FIG. 3. $K\alpha_1$ spectra obtain for $\theta = 22°$ $\vec{k} \parallel C$ and $\vec{k} \parallel A$ after the $K\alpha_2$ contribution has been subtracted. They are compared with the RPA result which has been smeared with the instrumental resolution function.

turn look different from the homogeneous RPA result. While some of the features in this spectrum no doubt depend on the details of the Be band structure, others may very well be signaling a

real breakdown of this simple RPA picture.

---

*Resident visitor from Columbia University, New York, N. Y. 10027.

[1]H. Watanabe, J. Phys. Soc. Jap. 11, 112 (1956).

[2]C. J. Powell, Proc. Phys. Soc., London 76, 593 (1960).

[3]G. Priftis, Phys. Rev. B 2, 54 (1970).

[4]A. Tanokura, N. Hirota, and T. Suzuki, J. Phys. Soc. Jap. 28, 1382 (1970).

[5]D. M. Miliotis. Phys. Rev. B 3, 701 (1971).

[6]D. Pines and D. Bohm, Phys. Rev. 92, 608 (1953).

[7]P. M. Platzman and P. A. Wolff, Waves and Interactions in Solid State Plasmas (Academic, New York, 1973); S. L. Adler, Phys. Rev. 126, 413 (1962); N. Wiser, Phys. Rev. 129, 62 (1963); M. S. Hague and K. L. Kliewer, Phys. Rev. B 7, 2416 (1972).

[8]N. G. Alexandropoulos, J. Phys. Soc. Jap. 31, 1790 (1971).

[9]M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Lett. 27, 1565 (1971).

[10]D. F. Dubois and M. G. Kivelson, Phys. Rev. 186, 409 (1969).

[11]A. E. O. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

[12]K. L. Kliewer and H. Raether, Phys. Rev. 30, 971 (1973); G. G. Cohen, N. G. Alexandropoulos, and M. Kuriyama, Solid State Commun. 10, 95 (1972).

New Ferroelastic-Ferroelectric Compound: Tanane

D. Bordeaux, J. Bornarel, A. Capiomont, J. Lajzerowicz-Bonneteau,
J. Lajzerowicz, and J. F. Legrand
Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale de Grenoble,
38041 Grenoble Cedex, France
(Received 7 May 1973)

We report here evidence for the first paraferroelectric transition observed in a pure molecular solid (without H bonds); we present results from x-ray diffraction, calorimetric and dielectric measurements, and direct optical observation of domain-wall displacement under an applied electric field.

During studies of crystallographic structure of organic free radicals, it has been found that one of these substances, nitroxyde tetramethyl-2, 2, 6, 6-piperidine oxyle ($C_9H_{18}NO$), named Tanane (Fig. 1), has three different phases.[1] In all phases, distances between all neighboring atoms of different molecules are compatible with normal Van der Waals interactions, and, in particular, there is no evidence for intermolecular hydrogen bonding. Two of these phases are connected by a phase change, analogous, from the point of view of symmetry, to that in potassium dihydrogen phosphate (KDP). We present here results

showing that this transition is of second order, with a net departure from the mean-field behav-
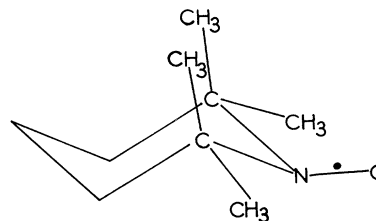

FIG. 1. The Tanane molecule is a saturated heterocycle having a "chair" conformation.
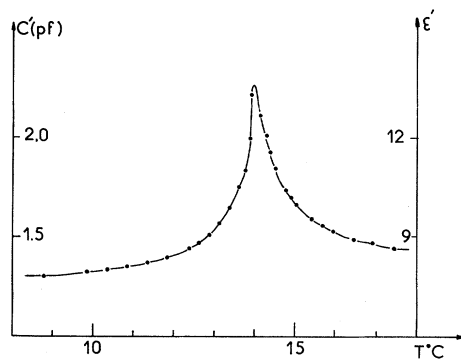
FIG. 2. Dielectric constant versus temperature. The dielectric measurements have been made with samples of 0.05-cm thickness and an area of the order of 0.2 cm^2 with a Wayne-Kerr capacitance bridge operating at 1592 Hz.

FIG. 3. C_p versus T. Calorimetric measurements have been made with a power-compensated calorimeter [E. Bonjour, M. Couache, and J. Pierre, Cah. Therm. 1B, 134 (1971)].

ior analogous with what has been found in other structural transitions. We have not been able to observe hysteresis loops because of the low mobility of the domain wall; nevertheless we observed domain-wall displacements in a dc electric field and an anomaly in the dielectric constant.

