PHYSICAL REVIEW B VOLUME 27, NUMBER 9 1 MAY 1983

Nonlinear elasticity in proper ferroelastics

P. Toledano,* M. M. Fejer, and B. A. Auld
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

(Received 19 July 1982)

Nonlinear elasticity in proper ferroelastics is investigated using the Landau theory of phase transitions. In proper ferroelastics, where certain combinations of strain components e_s correspond to the order parameter, coefficients in the Landau free energy are found to coincide with special combinations of elastic constants of second and higher orders, so that both linear and nonlinear elasticity can be directly accounted for by the Landau theory. Accordingly, four categories of strain-induced ferroelastics are distinguished and their nonlinear elastic properties are established. The temperature variation of the second-, third-, and fourth-order elastic constants is also described. A measure of the nonlinearity coefficient L_1, expressing the nonlinear elastic energy stored at a ferroelastic transition, is defined and calculated for each of the preceding categories of transitions. Numerical models are discussed for illustrative examples of type-I (TeO_2), type-II (V_3Si), and type-III ($LaNbO_4$) ferroelastics. In "pseudoproper" ferroelastics, where spontaneous strain is a secondary order parameter, elastic properties are accounted for in the Landau free energy via elastic energies of second and higher orders. With the use of the specific case of LaP_5O_{14}, it is shown that pseudoproper ferroelastics have distinctive elastic (linear and nonlinear) behavior, the magnitude of L_1 depending on the strength of the linear coupling between the order parameter and the spontaneous strain. Available examples of pseudoproper ferroelastics are briefly discussed.

I. INTRODUCTION

Evidence of nonlinear elastic behavior in a number of solids has been established in recent years by direct or indirect measurements, namely stress-strain curves showing strong deviations from Hooke's law,[1] development of higher-order harmonics in finite-amplitude wave propagating through the medium,[2] and variation in ultrasonic transmission velocities with applied stress.[3] In the equation of state of the solid, nonlinear elastic effects are characterized by the third- and higher-order elastic constants.[4] Thus third-order elastic constants (TOEC's) have been used to describe many anharmonic properties of solids.[5-7] In particular, they have been related to some features of materials undergoing structural phase transition, such as the temperature and pressure dependence of second-order elastic constants[8,9] (SOEC's) or the velocity discontinuity and anomalous damping of ultrasonic waves observed near the Curie point.[10,11]

Since the anharmonicity of the crystal lattice is enhanced by structural instabilities, one can expect a high degree of elastic nonlinearity in materials exhibiting structural transitions in the vicinity of the transition point. Moreover, for transitions involving large strains over a large range of values of the temperature or pressure, nonlinear elastic behavior should be also observable far from the Curie point, as the basic assumption of linear elasticity (i.e., infinitesimal strains) is not satisfied. This is the case for ferroelastic phase transitions, i.e., structural transitions giving rise to spontaneous strain components.[12] These components increase in the ferroelastic phase and can be several orders of magnitude larger than the standard thermal expansion of the lattice parameters.[13]

It is therefore not surprising to find out that most of the studies dealing with the nonlinear elastic properties of solids that undergo a phase transition are devoted to ferroelastic materials. Sets of values of TOEC's are available either for pure ferroelastics such as $KH_3(SeO_3)_2$ (Ref. 14), TeO_2 (Ref. 15), V_3Si (Ref. 16), and $SrTiO_3$ (Ref. 17), or for ferroelectric ferroelastics such as KH_2PO_4(KDP) (Ref. 18) and $BaTiO_3$ (Ref. 19). Although it appears necessary to include elastic nonlinearity in a phenomenological description of these compounds, a difficulty arises from the fact that most of the experimental data are partial or uncertain. This is due to the fact that direct measurements (i.e., stress-strain curves obtained by static compression) are subject to large experimental errors,[20] while indirect ones (i.e., the dependence of ultrasonic wave velocity on applied stresses and ultrasonic second-harmonic generation) involve many approximations and provide only linear combinations of the TOEC's.[21] Moreover, the suitability of the phenomenological approach used by a number of authors in calculating these constants, is in many cases controversial, as it does not take entirely into account the symmetry and physical characteristics of the system[22] considered.

The aim of this paper is to determine, for the various theoretical situations encountered in ferroelastic materials, the phenomenological behavior that may be expected for the third- and higher-order elastic constants, using the Landau theory of phase transitions.[23] It is shown that through such a thermodynamic description, one can obtain information about the higher-order elastic constants of the system from the variation of the strain components and SOEC's as a function of the temperature or pressure. Conversely, the variation of the higher-order elastic constants may help to discriminate which physical mechanism is responsible for the transition. The study is limited to purely ferroelastic transitions[12,13] (PFT's) for which the order-parameter symmetries and free-energy expansions have been systematically worked out in a recent paper.[24] Partially unpublished results[25] concerning ferroelastic transitions violating the Landau symmetric-cube condition,[23] excluded from Ref. 24, are also used.

It is now well known[26] that ferroelastic transitions are among the most frequently encountered type of structural phase transitions. Besides being associated with a symmetry-breaking spontaneous strain, they share a number of typical features: a stress-strain hysteresis loop (in the ferroelastic phase) disclosing the occurrence of several different strain states of definite crystallographic orientation (the ferroelastic domains), the possibility of switching the crystal from one state to another by applying an external stress, and anomalies in specific components of the elasticity tensor. In addition to the trivial group-subgroup relationship between phases, the symmetry change taking place at a ferroelastic transition is characterized by the fact that the thermal-expansion tensor of the ferroelastic [low-symmetry (LS)] phase has more independent components than that of the paraelastic [high-symmetry (HS)] phase. This condition arises from the fact that the spontaneous strain is represented by a symmetric second-rank traceless tensor. Because of this it follows that the point groups of the two phases belong to different crystal systems provided that the hexagonal and trigonal systems are grouped together.[13] The PFT's are defined by the additional condition that the same components of a vector are compatible with the crystal classes of the two phases[13] so that the ferroelastic phase will not be simultaneously ferroelectric.[24] The possible ferroelastic point-group changes (ferroelastic "species"[27]) and the corresponding macroscopic properties (such as the form of the spontaneous strain tensor and the number of orientational domains) have been listed by several authors[28-30] and are partly reviewed in Ref. 24 for PFT's.

In the framework of the Landau theory, the basis for a phenomenological description of the physical quantities affected by a phase transition is provided by the so-called Landau free energy[23] (LFE). This thermodynamic function has the form of a polynomial expansion whose terms are invariant under the symmetry operations of the HS space group. For a PFT the LFE expansion is restricted to two sets of variables: the order-parameter (OP) components $\{\eta_i\}$ spanning the irreducible representation (IR) driving the transition and the spontaneous-strain (SS) components $\{e_s\}$ relative to the considered symmetry change. Here the e_s are combinations of strain-tensor components, while the η_i may be either combinations of strain components or combinations of other degrees of freedom of the system, depending on the nature of the transition. Different situations can be distinguished on the basis of the relative symmetry of the OP and of the SS.

(1) When the OP and the SS have the same symmetry (i.e., when they belong to the same Brillouin-zone-center IR), the corresponding PFT is labeled as "proper."[31] However, depending on the physical nature of the OP, two distinct types of phenomenological behavior can be encountered:

(a) *Purely strain-induced transitions.* When the OP components coincide with some components e_s of the SS, the transition is described by a LFE of the type

$$F=F_1(e_s,c_s)+F_2(e_s,e_i,c_i)\ , \qquad (1)$$

where $F_1(e_s,c_s)$ is the OP expansion and $F_2(e_s,e_i,c_i)$ is the elastic energy of the crystal in the paraelastic phase minus the SS contribution already taken into account in F_1. In (1) the c_s and c_i are combinations of elastic constants of different orders associated respectively with the SS components e_s and with other combinations e_i of strain-tensor components. This situation occurs when the mechanical (acoustic) instability induces the transition,[32] the crystal being elastically "soft" and optically "hard." The homogeneous distortion of the unit cell occurring at the transition is accompanied by substantial elastic anomalies, a combination of SOEC's going to zero as the Curie point is approached from either side.

In this family of ferroelastic materials, nonlinear elasticity is naturally accounted for in the Landau theory by the coefficients of the quadratic, cubic, quartic, etc., invariants of the OP in the LFE, which are, respectively, combinations of SOEC's, TOEC's, FOEC's, etc. Actually the well-known nonparabolic distortion of the OP expansion $F_1(e_s)$ (or equivalently, the corresponding nonlinear stress-strain relationship) in the vicinity of the transition point clearly suggests the existence of nonlinear elastic effects. In Sec. II we show that even partial experimental determination of higher-order constants in a strain-induced ferroelastic allows one to undertake a more general quantitative description of the linear and nonlinear properties of the material. Conversely the Landau theory should help to estimate the values of the elastic constants of a proper ferroelastic whose salient features should be related to definite combinations of second- and higher-order elastic constants.

(b) *Pseudoproper transitions.* The OP components η_i do not coincide with the SS components but couple to them bilinearly. The η_i may correspond to atomic displacements associated with a soft zone-center optic mode (both the acoustic and optic soft modes being Raman active) or to some other degree of freedom of different physical nature (such as electronic effects). In this "pseudoproper" case, ferroelasticity results from a coupling of the SS components with the actual OP and the PFT is described by a LFE of the following type:

$$F = F_1(\eta_i) + F_2(e_i, e_s, c_i, c_s) + F_3(\eta_i, e_s) , \qquad (2)$$

where $F_1(\eta_i)$ is the OP extension, $F_2(e_i, e_s, c_i, c_s)$ is the linear *and* nonlinear elastic energy of the crystal (including the SS components), and $F_3(\eta_i, e_s)$ is a mixed invariant expressing the bilinear coupling between the OP and the SS components. In pseudoproper ferroelastics, the magnitude of the elastic nonlinear effects depends on the strength of the coupling between the SS components and the OP components. These effects are not directly accounted for in the OP expansion and must be introduced in the F_2 and F_3 terms of (2), not only on the basis of symmetry but also on empirical considerations that depend on the specific properties of the material.

