K, and for phase II in which they are nearly temperature independent.

spectroscopy, all of which have been interpreted to imply small structural distortions.[5,6] In phase II, near the I-II, transition the value of $e_5$ is small (approximately $-2e^{-3}$ $\pm 6.5e^{-5}$) but not zero.

The nature of these strains is revealed by diagonalizing the strain tensor,[18] $e_i$, to determine the magnitude (eigenvalue) [Fig. 2(a)], $\epsilon_1,\epsilon_2$, and $\epsilon_3$, and orientation (eigenvector) [Fig. 2(b)] of its principal axes, $\bar{\epsilon}_1$, $\bar{\epsilon}_2$, and $\bar{\epsilon}_3$.

One of the principal axes, $\epsilon_2$, is constrained by symmetry to lie along the two-fold monoclinic axis {0,1,0} in phases II and III, corresponding to to $\{1\bar{1}0\}_F$ of phase I, via the inverse matrix of Eq. (1). In phase II, the two "free" eigenvectors, $\bar{\epsilon}_1$ and $\bar{\epsilon}_3$, cluster to within $\pm 2°$ of **X** and **Z**, respectively for all temperatures. As $\mathbf{Z}\|1/c^*\|001$, this implies $\bar{\epsilon}_3\|11\bar{1}_F$. The other "free" eigenvector $\bar{\epsilon}_1\|\mathbf{X}\|\mathbf{a}$. Since $\bar{\epsilon}_1=\bar{\epsilon}_2\otimes\bar{\epsilon}_3$, $\bar{\epsilon}_1=11\bar{1}_F\otimes 1\bar{1}0_F=112_F$. The eigenvectors may be summarized as

$$\begin{pmatrix}\bar{\epsilon}_1\\ \bar{\epsilon}_2\\ \bar{\epsilon}_3\end{pmatrix}_{\mathrm{II}} \Bigg\| \begin{pmatrix}112_F\\ 1\bar{1}0_F\\ 11\bar{1}_F\end{pmatrix}, \tag{3}$$

and, together with the eigenvalues $\epsilon_3>0$ and $\epsilon_1\approx\epsilon_2<0$, confirm the pseudorhombohedral nature of phase II.

On cooling towards base temperature [Fig. 2(a)] in phase III, the $\epsilon_1$ and $\epsilon_3$ eigenvectors continuously rotate until they lie very close to 101 and $\bar{1}01$, corresponding to $001_F$ and $110_F$, i.e.,

$$\begin{pmatrix}\bar{\epsilon}_1\\ \bar{\epsilon}_2\\ \bar{\epsilon}_3\end{pmatrix}_{\mathrm{III,20\ K}} \Bigg\| \begin{pmatrix}001_F\\ 1\bar{1}0_F\\ 110_F\end{pmatrix}. \tag{4}$$

Without any change in symmetry, the mode of distortion of the lattice changes radically between phases II and III only by activating existing degrees of freedom. The rotation of the spotaneous strain ellipsoid is achieved by the activation of the $e_5$ shear component, of small magnitude and nearly temperature independent in phase II.

The total spontaneous strain can be represented by the scalar $e_s=\sqrt{\Sigma_i\epsilon_i^2}$. At 20 K, $ND_4PF_6$ has a value of 12.3%, making this a system with one of the largest spontaneous strains reported.[19]

In the I-II transition, the order parameters (OP's) are easy to identify: the primary OP, $\eta$, being the (optic) translation of the $ND_4$ group along the *y* axis, and the coupled secondary OP, the spontaneous strain.

The II-III, $C2/c-C2/c$, transition is governed by the identity, i.e., $\Gamma_1$, or $A_g$. Isosymmetric transitions are necessarily discontinuous: The simplest proof is that in a mean-field description the Landau condition is always violated, since $\Gamma_1\subset[\Gamma_1]$.[3] As the active representation is $\Gamma_1$, all powers of $\eta$ are allowed in the "Landau expansion."[20] The hypothetical phase diagram for such transitions consists of a line of first-order transitions terminating at the singular Landau critical point, where second-order behavior is found.[21]

The corresponding supercritical phenomenon is known as a crossover and is commonly associated with maxima in thermal expansion or compressibility, which do not separate thermodynamically distinct phases.[20] Associated with these are broad anomalies in $C_p$, e.g., $NH_4ReO_4$ where the $C_p$ anomaly extends over 150 K.[22]

The II-III transition is more gradual in nature than I-II, but there is a distinct latent heat, giving the appearance of a

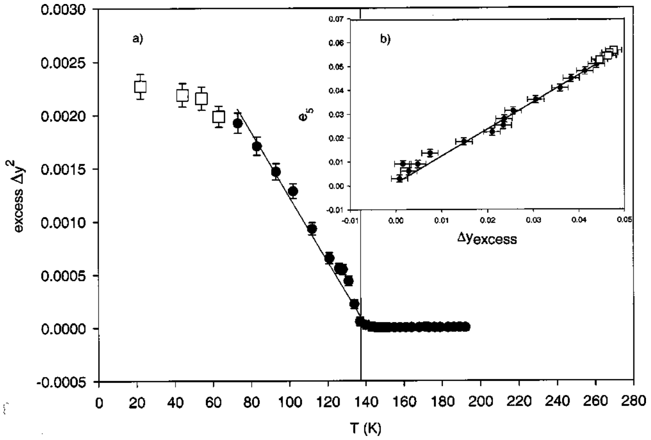

FIG. 3. (a) $\Delta y^2_{\mathrm{excess}}$ versus temperature in phase III. The fit represents behavior characteristic of second order. The deviation at $T < 60$ K (shown as □) is due to "saturation." (b) $e_5$ versus $\Delta y_{\mathrm{excess}}$. Coupling is linear throughout phase III, including the "saturation" range (□).