The two phases of interest are the tetragonal and the orthorhombic ones. The tetragonal is the high-temperature phase (space group $I\bar{4}2d$, point group $\bar{4}2m$), and the orthorhombic (space group $Fdd2$, point group $mm2$) appears at $T_c = 14 \pm 1°$C. We do not observe thermal hysteresis; if present, it is less than 0.1°C. The space groups are the same as in KDP, but evidently the two substances are not isomorphous. The high-temperature phase is piezoelectric, and we have, simultaneously, appearances in the low-temperature phase of a spontaneous polarization P_z and a spontaneous shear strain U_{xy}, both transforming according to the B_2 representation. If the transition is of second order both response functions (the dielectric susceptibility χ_{zz} and the elastic compliance S_{xyxy}) must diverge in the same way at T_c. In a "Landau" type of approach, if we write the quadratic part of the free energy as a function of P_z and U_{xy}, we have

$$F = \tfrac{1}{2}AP_z^2 + \tfrac{1}{2}CU_{xy}^2 - aU_{xy}P_z.$$

We have for χ_{zz} and S_{xyxy}

$$\chi_{zz} = C/(AC - a^2), \quad S_{xyxy} = A/(AC - a^2).$$

The system becomes unstable when $AC - a^2$ goes to zero, and this can happen either with A or C small, or a large (the two first cases correspond, respectively, to a ferroelectric and a ferroelas-
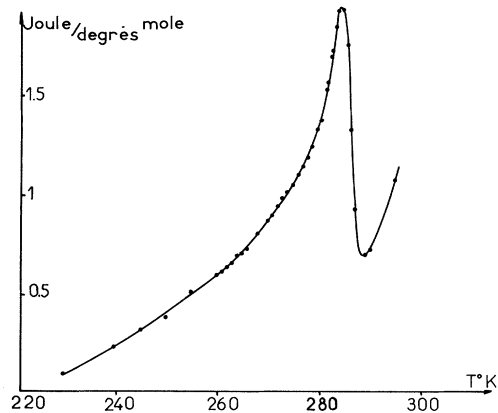
tic transition).

The crystal is very soft and sublimes easily (the melting point is about 38°C) so we are not able to obtain a very good capacitor for dielectric measurements. The value of the dielectric constant has therefore to be considered as an order-of-magnitude estimate. Nevertheless, there is a net anomaly at the Curie point (see Fig. 2).

Calorimetric measurements give a curve (Fig. 3) very characteristic of a second-order transition. The experimental data are consistent with a logarithmic singularity on the low-temperature side. As a result of the low melting point (38°C) we are not able to obtain significant data on the high-temperature side. We evaluate the change in entropy, ΔS, between 1.5 and 2.1 cal/deg mole. If we write $\Delta S = R\ln n$ we find that n is between 2 and 2.9.

At T_c the tetragonal symmetry is broken and the crystal becomes orthorhombic. This induces a twin or domain structure [the twinning planes are the tetragonal (100) or (010) planes (Fig. 4)]. As the symmetry operation which connects two domains is a $\bar{4}$ axis, the optical ellipsoid is rotated by 90° from one domain to another, and it is possible to make optical observations with a polarizing microscope (see Fig. 4). Domains appear at the Curie point when cooling, with a large distribution of domain widths varying from 10 μm to several millimeters. Usually the domain walls go from one edge of the crystal to the other. This behavior is very different from that observed in KDP.[2]
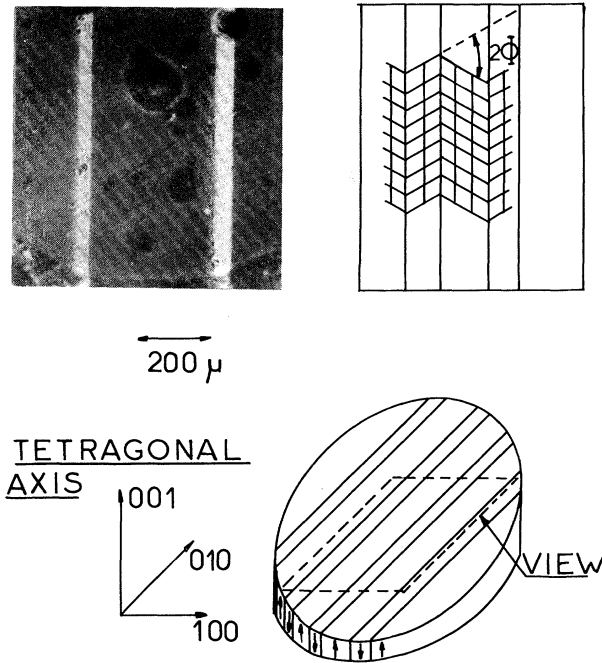
200 μ

TETRAGONAL
AXIS |001

FIG. 4. A picture of the domain structure with schematic representation of the spontaneous deformation and polarization.