A softening of the optic mode (or other effects) may also influence a proper PFT. In this case coupling terms, that may be bilinear, have to be added to (1). However, the distinction between proper and pseudoproper PFT's, even in a hybrid case, is not a formal one. It indicates which one of the mechanical, optical, or other (i.e., the primary OP) instabilities induces the transition and triggers the other one. In particular, the choice of an OP with components η_i distinct from the SS components means that the phase transition would still occur in a rigidly clamped lattice. Although they have some common features, proper and pseudoproper ferroelastics can be distinguished experimentally by certain dynamical and static properties.[33] In Secs. II and III we establish that their nonlinear elastic behavior differs in several important respects. Detailed numerical examples of proper ferroelastics, such as TeO_2 and V_3Si, and pseudoproper ones, such as LaP_5O_{14}, are discussed.

(2) The following types of phase transition may also occur in ferroelastic materials:

(a) When the sets of components $\{e_s\}$ and $\{\eta_i\}$ belong to different IR's, the transition is labeled as "improper,"[34,35] with the SS components e_s being nonlinearly coupled to the OP components η_i.

(b) When the OP components coincide with one set of strain components $\{e_i\}$ and another set corresponding to the same ferroelastic transition belongs to a different nonidentical IR, the PFT exhibits simultaneously proper and improper behavior.

(c) When the OP transforms according to a reducible representation, the transition results from a simultaneous instability with respect to several modes.

(d) When the PFT involves components belonging to higher-rank tensors in addition to the SS components.

Elastic nonlinear effects in all of these categories of PFT's are either secondary effects (as for improper transitions) or are accounted for less directly by a phenomenological model based on the Landau theory. Their description will not be discussed here.[36]

II. STRAIN-INDUCED FERROELASTIC TRANSITIONS

In this section we consider PFT's whose OP components are strain components transforming like a single IR of the paraelastic phase, so that the different domain orientations are completely characterized by the SS components. It is also assumed that the onset of SS affects strongly the transition in such a way that coupling with secondary atomic displacements (or other effects) can be neglected in a first approximation. Column 2 of Table I reviews the 32 ferroelastic species[27] which, on a symmetry basis, satisfy this condition. The corresponding SS components[28–30] and IR's are listed in column 3. Since the form of the SS and elastic constants of various orders depend exclusively on the Laue classes of the paraelastic and ferroelastic phases,[13] we have grouped the species according to their respective changes in the Laue class using the notation of Brugger[37] (column 1). Four types of transitions are distinguished which are shown below to have specific phenomenological behaviors. In particular, four distinct OP expansions only have to be considered, whose explicit form is given at the bot-

TABLE I. Symmetry changes, spontaneous strains, Landau free energies, and associated combinations of second-, third-, and fourth-order elastic constants (in the paraelastic and ferroelastic phases) for proper PFT's. The detailed meaning of the columns is explained in the text. The IR notation (column 3) refers to the tables of Zak *et al.* (Ref. 74) while the elastic constants (columns 5 to 10) are written in the Voigt contracted notation (Ref. 121). For the $mmm \rightarrow 2/m$ species the binary axis has been chosen along z. (PP denotes pseudoproper.)

1 Laüe-class change	2 Point-group change	3 Spontaneous strain components (IR)	4 Landau free energy	5 C_{2S}^0
Type I				
$0 \rightarrow M$	$mm2 \rightarrow 2$	$e_6(\tau_3)$	a	$\frac{C_{66}^0}{2}$
	$mmm \rightarrow 2/m$	$e_6(\tau_4)$		
$T_{\mathrm{I}} \rightarrow 0$	$422 \rightarrow 2^x22$ $4mm \rightarrow m^xm2$ $\bar{4}2m \rightarrow 2^x22$ $4/mmm \rightarrow m^xmm$	$\frac{(e_1-e_2)}{2}(\tau_3)$	a	$\frac{C_{11}^0-C_{12}^0}{4}$
	$422 \rightarrow 2^{xy}22$ $4mm \rightarrow m^{xy}m2$ $4/mmm \rightarrow m^{xy}mm$	$e_6(\tau_4)$	a	$\frac{C_{66}^0}{2}$
Type II				
$H_{\mathrm{I}} \rightarrow M,0$	$6mm \rightarrow 2$ $6/mmm \rightarrow 2^z/m$	$[\frac{1}{2}(e_2-e_1),e_6](\tau_6)$	b	$\frac{C_{11}^0-C_{12}^0}{2}$
	$622^* \rightarrow 222$ $6mm \rightarrow mm2$ $6/mmm \rightarrow mmm$	$[\frac{1}{2}(e_2-e_1),0](\tau_6)$	b	$\frac{C_{11}^0-C_{12}^0}{4}$
$H_{\mathrm{II}} \rightarrow M$	$6^* \rightarrow 2$ $6/m \rightarrow 2/m$	$[\frac{1}{2}(e_2-e_1),e_6](\tau_3+\tau_4)$	c	$\frac{C_{11}^0-C_{12}^0}{2}$
$C_{\mathrm{I}} \rightarrow 0,T_{\mathrm{I}},R_{\mathrm{I}}$	$\bar{4}3m \rightarrow 222$ $432 \rightarrow 222^x$ $m3m \rightarrow mmm^x$	$[\sqrt{3}(e_2-e_1),e_1+e_2-2e_3](\tau_3)$	b	$2(C_{11}^0-C_{12}^0)$
	$\bar{4}3m \rightarrow \bar{4}2m$ $432 \rightarrow 422$ $m3m \rightarrow 4/mmm$	$[0,e_1+e_2-2e_3](\tau_3)$	b	$3(C_{11}^0-C_{12}^0)$
	$432^* \rightarrow 32$ $m3m \rightarrow \bar{3}m$	$[e_4,e_4,e_4]\begin{bmatrix}\tau_5\\ \tau_4\end{bmatrix}$	d	$\frac{3}{2}C_{44}^0$
$C_{\mathrm{II}} \rightarrow 0$	$23 \rightarrow 222$ $m3 \rightarrow mmm$	$[\sqrt{3}(e_2-e_1),e_1+e_2-2e_3](\tau_2+\tau_3)$	c	$2(C_{11}^0-C_{12}^0)$

tom of Table I.

Let us examine successively the elastic (linear and nonlinear) characteristics of the different types of PFT, assuming that the external parameter is the temperature T, so that the high-temperature phase will generally be the paraelastic phase.

A. Type-I ferroelastics

This category contains the proper PFT's having an orthorhombic-to-monoclinic or a tetragonal-to-orthorhombic symmetry change. The transitions are induced by a one-dimensional IR fulfilling the

TABLE I. (*Continued.*)

6 C_{2S}	7 C_{3S}^0	8 C_{3S}	9 C_{4S}^0	10 C_{4S}	11 Examples
C_{66}	0	C_{666}	$\frac{C_{6666}^0}{24}$	C_{6666}	LaP_5O_{14} (PP), $KH_3(SeO_3)_2$ (PP)
j	0	P	$\frac{\alpha_1}{192}$	β_1	TeO_2 (P) $DyVO_4$ (PP)
C_{66}	0	C_{666}	$\frac{C_{6666}^0}{24}$	C_{6666}	$TbVO_4$ (PP)
$j+4C_{66}$	$\frac{C_{222}^0-C_{111}^0}{3}$	q	α_2	β_2	
j	$\frac{C_{222}^0-C_{111}^0}{12}$	P	α_3	β_1	
$j+4C_{66}$	$\frac{1}{3}(C_{222}^0-C_{111}^0)$ l_1	q,r	α_4	β_2	
i	$4l_3$	s	$2\alpha_1$	β_3	
k	l_3	t	$\frac{3}{4}\alpha_1$	β_4	V_3Si (P), InTl (P), $NiCr_2O_4$ (PP)
$2C_{44}+C_{66}$	$\frac{C_{456}^0}{6}$	C_{456}	$\frac{C_{4444}^0}{8}$	C_{4444}	$RbAg_4I_5$ (PP) KNO_2
i	l_2 $6\sqrt{3}(C_{112}^0-C_{113}^0)$	s,u	$2\alpha_1$	β_3	$K_2Mn_2(SO_4)_3$

Landau-Lifshitz criteria,[23] so that they can possibly be second order. Thus the OP has only one component e_s [either $(e_1-e_2)/2$ or e_6, in the standard Voigt notation for the subscripts] and the LFE can be written, for a second-order transition, as

$$F(T,e_s)=F(T,0)+C_{2s}^0e_s^2+C_{4s}^0e_s^4+\frac{1}{2}\sum_{i,j\neq s}C_{ij}^0e_ie_j+e_s^2\sum_{i\neq s}C_{3is}^0e_i\ . \tag{3}$$

Here $F(T,0)$ accounts for the standard thermal ex-

TABLE I. (*Continued.*)

1 Laüe-class change	2 Point-group change	3 Spontaneous strain components (IR)	4 Landau free energy	5 C^0_{2S}
Type III				
$M \rightarrow N$	$2/m \rightarrow \bar{1}$	$e_6(\tau_2);e_4(\tau_2)$	a	$\frac{C^0_{66}}{2},\frac{C^0_{44}}{2}$
$T_{\text{II}} \rightarrow M$	$4 \rightarrow 2$ $4/m \rightarrow 2/m$	$(e_1-e_2)(\tau_2);e_6(\tau_2)$	a	$\frac{C^0_{11}-C^0_{12}}{4},\frac{C^0_{66}}{2}$
Type IV				
$R_{\text{II}} \rightarrow N$	$\bar{3} \rightarrow \bar{1}$	$[\frac{1}{2}(e_2-e_1),e_6](\tau_2+\tau_3)$; $[e_5,e_4](\tau_3)$	c	$\frac{1}{2}(C^0_{11}-C^0_{12})$, C^0_{44}
$R_{\text{I}} \rightarrow N,M$	$\bar{3}m \rightarrow \bar{1}$	$[\frac{1}{2}(e_2-e_1),e_6](\tau_3)$; $[e_5,e_4](\tau_3)$	b	$\frac{1}{2}(C^0_{11}-C^0_{12})$, C^0_{44}
	$\bar{3}m \rightarrow 2/m$	$[\frac{1}{2}(e_2-e_1),0](\tau_3)$; $[e_4,0](\tau_3)$		$\frac{1}{4}(C^0_{11}-C^0_{12})$, $\frac{C^0_{44}}{2}$