slightly broadened λ anomaly.[3] This implies that this transition is first order, as demanded by the Landau condition. Since no symmetry is broken, $\eta$ for such transitions transforms as a modification of the behavior of an existing degree of freedom, in this case $\Delta y$ inherited from phase II [Fig. 1(a)]. A break in slope is evident at the II-III transition. A curve has been fitted through the values of $\Delta y$ in phase II, on the basis of a standard first-order 2-4-6 Landau potential, representing the I-II transition. The II-III OP is the excess quantity $\Delta y_{\mathrm{excess}}$, the difference between the observed and extrapolated values of $\Delta y$. Figure 3(a) shows a plot of $\Delta y^2_{\mathrm{excess}}$ vs temperature. It is clearly linear for $T > 60$ K, showing that the transition is close to being second order. For $T < 60$ K, the points curve away from the relationship. This departure is due to "order-parameter saturation:" the third law of thermodynamics requires that $\partial\eta/\partial T = 0$ at 0 K. Hence such Landau relationships must be violated at low temperatures.[23] Figure 3(b) shows a plot of $e_5$ and $\Delta y_{\mathrm{excess}}$ showing a strong proportionality, over the entire range of phase III, *including* the region of OP saturation. This shows that it is not an artifact of the extrapolation. The relationship $\epsilon_5 \propto \eta$ is that expected of a $\Gamma$-point transition.

Despite the absence of a symmetry change through the II-III transition, the strains in phase III have a very different character from that of phase II. The II-III transition may be triggered by $\eta$ exceeding a critical value which the structure cannot accommodate without changing the "sense" of distortion. This is remiscent of a class of isosymmetric transitions that occur under pressure,[20] whereby the dominant compression mechanism changes discontinuously, beyond a critical pressure; e.g., $\alpha$-$PbF_2$,[24] $Na_3MnF_6$.[25] This may be accompanied by a change in coordination, and in this case the coordination ammonium decreases from 14 to 12.[14]

Our data show the II-III transition to be close to second order. The detailed NMR measurements show a distinct discontinuity in $T_1$ of $^{19}$F at the I-II transition. At the II-III transition the slope of $T_1$ of both $^{19}$F and D change, but any discontinuity is within the resolution.[5]

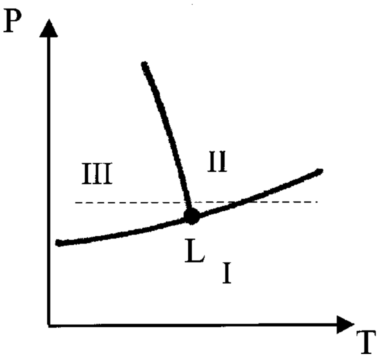

FIG. 4. Hypothetical phase diagram. The II-III transition is in the vicinity of the Landau critical point.

How is it that a transition can be shown that it must be discontinuous (Landau condition), is discontinuous (latent heat), yet appears continuous by, e.g., both NMR and diffraction? There appears to be a contradiction. A similar apparent contradiction was found in $V_3Si$, with its gradual transition from cubic to tetragonal. While not isosymmetric, a third-order invariant is allowed in the Landau expansion and for a long time was used as an appparent exception to the Landau condition, since, e.g., X-ray measurements appeared to show it to be continuous.[21,26] However, it was eventually shown that this too was first order using a dilatometer.[26]

It may be that many slightly discontinuous isosymmetric transitions appear more continuous than they really are. The Landau condition does not place a minimum size on the discontinuity. While there are many examples of weakly discontinuous transitions, isosymmetric ones may be particularly prone to misidentification. Many phase-sensitive methods will not be capable of distinguishing between the two "identical" structures, in the limit of small discontinuities.

In the case of diffraction, there are no new peaks, but one may expect to see a discontinuity in the diffraction pattern, i.e., an offset in $2\theta$ due to the coupled strains. However, for small $\Delta\eta$, and, therefore, $\Delta e_i$ this may be within the resolution limit. The small discontinuity in $\eta$ and $e_i$ may be further smoothed by coexistence near $T_{\mathrm{tr}}$, where the proportions of domains of "identical" phase II and phase III change gradually. The values extracted of $\eta$ and $e_i$ may therefore be weighted by the presence of both phases through the coexistence range. One may therefore only have to be in the vicinity of the Landau critical point to see apparently continuous behavior from diffraction. A hypothetical phase diagram is shown in Fig. 4, with the temperature path marked.

In the case of NMR, for small $\Delta\eta$, the local environment will be essentially the "same," and, in this case also, the discontinuity may also be smeared by coexistence. While such phase-sensitive techniques may be "fooled" in this limit, calorimetry, a bulk technique, will directly display the discontinuity in $\eta$ via the latent heat generated through the transition region.

In this case the spontaneous strains are large. Had the coupling between the optic distortion and strain been small, it is easy to envisage missing the transition entirely. This brings us to the more general point that isosymmetric transitions are probably more common than realized. Structural examination at a few isolated points in $(T,p)$ may miss such transitions entirely. This may explain the comparatively rare reporting of such transitions, especially in insulators.

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