FIG. 5. Spontaneous deformation versus $T - T_c$.

It was not possible to obtain a hysteresis loop at 50 Hz because the domain-wall mobility was too small, but in an applied dc field, movements of the domain walls were observed. A film has been made, and for a field of 10 kV/cm we measure a velocity of the order of 10^{-2} cm/sec. 1° below T_c the switching time is of the order of 30 sec, and 10° below T_c of the order of 30 min.

We are not able to measure the spontaneous polarization, but as we know the value of the dipole moment[3]—mainly due to the NO group—and the orientation of the molecule,[1] we can find a value of P_s of about 1 μC/cm².

We can measure the deformation angle $\varphi = U_{xy}$ (Fig. 4) by the following method: We position the crystal so as to get a Bragg reflection, let us say the 600 for one type of domains, and without changing the x-ray setting we rotate the crystal until we get the 600 Bragg reflection from other domains related to the original ones by a 010 symmetry operation. The angle of rotation θ $= 2\varphi$ gives us directly the order parameter. Experiments have been done with a Siemens x-ray diffractometer. We have plotted (Fig. 5) the value of φ versus the temperature; several points should be noticed:
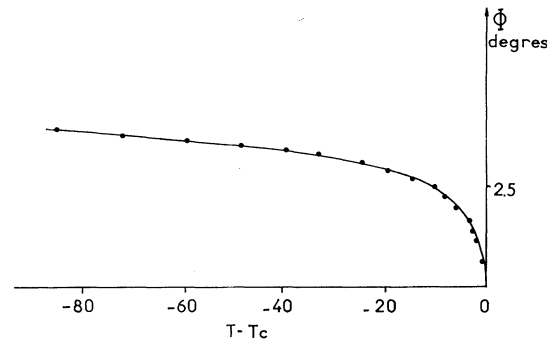
(1) The deformation angle is quite high com-

pared to KDP (4° compared to 0.5°).

(2) The variation of the order parameter U_{xy} as a function of $T - T_c$ is very different than for KDP; we find that $U_{xy} \sim (T - T_c)^\beta$, with β equal 0.34 ± 0.01, showing a net departure from mean field behavior and displaying a critical behavior.

(3) It is remarkable that this transition obeys a criterion of "universality": The behavior of the order parameter near the transition point is the same as for two other structural phase transitions with very different mechanisms and symmetries[4] (AlLaO₃ and SrTiO₃). Several authors[5] have said that the "classical" behavior is obeyed if the system is anisotropic with dipolar or piezoelectric interactions. We see here that this cannot be applied to Tanane unless these interactions are negligible. This once again makes questionable the role of dipolar interactions on the nature of singularities near the transition point.

The mechanism of the transition is due to the flexibility of the molecule. Tanane has a chair conformation (Fig. 1) with the possibility of inversion[6]; in the high-temperature phase the two forms are inverting, but in the low-temperature phase they freeze with all their NO groups having the same z component. The system can therefore be represented by an Ising model. There is another possibility for the mechanism of the transition: a rotation of the molecule of 180° around the twofold [100] axis. From steric considerations the first process is more likely.[7]

We can conclude from all this data that Tanane has a ferroelastic-ferroelectric transition of an order-disorder type. It is believed to be the first nonhydrogen-bonded molecular crystal in which the existence of a ferroelectric phase has been firmly established.

ing in the dielectric measurements, and M. Thomas for the x-ray measurements.

[1]A. Capiomont, D. Bordeaux, and J. Lajzerowicz, C. R. Acad. Sci., Ser. C 275, 317 (1972).
[2]J. Bornarel and J. Lajzerowicz, Ferroelectrics 4, 177 (1972).
[3]E. G. Rozantsev and E. N. Gur'yanova, Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 979.
[4]K. A. Müller and W. Berlinger, Phys. Rev. Lett. 26, 13 (1971).
[5]J. Villain, Solid State Commun. 8, 295 (1970), and J. Phys. (Paris), Colloq. 32, C1-646 (1971); A. P. Levanyuk and A. A. Sobyanine, Pis'ma Zh. Eksp. Teor. Fiz. 11, 540 (1970) [JETP Lett. 11, 371 (1970)].
[6]A. Rassat, Pure Appl. Chem. 25, 623 (1971).
[7]A. Capiomont and J. Lajzerowicz, to be published.