$a = C^0_{2S}e_S^2 + C^0_{4S}e_S^4$

$b = C^0_{2S}(e_{S1}^2 + e_{S2}^2) + C^0_{3S}(e_{S2}^3 - 3e_{S2}e_{S1}^2) + C^0_{4S}(e_{S1}^2 + e_{S2}^2)^2$

$c = b + C^{0\prime}_{3S}(e_{S1}^3 - 3e_{S1}e_{S2}^2)$

$d = C^0_{2S}(e_{S1}^2 + e_{S2}^2 + e_{S3}^2) + C^0_{3S}e_{S1}e_{S2}e_{S3} + C^0_{4S}(e_{S1}^4 + e_{S2}^4 + e_{S3}^4)$

$i = C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}$

$j = C_{11} + C_{22} - 2C_{12}$

$k = C_{11} + C_{12} + 2C_{33} - 4C_{13}$

$l_1 = [2(C^0_{222} - C^0_{111}) - 9C^0_{116}]/24$

$l_2 = -4C^0_{111} + 6(C^0_{112} + C^0_{113}) - 8C^0_{123}$

$l_3 = 3C^0_{112} - 2C^0_{123} - C^0_{111}$

$P = C_{111} - C_{222} - 3(C_{112} - C_{122})$

$q = 12(C_{166} - C_{266}) - P$

$r = 6(C_{126} - C_{116} - C_{226}) - P$

$s = \frac{3}{2}(C_{112} + C_{122} + C_{113} + C_{223} + C_{133} + C_{233}) - 6C_{123} - (C_{111} + C_{222} + C_{333})$

$t = C_{111} - 4C_{333} - 9C_{112} + 6(C_{133} - C_{113} - C_{123})$

$u = 2\sqrt{3}(C_{112} - C_{113} - C_{122} + C_{223} + C_{133} - C_{233})$

$v = C_{555} - 3C_{445}$

$w = C_{444} - 3C_{455}$

pansion of the lattice parameters in the paraelastic phase; C^0_{2s} and C^0_{4s} are, respectively, certain combinations of SOEC and FOEC of the paraelastic phase; the subscripts indicate that they correspond to a certain SS. For instance, if the SS is $e_s=(e_1-e_2)/2$, then $C^0_{2s}=(C^0_{11}-C^0_{12})/2$, whereas for $e_s=e_6$, $C^0_{2s}=C^0_{66}/2$. The C^0_{3is} are combinations of TOEC's expressing the coupling of e_s with components $e_i \neq e_s$ of the strain tensor. Since we are dealing with possibly continuous transitions, only terms up to the fourth order in e_s and to the second order in e_i (and their combinations, which are implicitly of fourth order in e_s) have been kept. The case of first-order transitions involving higher-degree terms (such as sixth order in e_s and third and fourth order in e_i) is discussed briefly below. As usual in the Landau theory[23] all the coefficients are assumed in the simplest model to be constants, except C^0_{2s} which varies linearly with T. This gives

$$C^0_{2s}=a(T-T_c) ,$$

TABLE I. (*Continued.*)

6	7	8	9	10	11
C_{2S}	C_{3S}^0	C_{3S}	C_{4S}^0	C_{4S}	Examples
C_{66}, C_{44}	0;0	$C_{666}; C_{444}$	$\frac{C_{6666}^0}{24}; \frac{C_{4444}^0}{24}$	$C_{6666}; C_{4444}$	
j, C_{66}	0;0	$P; C_{666}$	$\alpha_1; \frac{C_{6666}^0}{24}$	$\beta_1; C_{6666}$	$LaNbO_4$ (P), $BiVO_4$ (PP)
$C_{11}-C_{12}$, C_{44}	$\left\{\begin{matrix} \frac{1}{3}(C_{222}^0-C_{111}^0); & \frac{2}{3}C_{444}^0 \\ l_1 & \frac{2}{3}C_{555}^0 \end{matrix}\right.$	$\left\{\begin{matrix} q \\ r \end{matrix}\right. ; \begin{matrix} v \\ w \end{matrix}$	$\alpha_4; \frac{C_{4444}^0}{4}$	$\beta_2; C_{4444}$	
$C_{11}-C_{12}$, C_{44}	$\frac{1}{3}(C_{222}^0-C_{111}^0)$; $\frac{2C_{444}^0}{3}$	$q; w$	$\alpha_2; \frac{C_{4444}^0}{4}$	$\beta_2; C_{4444}$	NaN_3 (PP)
j, C_{44}	$\frac{1}{12}(C_{222}^0-C_{111}^0)$; $\frac{2C_{444}^0}{3}$	q, w	$\alpha_3; \frac{1}{24}C_{4444}^0$	$\beta_1; C_{4444}$	*S*-triazine

$\alpha_1 = C_{1111}^0 - 4C_{1112}^0 + 3C_{1122}^0$

$\alpha_2 = \frac{1}{216}(-71C_{1111}^0 - 376C_{1112}^0 + 270C_{1122}^0 + 56C_{1166}^0)$

$\alpha_3 = \frac{1}{216}(-23C_{1111}^0 - 64C_{1112}^0 + 54C_{1122}^0 + 8C_{1166}^0)$

$\alpha_4 = \alpha_2 + \frac{1}{216}(5C_{1111}^0 + C_{1112}^0 + C_{1166}^0)$

$\beta_1 = C_{1111} + C_{2222} - 4C_{1112} + 6C_{1122} - 4C_{1222}$

$\beta_2 = \beta_1 + 4(C_{1166} + C_{2266} + 2C_{1266} + 2C_{6666})$

$\beta_3 = C_{1111} + C_{2222} + C_{3333} + 3(C_{1122}\ C_{1133} + C_{2233})$
$\quad - 2(C_{1112} + C_{1113} + C_{1222} + C_{2223} + C_{1333} + C_{2333})$

$\beta_4 = C_{1111} + 3C_{1122} + 4C_{1112} - 32C_{1333}$
$\quad + 8(C_{3333} - C_{1113}) + 3(C_{1133} - C_{1123} + C_{1233})$

where T_c is the critical temperature and $a > 0$. Columns 5, 7, and 9 of Table I give, respectively, the explicit combinations of SOEC's, TOEC's, and FOEC's of the paraelastic phase for the 32 species considered; the data of column 5 are consistent with the partial results published by Boccara,[28] Aubry and Pick,[30] and Cowley.[38] Columns 6, 8, and 10 of Table I provide the corresponding combinations in the ferroelastic phase. The determination of expressions for C_{2s}, C_{3s}, and C_{4s} makes use of the form of the SS tensor and the relationships between the elastic constants in a given symmetry class (Ref. 37 for SOEC's and TOEC's, and Refs. 39 and 40 for FOEC's). Imposing the requirement that the equilibrium values of the SS components are zero in the paraelastic phase yields the factored expressions for C_{2s}, C_{3s}, and C_{4s}. The constants C_{2s}^0, C_{3s}^0, and C_{4s}^0 are then deduced from C_{2s}, C_{3s}, and C_{4s} by taking into account the additional symmetries of the paraelastic phase and the corresponding numerical coefficients.

The stresses conjugate to e_s and e_i are given by

$$\sigma_s = \partial F/\partial e_s = 2C_{2s}^0 e_s + 4C_{4s}^0 e_s^3 + 2e_s \sum_{i\neq s} C_{3is}^0 e_i \ ,$$

$$\sigma_i = \partial F/\partial e_i = \sum_{j\neq s} C_{ij}^0 e_j + C_{3is}^0 e_s^2 \ ,$$

so that the equilibrium values of e_s and e_i at zero stresses are

$$e_i = e_s = 0$$

in the HS phase and

$$e_i = -\sum_j S_{ij}^0 C_{3js}^0 e_s^2$$

and

$$e_s = \pm \left[-\frac{C_{2s}}{\beta'} \right]^{1/2} = \pm \left[\frac{a(T_c - T)}{\beta'} \right]^{1/2}$$

in the LS phase, where the S_{ij}^0 are elastic compliances corresponding to the C_{ij}^0. Note that

$$\beta' = 2C_{4s}^0 - \sum_{i\neq s} \sum_j C_{3is}^0 C_{3js}^0 S_{ij}^0$$

is the renormalized fourth-degree coefficient ($\beta' > 0$ and $C_{ii}^0 > 0$ for a continuous transition). The temperature dependence of $|e_s|$ and $|e_i|$ is given in Figs. 1(a) and 1(b), the slopes of e_s^2 and e_i being, respectively, a/β' and $-(a/\beta')\sum_{i\neq s} C_{3is}^0 S_{ij}^0$. The second derivatives of (3) with respect to the strains give the values of the SOEC's:

$$C_{2s} = \frac{\partial^2 F}{\partial e_s^2} = \begin{cases} 2C_{2s}^0 \\ -8C_{2s}^0 \dfrac{C_{4s}^0}{\beta'} \end{cases} \tag{4}$$

in the HS phase and in the LS phase, respectively,

$$C_{ij} = \frac{\partial^2 F}{\partial e_i \partial e_j} = C_{ij}^0 \quad (i,j \neq s) \tag{5}$$

in both phases, and

$$C_{is} = \frac{\partial^2 F}{\partial e_s \partial e_i} = \begin{cases} 0 \quad (i \neq s) \\ 2C_{3is}^0 e_s \quad (i \neq s) \end{cases} \tag{6}$$

in the HS phase and in the LS phase, respectively. It must be pointed out that when C_{2s}, C_{ij} $(i,j\neq s)$ and C_{is} $(i\neq s)$ represent combinations of SOEC's, one should expect the individual SOEC contributing to these combinations to have a temperature dependence which does not appear explicitly in (4), (5), and (6). For instance, in the 422→2^x22 species the constancy of $C_{ij}^0 = \frac{1}{2}(C_{11} + C_{12})$ in both phases results from an exact compensation of two opposing linear temperature variations for C_{11} and C_{12}. The temperature variations of C_{2s} and $|C_{is}|$ are shown on Figs. 1(c) and 1(d). We can see that the slopes of C_{2s} and C_{is}^2 give the values of C_{4s}^0 and C_{3is}^0, respectively.