Number-Displacement Degrees of Freedom in Nuclear Rotational Theory*

John O. Rasmussen†
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

and

Chin W. Ma
Physics Department, Indiana University, Bloomington, Indiana 47401

A new degree of freedom associated with shifting of particles between the even-parity-orbitals system and the odd-parity-orbitals system is introduced in the study of the nuclear rotational problem. It is found that this new mode contributes significantly to the deviation from the $I(I+1)$ rule, with correction terms comparable to the Coriolis anti-pairing effect.

In theoretical calculations of the nuclear rotational spectrum, several specific collective degrees of freedom have been considered as influencing deviations from the $I(I+1)$ energy spacings. There are the proton and neutron pairing correlations involved in the Coriolis antipairing (CAP) effect. There are the β- and γ-vibrational degrees of freedom involved in shape-change effects. There is also a fourth-order cranking effect that may be expressed in terms of an additional collective degree of freedom.

The total energy E of a deformed rotating system may be expressed in terms of these collective degrees of freedom as[1]

$$E = \sum_i \tfrac{1}{2} C_i (X_i - X_{i0})^2 + I(I+1)/2J(X_i), \tag{1}$$

where X_i ($i = 1, 2, 3, ...$) describes the various degrees of freedom, C_i is the spring constant associated with the ith degree of freedom, and $J(X_i)$ is the moment of inertia. The rotational solution may be obtained by minimizing the total energy of Eq. (1) with respect to each of the X_i at a given angular momentum I.

In this note we shall identify a new degree of freedom which will affect both the moment of inertia and the potential energy of Eq. (1). We first express the moment of inertia J in terms of the cranking formula of Inglis[2] and Belyaev[3]:

$$J = 2\hbar^2 \sum_{\Omega_\alpha > 0} \frac{\langle \alpha' | j_x | \alpha \rangle}{E_{\alpha'} + E_\alpha} (U_{\alpha'} V_\alpha - U_\alpha V_{\alpha'})^2, \tag{2}$$

where $|\alpha\rangle$ is the deformed single-particle state with α denoting the appropriate quantum numbers, Ω_α is the projection of the angular momentum on the symmetry axis, E_α is the quasiparticle energy, and U_α and V_α are the probability coefficients defined by

$$\left.\begin{matrix} U_\alpha^2 \\ V_\alpha^2 \end{matrix}\right\} = \frac{1}{2}\left[1 \pm \frac{\epsilon_\alpha - \lambda}{[(\epsilon_\alpha - \lambda)^2 + \nu^2]^{1/2}}\right], \tag{3}$$

with ϵ_α the single-particle energy, ν the pairing-correlation parameter, and λ the chemical potential. In usual practice, the chemical potential takes two values, λ_p for the proton system and λ_n for the neutron system. What interests us here is the fact that the even-parity orbital systems and odd-parity orbital systems make separable contributions to the moment of inertia, since the operator j_x has even parity. Thus, it is possible that the nuclear system could change its moment of inertia by shifting nucleons between the two orbital systems of opposite parity. In other words, the nuclear system might assume unequal chemical potentials (λ_+ and λ_-) for the different-parity orbital systems in order to min-
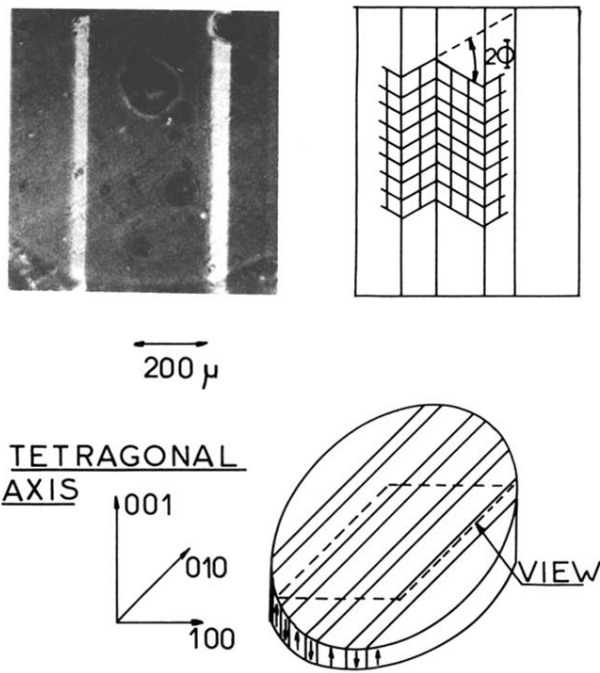
200 μ

TETRAGONAL
AXIS
001
010
100

VIEW

FIG. 4. A picture of the domain structure with schematic representation of the spontaneous deformation and polarization.