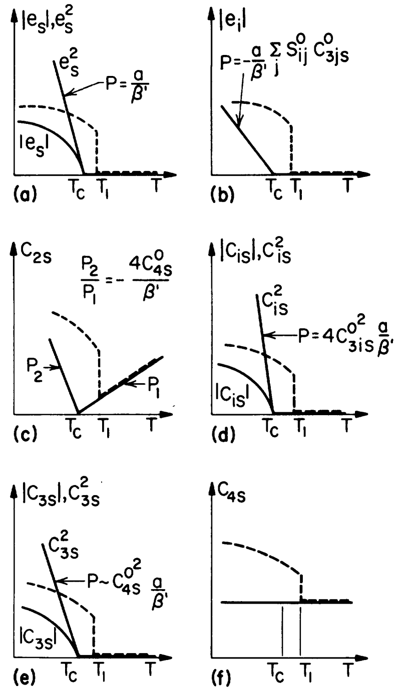

FIG. 1. Temperature dependence of spontaneous strains, SOEC's, TOEC's, and FOEC's for a type-I proper PFT. (a) SS modulus. (b) Nonspontaneous components of the strain-tensor. (c) SOEC combination associated with the SS. (d) Modulus of SOEC's that couple spontaneous and nonspontaneous components of the strain tensor. (e) Modulus of the combination of TOEC's associated to the SS. (f) FOEC combination associated with the SS. Solid and dashed lines correspond, respectively, to second- and first-order transitions (C_s^2, C_{is}^2, and C_{3s}^2 are shown only for the second-order case). Note that the slopes P, P_1, and P_2 in the ferroelastic phase depend exclusively on the elastic constant values of the paraelastic phase, $\beta' = 2C_{4s}^0 - \sum_{i\neq s} \sum_j C_{3is}^0 C_{3js}^0 S_{ij}$.

The third derivatives of (3) yield expressions for the TOEC. In this case the C_{3is} combinations are temperature independent, while

$$C_{3s} = \frac{\partial^3 F}{\partial e_s^3} = 24C_{4s}^0 e_s = \begin{cases} 0 \\ \pm 24C_{4s}^0 \left[\dfrac{a(T_c - T)}{\beta'} \right]^{1/2} \end{cases} \tag{7}$$

in the HS phase and in the LS phase, respectively. The vanishing of the C_{3s} combination of TOEC's at the Curie point is a distinctive property of the type-I PFT under consideration. As is illustrated below in the example of paratellurite, the individual TOEC involved in this combination will also be generally temperature dependent, their respective contributions summing positively with one another. Figure 1(e) shows the variation of $|C_{3s}|$ and C_{3s}^2. Finally,

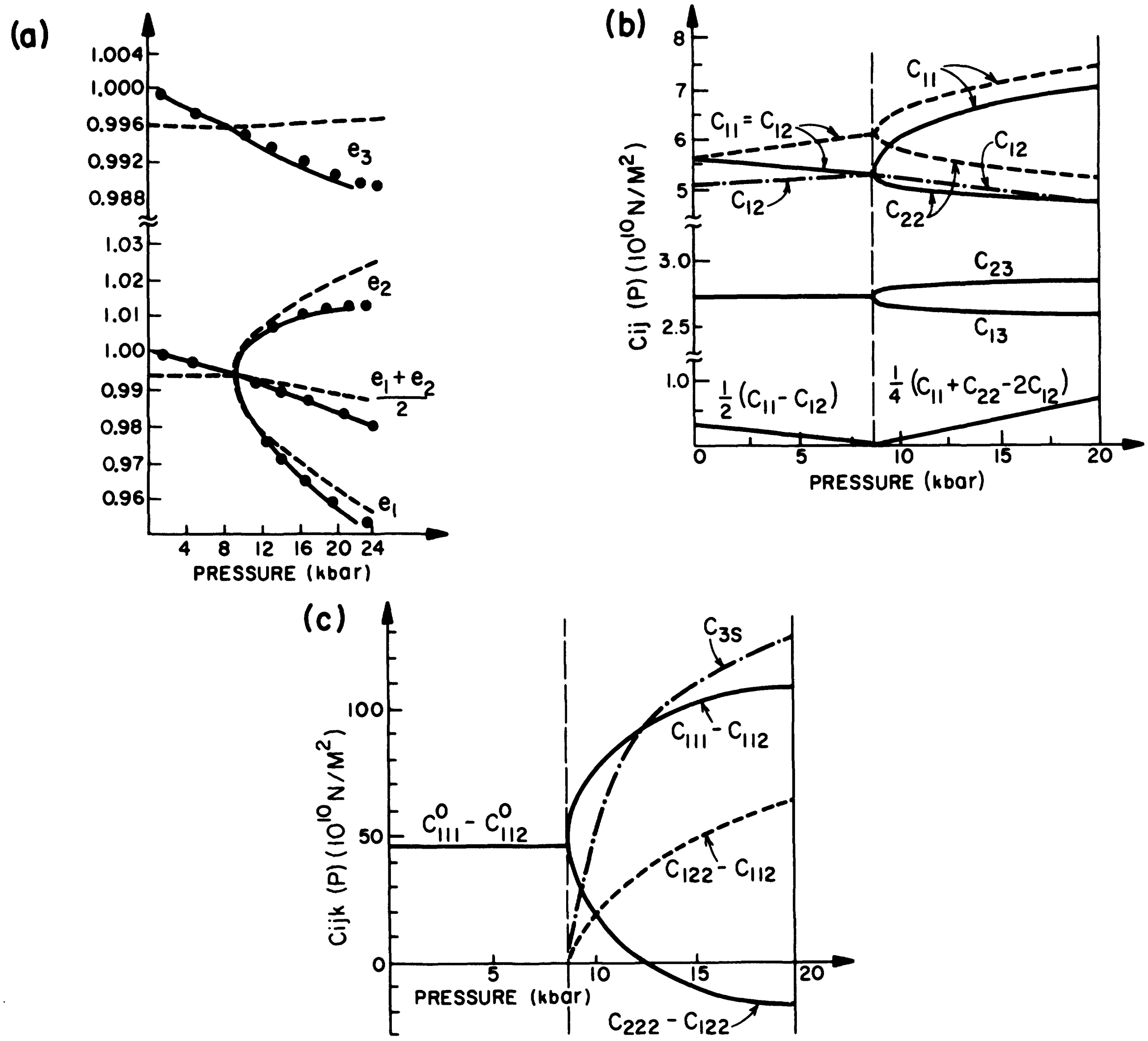

FIG. 2. Pressure dependence of the strain components, SOEC's, and TOEC's for TeO_2. (a) Components e_1, e_2, and e_3 of the strain tensor. Dashed lines: Calculated values following Table III. Solid lines: Experimental curves from Ref. 43. Dots: calculated values taking into account compressibilities of the LP phase given in Ref. 42. (b) SOEC's following Table II (solid lines). For C_{11}, C_{12}, and C_{22}, the dashed lines represent corrected values taking into account a pressure dependence of $(C^0_{11}+C^0_{12})$ (see text). (c) Linear combination of TOEC's following Eq. (12).

the fourth derivative of F with respect to strain components provide the C_{4s} combination of FOEC's which is constant and equal to $24C^0_{4s}$ [Fig. 1(f)].

The preceding results are valid for a second-order phase transition assuming that only the lowest-degree couplings between e_s and the other components e_i of the strain tensor influence the transition. Higher-degree couplings can be introduced to explain the anomalous variation of some of the e_i. For a first-order transition one has to add to Eq. (3) sixth-degree terms (at least), and so the LFE becomes

$$F'=F+C^0_{6s}e_s^6+\sum_{i,j,k\neq s}c^0_{ijk}e_ie_je_k+e_s^2\sum_{i,j\neq s}C^0_{4ijs}e_ie_j \;. \tag{8}$$

Here C^0_{6s} is a positive combination of sixth-order elastic constants[40] (SIOEC's) of the HS phase, while C^0_{ijk} are TOEC's and C^0_{4ijs} are FOEC's expressing the coupling of e_s^2 to products e_ie_j of the strain tensor. Figures 1(a)–1(f) give in dashed lines the qualitative behavior of the strain component and elastic constants of various orders, for a first-order transition. It should be noted that the upward shift of the transition temperature and the discontinuities of the physical quantities described in Fig. 2 provide information about the TOEC's, FOEC's, and SIOEC's. In addition to these discontinuous changes, first-order transitions can be distinguished by the nonvanishing (though small) value of C_{2s} at T_c and by the increasing of C_{4s} with temperature in the LS phase.

Introducing higher-order elastic constants in the LFE expresses the fact that, due to the larger magnitude of the SS components, elastic nonlinearity in the LS phase should be greater for ferroelastics undergoing a first-order phase transition than for a second-order transition. In order to verify this assumption and, more generally, to estimate the elastic nonlinearity "stored" at the transition, we now define the "degree of nonlinearity":

$$L_1=\frac{\frac{1}{6}C_{3s}e_s^3+\frac{1}{24}C_{4s}e_s^4+\frac{1}{120}C_{5s}e_s^5+\frac{1}{720}C_{6s}e_s^6+\cdots}{\frac{1}{2}C_{2s}e_s^2} \tag{9}$$

which expresses the deviation from linearity obtained in a virtual stress-strain relationship $\sigma_s(e_s)$. In other words, the same value should be obtained for L_1 by applying to the undeformed state (the paraelastic state) a real stress σ_s inducing a (nonspontaneous) strain e_s. For a second-order phase transition ($C_{5s}=C_{6s}=0$), we find using (4) and (7) $L_1=\frac{5}{4}$, while for a first-order one we find

$$L_1=\frac{5C_{4s}^0+42C_{6s}^0e_s^2}{4C_{4s}^0+15C_{6s}^0e_s^2}>\frac{5}{4}\ .$$

The preceding ratios reveal that in the ferroelastic phase, the *nonlinear contribution to the elastic energy is always larger than the linear contribution.* This may appear surprising in view of the relatively good fit to experimental results obtained with models which apparently neglect the nonlinear elastic energy. However, one must bear in mind that the measured values of SOEC's are *renormalized values which implicitly contain nonlinear elastic contributions.* In other words, a phenomenological model taking explicitly into account elastic constants of an order higher than two *decouples* the linear and nonlinear elastic energies stored at the transition. On the other hand, the magnitude of the virtual stress σ_s is very large because spontaneous strains arising at a PFT are several orders of magnitude larger than those strains usually induced in measurements of elastic constants. Let us also stress that the degree of nonlinearity (9) does not express the intrinsic nonlinear elasticity of the material undergoing a phase transition, but only the part which is related to the onset of the spontaneous strain in the ferroelastic phase. In particular, from the very definition of e_s it follows that $L_1=0$ in the paraelastic phase. Finally, we must note that the universal constant value found for L_1 in the case of a second-order transition is illustrative of the *equilibrium* values of physical quantities below the transition, and does not apply in the critical regime which dominates in the vicinity of T_c.

In column 11 of Table I most of the presently known purely ferroelastic materials have been classified according to their point-group changes. Among type-I PFT paratellurite TeO_2 appears as the only confirmed example of a proper ferroelastic possessing a strain-induced phase transition. However, the relative abundance of elastic (linear and nonlinear) data for this material allows one to check in a rather accurate manner the theoretical model based on a LFE of the type given in Eq. (3).

Paratellurite undergoes a pressure-induced second-order phase transition at ($P_c=8.85$ kbar, $T=20\,^\circ\mathrm{C}$) driven by the soft acoustic shear mode propagating along a $\langle 110\rangle$ direction and polarized along a $\langle 1\bar{1}0\rangle$ direction.[41] No soft (Raman-active) zone-center optic modes have been observed in the low-pressure (HS) phase, and no evidence was found for any strong coupling of the soft mode to any other acoustic mode, although small anomalies in some of the elastic constants unrelated to the acoustic mode were observed.[42] According to the reported point-group change $422\rightarrow 2^x22$, (3) takes the explicit form

$$\begin{aligned}F=&\tfrac{1}{4}(C_{11}^0-C_{12}^0)(e_1-e_2)^2+\tfrac{1}{192}(C_{1111}^0-4C_{1112}^0+3C_{1122}^0)(e_1-e_2)^4+\tfrac{1}{4}(C_{11}^0+C_{12}^0)(e_1+e_2)^2\\&+C_{13}^0(e_1+e_2)e_3+\tfrac{1}{2}C_{33}^0e_3^2+C_{44}^0e_4^2+C_{66}^0e_6^2+\tfrac{1}{8}(C_{111}^0-C_{112}^0)(e_1-e_2)^2(e_1+e_2)\\&+\tfrac{1}{4}(C_{113}^0-C_{123}^0)(e_1-e_2)^2e_3\ .\end{aligned} \tag{10}$$

Worlton and Beyerlein[43] and McWhan *et al.*[44] have used (10), neglecting the contributions of e_4 and e_6, to account for the pressure dependence of the lattice parameters a and b. On the other hand, Fritz and Peercy[45] have taken into consideration terms of third and fourth degree in (e_1+e_2) with pressure-dependent elastic constants, to explain the slopes of the inverse susceptibility $C_{11}-C_{12}$ and the small discontinuities in the pressure derivative of $a+b$. However, these authors were able to undertake only a qualitative comparison, as the numerical values were known[46,47] only for the SOEC's at that time. Recently Antonenko *et al.*[15] measured the complete set of TOEC's at atmospheric pressure (AP) so that we can undertake a numerical model giving the relevant quantities involved at the transition and, in turn, a close check of the validity of (10).

The measured values of the SOEC's and TOEC's

TABLE II. Experimental and calculated values of SOEC's, TOEC's, and FOEC's for TeO_2 (in units of 10^{10} N/m^2).

Measured values ($T=20C,P=1$ bar)			Calculated values ($T=20C,P=20$ kbar)		
SOEC (Ref. 47)	TOEC (Ref. 49)		SOEC	TOEC	FOEC
$C^0_{11}=5.6$	$C^0_{111}=-16$	$C^0_{155}=3.6$	$C_{11}=7.17$ (7.65)	$C_{111}-C_{112}=106.12$	$C^0_{1111}-4C^0_{11112}+3C^0_{1122}=5330$
$C^0_{12}=5.16$	$C^0_{112}=-60$	$C^0_{166}=-64$	$C_{22}=4.81$ (5.29)	$C_{222}-C_{122}=-18.12$	
$C^0_{13}=2.72$	$C^0_{113}=-14$	$C^0_{333}=-211$	$C_{12}=4.77$ (5.25)	$C_{111}-C_{222}=62.12$	
$C^0_{44}=2.70$	$C^0_{123}=-11$	$C^0_{344}=-5.4$	$C_{13}=2.64$	$C_{122}-C_{112}=62.12$	
$C^0_{33}=10.51$	$C^0_{133}=18$	$C^0_{366}=-26$	$C_{23}=2.80$	$C_{3S}=\frac{1}{2}[C_{111}-C_{222}-3(C_{112}-C_{122})]$ $=124.24$	
$C^0_{66}=6.65$	$C^0_{144}=-4.1$	$C^0_{456}=-25$	$\frac{C_{2S}}{4}=\frac{C_{11}+C_{22}-2C_{12}}{4}$ $=0.61$		
$C^0_{11}-C^0_{12}=0.44$	$C^0_{111}-C^0_{112}=44$				
$C^0_{11}+C^0_{12}=10.76$	$C^0_{113}-C^0_{123}=-3$				

at AP and room temperature (RT) are collected in Table II. Expressions for the strain components e_1+e_2, e_3, and e_1-e_2 in the high-pressure (HS) ferroelastic phase are given in Table III. In this table we can see that a complete numerical model requires knowledge of the FOEC combination $C^0_{1111}-4C^0_{1112}+3C^0_{1122}$, but since no measurements have yet been performed for the FOEC's, we must evaluate this parameter from other experimental data. Let us take the slope of the elastic constant $(C_{11}-C_{12})/2$ in the paraelastic low-pressure (LP) phase determined by Peercy *et al.*,[42] which gives the value $a=2.44$, and take the square of the SS as a function of pressure plotted by Worlton and Beyerlein[43] which indicates the ratio $a/\beta'=2.50\times10^{-12}$ m^2/N. From these values we can deduce that $\beta'=0.97\times10^{12}$ N/m^2 and $\beta=1.11\times10^{12}$ N/m^2. We can then express the strain components as a function of pressure:

$$
\begin{aligned}
e_1&=C(P-P_c)-D(P-P_c)^{1/2}\,,\\
e_2&=-C(P-P_c)+D(P-P_c)^{1/2}\,, \qquad (11)\\
e_3&=E(P-P_c)\,,
\end{aligned}
$$

with $P-P_c$ in kbar, $C=1.63\times10^{-4}$, $D=0.77\times10^{-2}$, and $E=0.96\times10^{-4}$. Equations (11) are shown in Fig. 2(a) and the same figure gives (solid lines) the experimental curves (Ref. 43). The discrepancy is due to the fact that we have not taken into account the compressibilities of the LP phase corresponding to a slow decrease of 8.1×10^{-4} $kbar^{-1}$ along the a axis and of 6.1×10^{-4} $kbar^{-1}$ along the c axis.[42,43,48] Extrapolating the corrections to the HP phase we can obtain [dotted lines on Fig. 2(a)] a very close fit between the two curves.

The second derivatives of F with respect to e_1, e_2, and e_3 give expressions for the SOEC's in the HP and LP phases (Table III). The curves for C_{11}, C_{12}, C_{22}, C_{13}, and C_{23} are given in Fig. 2(b). For C_{13} and C_{23}, no experimental data are available for checking the variation given in Table III. On the other hand, we find that

$$
\frac{1}{2}\,\frac{(C_{11}+C_{22}-2C_{12})(P>P_c)}{(C_{11}-C_{12})(P<P_c)}=2.76\,,
$$

which is very close to the ratio found by Peercy *et al.*[42] However, our results show that C_{11} *decreases* with increasing pressure from 5.6×10^{10} N/m^2 at AP, to 5.38 N/m^2 at $P=P_c$, while the experimental curve reveals an *increase* of about 0.4×10^{10} N/m^2 in the same range of pressures. This discrepancy can be corrected if we assume that $(C^0_{11}+C^0_{12})/2$ depends on pressure according to the law $(C^0_{11}+C^0_{12})/2=\alpha_0P+P_0$ with $P_0=5.38\times10^{10}$ N/m^2 and $\alpha_0=2.4$. In Fig. 2(b) the corrected curves

TABLE III. Pressure dependence of strain components and pressure dependence of SOEC's.

Pressure dependence of strain components	Pressure dependence of SOEC's
$e_1-e_2=\pm\left[\frac{a}{\beta'}(P-P_c)\right]^{1/2}$ $e_1+e_2=A\frac{a}{\beta'}(P-P_c)$ $e_3=B\frac{a}{\beta'}(P-P_c)$ $A=\frac{1}{4}\left[\frac{2C^0_{13}(C^0_{113}-C^0_{123})-C^0_{33}(C^0_{111}-C^0_{112})}{C^0_{33}(C^0_{11}+C^0_{12})-2C^0_{13}}\right]=-1.21$ $B=-\frac{A}{4}\left[\frac{C^0_{113}-C^0_{123}-C^0_{13}}{C^0_{33}}\right]=0.385$ $\beta=\frac{C^0_{1111}-4C^0_{1112}+3C^0_{1122}}{48}$ $\beta'=\beta+\frac{C^0_{111}-C^0_{112}}{4}A+\frac{C^0_{113}-C^0_{123}}{2}B$	Paraelastic phase (LP) $C_{11}=C_{22}=\frac{C^0_{11}+C^0_{12}}{2}+a(P_c-P)$ $C_{12}=\frac{C^0_{11}+C^0_{12}}{2}-a(P_c-P)$ $C_{13}=C_{23}=C^0_{13}$ Ferroelastic phase (HP) $C_{11}=\frac{C^0_{11}+C^0_{12}}{2}+F(P-P_c)+G(P-P_c)^{1/2}$ $C_{22}=\frac{C^0_{11}+C^0_{12}}{2}+F(P-P_c)-G(P-P_c)^{1/2}$ $C_{12}=\frac{C^0_{11}+C^0_{12}}{2}-F(P-P_c)$ $\frac{C_{11}+C_{22}-2C_{12}}{4}=F(P-P_c)$ $C_{33}=C^0_{33};\ C_{44}=C^0_{44},\ C_{66}=C^0_{66}$ $F=2a\frac{\beta}{\beta'}\times 10^8=5.58\times 10^8$ $G=\frac{C^0_{111}-C^0_{112}}{2}\left[\frac{a}{\beta'}\right]^{1/2}\times 10^4=3.48\times 10^9$

are given in dashed lines for C_{11} and C_{12}. In Table II the uncorrected and corrected values are given at $P=20$ kbar. Furthermore, the simple LFE (10) does not account for the linear increase of C_{33} reported in the two phases and for the small anomalies indicated at the transition for C_{44} and C_{66}.[42] These features can be obtained respectively by providing a linear increasing of C^0_{33} with pressure (of 1.27% kbar^{-1} following Ref. 42) and by adding to (10) the higher-degree coupling terms:

$$(C^0_{1144}+C^0_{1155}-2C^0_{1244})(e_1-e_2)^2e_4^2$$

and

$$(C^0_{1166}-C^0_{1266})(e_1-e_2)^2e_6^2\ .$$

These refinements of (10) are consistent with the phenomenological model of Fritz and Peercy[45] though they consider unnecessarily third- and fourth-degree terms in (e_1+e_2) and a coupling between $(e_1+e_2)^2$ and $(e_1-e_2)^2$. Conversely the model of Uwe and Tokumoto,[49] which takes the SS as a secondary OP (the primary OP being an internal displacement of oxygen atoms) appears unjustified in view of its little predictive value.

Let us now determine expressions for the nonlinear elastic constants as a function of pressure. Seven TOEC's can be derived from (10), of which four are pressure dependent in the HP phase, namely C_{111}, C_{222}, C_{112}, and C_{122}. We can write that

$$\begin{aligned} C_{111}-C_{112}&=C^0_{111}-C^0_{112}+H(P-P_c)^{1/2}\ ,\\ C_{222}-C_{122}&=C^0_{111}-C^0_{112}-H(P-P_c)^{1/2}\ ,\\ C_{111}-C_{222}&=C_{122}-C_{112}\\ &=H(P-P_c)^{1/2}\ ,\\ C_{3s}&=\frac{C_{111}-C_{222}-3(C_{112}-C_{122})}{2}\\ &=2H(P-P_c)^{1/2}\ , \end{aligned} \tag{12}$$

with $H=12\beta(a_0/\beta')^{1/2}\times 10^4=18.38\times 10^{10}$ [$(P-P_c)$ in kbar].

Curves corresponding to (12) are shown in Fig.

2(c) and the values of the combinations of TOEC's at 20 kbar are given in Table II. As pointed out in the general case, we verify the vanishing of C_{3s} at $P=P_c$ (due here to the simultaneous vanishing of $C_{111}-C_{222}$ and $C_{122}-C_{112}$). We can see that the nonlinear elasticity cannot be evaluated from the mere values of the individual constants but only from particular combinations of TOEC's, especially those combinations C_{3s} given in Table I. In TeO_2 it appears that, while each TOEC entering in C_{3s} is small and negative (at AP), their resulting contributions produce a large positive value for C_{3s}. This expresses the fact that the deviation from Hooke's law increases *more rapidly* as the stress σ_s conjugate to e_s increases, whereas a negative value for C_{3s} is interpreted as a *slower increase* in elastic nonlinearity with increasing stress. We can note also that the ratio

$$L_2=C_{3s}/C_{2s} \qquad (13)$$

provides, complementarily to L_1, a suitable estimate of the magnitude of the elastic nonlinearity induced by the onset of the SS in the ferroelastic phase. In TeO_2 we have $L_2 \simeq 50$ at $P=20$ kbar, which is about ten times larger than the average values for the corresponding individual TOEC and SOEC.

The preceding considerations can be extended to the FOEC's. Using (10) we find that the FOEC's are constant and equal to their value at AP. In particular,

$$C_{4s}=\frac{C_{1111}+C_{2222}-4(C_{1112}+C_{1222})+6C_{1122}}{2}=48\beta$$

$$=C^0_{1111}-4C^0_{1112}+3C^0_{1122}=5.33\times 10^{13}$$

in units of N/m^2. Using the numerical values of C_{2s}, C_{3s}, and C_{4s} at $P=20$ kbar, and taking[43] $e_s(P=20 \text{ kbar})=5.2\times 10^{-2}$ we can evaluate the ratio (9). We obtain

$$L_1 \simeq 1.36 ,$$

whereas the theoretical expressions for C_{2s}, C_{3s}, and C_{4s} give the standard value of $\frac{5}{4}$. This difference must be attributed to the fact that the numerical values used to calculate L_1 are a mixture of corrected numbers (for C_{2s}) and uncorrected ones (for C_{3s} and C_{4s}).

Thus the example of TeO_2 illustrates fairly accurately the general considerations developed at the beginning of this section. Conversely, the qualitative and quantitative fitting of the model based on (10), though it requires adjustment to account for the complete set of experimental data, confirms both the choice of the SS as the primary OP, and the necessity of including elastic nonlinearity (i.e., higher-order elastic constants) in the interpretation of the phase transition in TeO_2.

B. Type-II ferroelastics

To this category belong ferroelastics undergoing a transition from a hexagonal or cubic paraelastic phase, induced by an IR which violates the Landau condition.[23] Accordingly their LFE possesses cubic terms and the transitions are necessarily discontinuous.[50,51] The fact that a majority of strain-induced transitions should be first order was first noticed by Anderson and Blount,[52] and more recently the symmetry aspects of the ferroelastic transitions violating the Landau condition were systematically worked out.[25,50] In column 4 of Table I, we see that three LFE's describe the features of type-II PFT's. Two of them, namely *b* and *c*, correspond to a two-component OP and the one labeled *d* is formed by a three-component OP. For *b* and *d*, the existence of only one cubic invariant leaves the possibility of a continuous transition at an isolated point of the phase diagram. Two cubic invariants can be constructed for the *c*-type LFE and a continuous transition is thus strictly forbidden.[53] It should be noted that for the three species 622→222, 6→2, and 432→32 (designated by an asterisk in column 2 of Table I) the corresponding IR's violate simultaneously the Lifshitz condition.[23] This means that for a weakly discontinuous transition an incommensurate phase instead of the ferroelastic phase may appear at low temperature.

If we want to determine the qualitative behavior of type-II ferroelastics the multidimensional character of the OP's can be ignored and we can use the following LFE:

$$F(T,e_s)=F(T,0)+C^0_{2s}e_s^2+C^0_{3s}e_s^3+C^0_{4s}e_s^4 + e_s^2\sum_{i\neq s} C^0_{3is}e_i+\tfrac{1}{2}\sum_{i,j\neq s} C^0_{ij}e_ie_j \; , \qquad (14)$$

where the notation is identical then to that of (3). Actually (14) differs from (3) only by the addition of the cubic term $C^0_{3s}e_s^3$, C^0_{3s} being a combination of TOEC's of the paraelastic phase given in column 7 of Table I. As the discussion of (14) is very similar to that of (3), we can restrict ourselves to a summary of the results:

(1) The transition takes place at the critical temperature

$$T_c=T_0+\frac{(C^0_{3s})^2}{2\beta' a} \; ,$$

with

$$\beta'=2C^0_{4s}-\sum_{i\neq s}\sum_{j} C^0_{3is}C^0_{3js}S^0_{ij}$$

corresponding to equal stability of the paraelastic and ferroelastic phases, defined by $F-F_0 = \partial F/\partial e_s = 0$. The Curie temperature is located between $T_{\mathrm{I}} = T_0 + \frac{9}{16}(C^0_{3s})^2/\beta' a$ where the ferroelastic phase becomes metastable, and T_0 where the paraelastic phase becomes unstable. However, T_c is only a theoretical value and for a real first-order transition, where thermal hysteresis is observed, the phase change effectively occurs between T_0 and T_c in the temperature range where the paraelastic phase is metastable.

(2) In the ferroelastic phase the equilibrium value of the SS is given by

$$e_s = -\frac{3C^0_{3s} \pm [9(C^0_{3s})^2 - 16\beta' C^0_{2s}]^{1/2}}{4\beta'}$$

with a discontinuous jump at T_c equal to $\Delta e_s = -C^0_{3s}/\beta'$. We see that depending on the sign of the TOEC combinations we have a positive or negative value for e_s and a downward or upward jump at T_c. For the cubic to tetragonal type-II PFT, where the LFE is of the b type, it has been pointed out by some authors[51,54] that it is the sign of C^0_{3s} which determines whether the ratio of the cubic c and tetragonal a parameters is greater or smaller than unity [if $C^0_{3s} < 0$, $e_s \simeq (c/a - 1) > 0$ so that $c > a$].

(3) The curves of the SOEC as a function of temperature derived from (14) have the same shape as first-order transitions in type-I PFT [dashed lines in Figs. 1(c) and 1(d)]. In particular, the C_{2s} combination does not vanish at T_c and undergoes a jump upward of $\Delta C_{2s} = 7(C^0_{3s})^2/\beta'$. For the C_{is} components $(i \neq s)$ the discontinuous jump is equal to $\Delta C_{is} = -2(C^0_{3is}C^0_{3s}/\beta')$ and its sign depends on the respective signs of C^0_{3is} and C^0_{3s}. Unlike the type-I PFT, the C_{3s} combination of TOEC's does not vanish at T_c. On the other hand, the FOEC combination C_{4s} *remains constant* as for *second-order* transitions of the type I.

(4) The variation of the stress σ_s conjugate to e_s is given by

$$\sigma_s = 2C^0_{2s}e_s + 3C^0_{3s}e_s^2 + 4C^0_{4s}e_s^3 ,$$

which contains a quadratic contribution, so that deviations from Hooke's law are more completely accounted for than in the type-I PFT for which only odd degrees of the SS components appear in the stress-strain relation. Using (9), we can calculate the degree of elastic nonlinearity in the ferroelastic phase. We find here

$$L_1 = \frac{C^0_{3s}e_s + \frac{5}{2}\beta e_s^2}{C^0_{2s} + 3C^0_{3s}e_s + 3\beta e_s^2} .$$

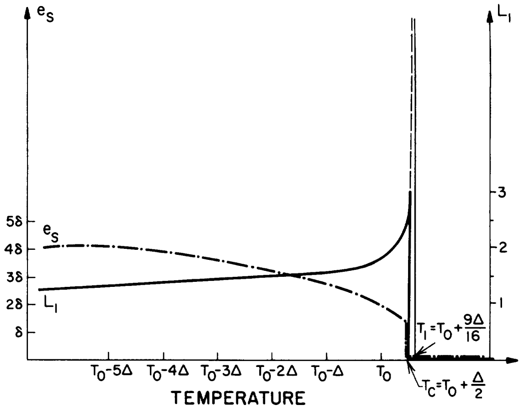

FIG. 3. Variation as a function of temperature of the spontaneous strain. e_s and the degree of nonlinearity L_1 for type-II ferroelastics described by the simplified LFE (14). The Curie temperature T_c is located between $T_{\mathrm{I}} = T_0 + 9\Delta/16$ [$\Delta = (C^0_{3s})^2/a\beta'$], where the ferroelastic phase becomes metastable and T and T_0, where the paraelastic phase becomes instable. The jump e_s at T_c is

$$\Delta e_s = \frac{4\delta}{3}\delta = -\frac{3}{4}\frac{C^0_{3s}}{a\beta'},\quad C^0_{3s} < 0 .$$

Note that $L_1(T)$ should become infinite at T_{I}.

Figure 3 shows that $L_1(e_s)$ jumps sharply at the transition point [$L_1(T_c) \cong 3$] then slowly decreases with decreasing temperature. For instance, at $T_f = T_0 - \frac{9}{2}(C^0_{3s})^2/\beta' a$ we have $e_s(T_f) = 4e_s(T_c)$ and $L_1(T_f) = 1.44$. However, the preceding numbers are only an indication of the magnitude of elastic nonlinearity in type-II ferroelastics, as they are deduced from the simplified one-component LFE (14). A quantitative estimate of nonlinear effects for a given system must take into account the actual symmetry of the corresponding OP.

The above model will now be illustrated considering the example of the martensitic transition in the *A*15 compound V_3Si. Since its discovery by Batterman and Barrett[55,56] the 21-K cubic (*Pm*3*n*) to tetragonal (*P*4$_2$/*mmc*) transition in V_3Si has been the subject of intensive studies dealing especially with its elastic anomalies and their relationship to the superconducting transition at 17 K.[57] The temperature dependence of the lattice parameters,[56,58] the variation of strain under applied stress,[59] and the SOEC values in both phases[60,61] have been determined with great accuracy. In particular, a stress-strain curve strongly deviating from linearity[59] and the observation of acoustic second-harmonic generation[62] are proofs that elastic nonlinearity must be considered as an essential feature of the material.[64,65] Accordingly, theoretical calculations of TOEC's and FOEC's have been performed[16,63,64] to account for the anharmonic behavior of V_3Si. Although neither has a soft optic mode been observed[66] nor is there clear evidence of coupling with any electronic effects,[67] the various models based on the Landau theory, which were proposed for the structural transition in V_3Si (Refs. 68 and 69) have discarded the SS as a primary OP. In particular, the current model by Bhatt and McMillan[69] hypothesized that the cubic tetragonal distortion results from a secondary coupling to an optic mode which is in turn coupled to a charge-density wave instability taken as the primary OP.

The SS is not chosen as the transition OP (in spite of an observed ferroelastic symmetry change,[70] acoustic-phonon softening[66] and elastic anomalies[60,71] that strongly suggest such a choice) because of the contradiction between the apparent second-order character of the transition and the existence of a cubic invariant allowed by the symmetry properties of the SS (i.e., the violation of the Landau condition). This contradiction was first noticed by Anderson and Blount,[52] who proposed that some hidden parameter, eventually connected to the superconducting transition close to 17 K, should be the actual OP. However, though the early experiments have effectively found the 21-K transition to be continuous, recent accurate results[72] show that the transition is indeed weakly first order, as in the isomorphous compound Nb_3Sn.[73] This crucial fact disproves the argument raised by Anderson and Blount and lends credence to a model consistent with the symmetry of the system (i.e., involving the SS as the natural transition parameter). We shall now develop such a model and show that, with the exception of the low-temperature rigidity, it describes accurately the set of elastic data available for V_3Si.

In Table I we can see that the point-group change $m3m \rightarrow 4/mmm$ corresponds to the onset of a two-component SS $[e_{s1}=\sqrt{3}(e_2-e_2),\ e_{s2}=2e_3-e_1-e_2]$ transforming like a two-dimensional IR (τ_3) at the Brillouin-zone center. As the corresponding OP expansion is of the b type,[50,51] we construct the explicit form of $F_1(e_{s1},e_{s2},C_s)$ in (1) using the expressions of C^0_{2s}, C^0_{3s}, and C^0_{4s} given in Table I. The other components of the strain tensor have the transformation properties of the three-dimensional IR (τ_4),[74] which allows quadratic coupling to e_{s1} and e_{s2}. Taking into account the various terms allowed by symmetry up to the fourth degree in e_{s1} and e_{s2}, we can thus write the complete LFE:

$$\begin{aligned}F(T,e_{s1},e_{s2})=F(T,0,0)&+\frac{C^0_{11}-C^0_{12}}{12}(e^2_{s1}+e^2_{s2})+\frac{(C^0_{111}+2C^0_{123}-3C^0_{112})}{36}(e^3_{s2}-3e_{s2}e^2_{s1})\\&+\tfrac{1}{72}(C^0_{1111}-4C^0_{1112}-3C^0_{1122})(e^2_{s1}+e^2_{s2})^2+\tfrac{1}{2}C^0_{44}(e^2_4+e^2_5+e^2_6)\\&+\tfrac{1}{6}(C^0_{11}+2C^0_{12})(e_1+e_2+e_3)^2+\tfrac{1}{6}(C^0_{111}-C^0_{123})(e_1+e_2+e_3)(e^2_{s1}+e^2_{s2})\\&+\tfrac{1}{3}(C^0_{144}+2C^0_{155})(e_1+e_2+e_3)(e^2_4+e^2_5+e^2_6)\\&+\tfrac{1}{6}(C^0_{144}-C^0_{155})[\sqrt{3}e_{s1}(e^2_5-e^2_6)+e_{s2}(2e^2_4-e^2_5-e^2_6)]\ .\end{aligned}\tag{15}$$

The stresses conjugate to e_{s1}, e_{s2}, $e=e_1+e_2+e_3$, e_4, e_5, and e_6 are given in Table IV. The equilibrium values at zero stresses in the LT phase are

$$\begin{aligned}e_{s2}&=\frac{-\beta_1\pm[\beta_1^2-16\beta'(C^0_{11}-C^0_{12})]^{1/2}}{4\beta'}\ ,\\e_1&=-\frac{e_{s2}}{6}-\frac{A}{6}e^2_{s2}=e_2\ ,\\e_3&=\frac{e_{s2}}{3}-\frac{A}{6}e^2_{s2}\ ,\end{aligned}\tag{16}$$

with

$$A=\frac{C^0_{111}-C^0_{123}}{C^0_{11}+2C^0_{12}}$$

and

$$\beta'=\frac{\beta_2}{3}-A(C^0_{111}-C^0_{123})\ .$$

The SOEC values at 300 K have been measured by Testardi *et al.*[60] and a theoretical determination of the TOEC's has been performed by Menon and Philip[16] based on a model of nearest-neighbor central interaction. These data (collected in Table V) allow

TABLE IV. Stresses conjugate to e_{s1}, e_{s2}, $e=e_1+e_2+e_3$, e_4, e_5, and e_6 for V_3Si.

$$\sigma_{s1}=\frac{C_{11}^0-C_{12}^0}{6}e_{s1}-\frac{\beta_1}{6}e_{s1}e_{s2}+\frac{\beta_2}{18}e_{s1}(e_{s1}^2+e_{s2}^2)$$

$$+\frac{C_{1111}^0-C_{123}^0}{3}ee_{s1}+\frac{\sqrt{3}}{6}(C_{144}^0-C_{155}^0)(e_5^2-e_6^2)$$

$$\sigma_{s2}=\frac{C_{11}^0-C_{12}^0}{6}+\frac{\beta_1}{12}(e_{s2}^2-e_{s1}^2)+\frac{\beta_2}{18}e_{s2}(e_{s1}^2+e_{s2}^2)$$

$$+\frac{C_{111}^0-C_{123}^0}{3}ee_{s2}+\tfrac{1}{6}(C_{144}^0-C_{155}^0)(2e_4^2-e_5^2-e_6^2)$$

$$\sigma_e=\frac{C_{11}^0+2C_{12}^0}{3}e+\frac{C_{111}^0-C_{123}^0}{6}(e_{s1}^2+e_{s2}^2)+\frac{(C_{144}^0+2C_{155}^0)}{3}(e_4^2+e_5^2+e_6^2)$$

$$\sigma_4=C_{44}^0e_4+\tfrac{2}{3}(C_{144}^0+2C_{155}^0)ee_4+\tfrac{2}{3}(C_{144}^0-C_{155}^0)e_4e_{s2}$$

$$\sigma_s=C_{44}^0e_5+\tfrac{2}{3}(C_{144}^0+2C_{155}^0)ee_5+\tfrac{1}{6}(C_{144}^0-C_{155}^0)(2\sqrt{3}e_{s1}e_5-2e_{s2}e_5)$$

$$\sigma_6=C_{44}^0e_6+\tfrac{2}{3}(C_{144}^0+2C_{155}^0)ee_6+\tfrac{1}{6}(C_{144}^0-C_{155}^0)-(2\sqrt{3}e_{s1}e_6-2e_{s2}e_6)$$

$$\beta_1=C_{111}^0+2C_{123}^0-3C_{112}^0$$

$$\beta_2=C_{1111}^0-4C_{1112}^0-3C_{1122}^0$$

us to estimate the value of A and β_1 We have $A=3.975$ and $\beta_1=-21.3\times10^{10}$ N/m^2. The negative value of β_1 is consistent with the observed expansion of the c parameters[56] ($c/a>1$), and its small magnitude is consistent with the weakly first-order character of the 21-K transition. From the accurate data given by Mailfert *et al.*[61] for the lattice parameters we can deduce the values of e_1, e_3, and e_{s2} at 4.6 and 20 K (Table VI). Accordingly, it appears that in the whole range of temperature of the ferroelastic phase we can neglect the quadratic contribution of e_{s2} in (16) which is of the order of 10^{-7}. Thus the ratio e_1/e_3 has the theoretical value of $-\frac{1}{2}$ which is roughly satisfied by the experimental curves of Batterman and Barrett[56] (the data of Ref. 60 give, respectively, $e_1/e_3=-0.422$ at 20 K and

TABLE V. Experimental and calculated values of SOEC's, TOEC's, and FOEC's for V_3Si.

	SOEC (10^{10} N/m^2) Measured values (Ref. 70)		SOEC (10^{10} N/m^2) Calculated values			TOEC and FOEC (10^{10} N/m^2)		Calculated values		
	300 K	4.2 K	22 K	20 K	4.6 K	$T=300$ K (Ref. 16)		22 K	20 K	4.6 K
C_{11}	28.70	17.95	17.62	17.62	17.06	$C_{111}^0=-219.9$	$\frac{1}{6}C_{3S}$:	-21.3	140.90	212.38
C_{12}	12.02	17.65	17.56	17.68	18.11	$C_{112}^0=-72.8$	$C_{333}-C_{111}$:	0	120.78	182.04
C_{44}	8.096	7.61	8.096	8.116	8.128	$C_{144}^0=-11.9$	$C_{113}-C_{112}$:	0	40.26	60.68
C_{13}			17.56	17.56	17.81	$C_{166}^0=-70$	$C_{113}-C_{133}$:	0	80.52	121.36
C_{33}			17.62	17.38	16.68	$C_{123}^0=-9.9$				
C_{66}			8.096	8.086	8.080	$C_{456}^0=-14.9$				
$\frac{1}{3}(C_{11}+2C_{12})$	17.58	17.75	17.58	17.66	17.76	$C_{111}^0+2C_{123}^0-3C_{112}^0$ $=-21.3$				
$\frac{1}{2}(C_{11}-C_{12})$	8.38	0.15	0.03	-0.03	-0.55	$C_{1111}^0+4C_{1112}^0-3C_{1122}^0$ $=5.49\times10^4$				
$\frac{1}{3}C_{2S}$			0.02	-0.06	-0.903					
$\frac{2C_{44}}{C_{11}-C_{12}}$	9.65	505.0	269.86	270.53	14.77					

TABLE VI. Experimental values of lattice parameters for two samples of V_3Si (after Ref. 61) and subsequent values of strain components and relative volume change.

V_3Si samples	T (K)	a (Å) (Ref. 60)	c (Å)	$e_1\times10^4$	$e_3\times10^4$	$e_{s2}\times10^4$	$\frac{e_1}{e_3}\times10^4$	$\frac{\Delta V}{V}\times10^4$
No. 1	4.6	4.71471	4.72645	−6.97	17.9	8.29	−0.390	3.9
	20.0	4.71571	4.72346	−4.9	11.6	5.50	−0.422	1.8
	22.0	4.71800		0.0	0.0	0.0	0.0	0.0
No. 2	4.6	4.71480	4.72522	−6.36	15.7	7.35	−0.405	2.9
	19.2	4.71542	4.72373	−5.05	12.56	5.87	−0.402	2.3
	24.1	4.71780		0.0	0.0	0.0	0.0	0.0

$e_1/e_3=-0.402$ at 19.6 K for two different samples of V_3Si). On the other hand, the upper limit of $\Delta V/V$ across the transition point is about 10^{-4} (see Table VI), which agrees reasonably with the 10^{-5} discontinuous expansion reported by Chandrasekhar and Ott[72] at T_c.

The jump of the OP at T_c can be approximated by the value of e_{s2} at 20 K.[61] We have $\Delta e_{s2}=5.50\times10^{-4}=-\beta_1/2\beta'$, so that $\beta'=1.75\times10^{14}$ N/m^2 and $\beta_2=5.49\times10^{14}$ N/m^2. This value differs by 2 orders of magnitude from the FOEC values given by Barsch.[64] However, his calculations are based on very crude approximations, as the ratio between the FOEC's and TOEC's in V_3Si is arbitrarily deduced from the same ratio available for alkali halides. Moreover, the combinations of the third- and fourth-degree terms used in Ref. 63 are incorrect on the basis of symmetry.

To express the temperature dependence of second- and higher-order elastic constants in V_3Si we also need to estimate the value of the a coefficient in $C_{11}^0-C_{12}^0=a(T-T_0)\cong a(T-T_c)$. Using 16 at $T=300$ K, we find $a\simeq6\times10^8$ N/m^{2}K. The SOEC's can thus be expressed (Table VII) with coefficients that are numerically determined. The variation of the C_{ij} as a function of temperature is shown in Fig. 4(a). In Table V, we give the corresponding values on both sides of the transition point (20 and 22 K) and at 4.6 K. A comparison of the theoretical curves with the measurements by Testardi *et al.*[60] and the experimental curves obtained by Testardi and Bateman[71] for C_{11}, C_{44}, and $C_{11}-C_{12}$ leads to the following conclusions.

(1) The bulk modulus $C_{11}+2C_{13}$ remains practically constant though it increases slightly in the low-temperature phase, where

$$C_{11}+2C_{12}\simeq(52.74\pm399e_s)\times10^{10}\ ,$$

in units of N/m^2.

(2) Only two constants are strongly affected by the transition: C_{11}, which at 4.6 K is smaller by about 60% than its 300-K value, and concurrently C_{12}, which increases by one-third from its room-temperature value. Consequently, $C_{11}-C_{12}$ nearly vanishes at the transition point. However, though for $C_{11}-C_{12}$ our results are in fairly good agree-

TABLE VII. Calculated expressions for the temperature dependence of SOEC's in the ferroelastic phase of V_3Si.

$$C_{11}=\tfrac{2}{3}(C_{11}^0-C_{12}^0)+\frac{C_{11}^0+2C_{12}^0}{3}(C_{111}^0-C_{112}^0)e_{s2}[\beta''-A(C_{111}^0-C_{123}^0)]\frac{e_{s2}^2}{3}$$

$$C_{12}=-\tfrac{1}{3}(C_{11}^0-C_{12}^0)+\frac{C_{11}^0+2C_{12}^0}{3}+2(C_{123}^0-C_{112}^0)e_{s2}+A(C_{111}^0-C_{123}^0)\frac{e_{s2}^2}{3}$$

$$C_{13}=-\tfrac{1}{3}(C_{11}^0-C_{12}^0)+\frac{C_{11}^0+2C_{12}^0}{3}-(C_{123}^0-C_{122}^0)e_{s2}-\beta''\frac{e_{s2}^2}{3}$$

$$C_{33}=\tfrac{2}{3}(C_{11}^0-C_{12}^0)+\frac{C_{11}^0+2C_{12}^0}{3}+2(C_{111}^0-C_{112}^0)e_{s2}+2\beta''\frac{e_{s2}^2}{3}$$

$$C_{44}=C_{44}^0+\tfrac{2}{3}(C_{144}^0-C_{155}^0)e_{s2}-A(C_{144}^0+2C_{155}^0)\frac{e_{s2}^2}{3}$$

$$C_{55}=C_{66}=C_{44}^0-\tfrac{1}{3}(C_{144}^0-C_{155}^0)e_{s2}-A(C_{144}^0+2C_{155}^0)\frac{e_{s2}^2}{3}$$

$$\beta''=\beta_2-A(C_{111}^0-C_{123}^0)$$

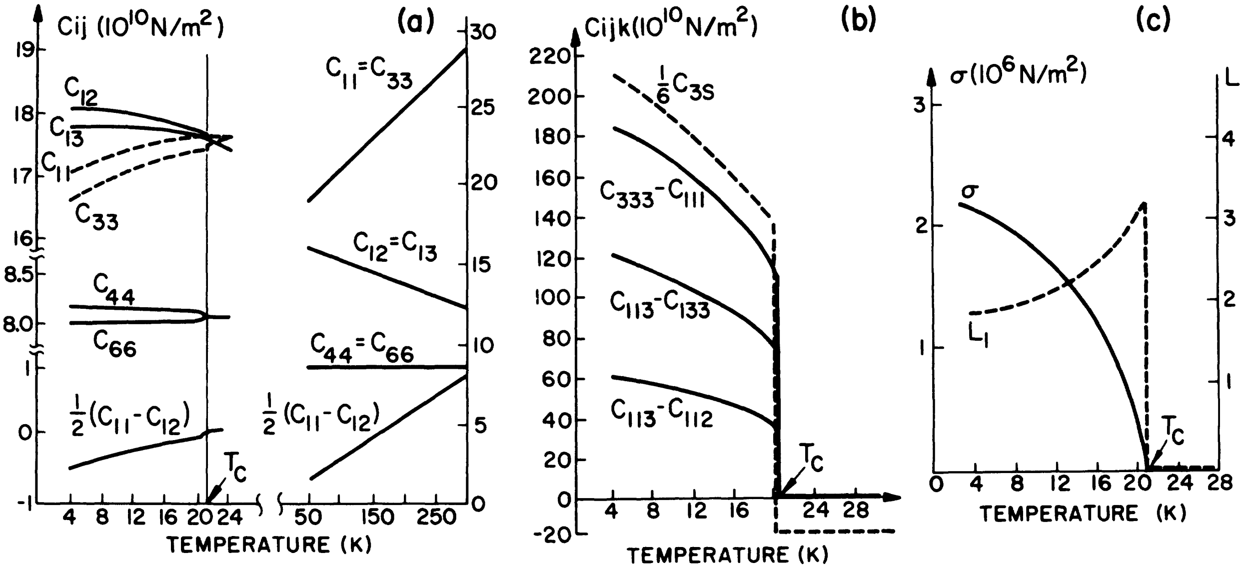

FIG. 4. Temperature dependence of elastic constants, degree of nonlinearity and stress conjugate to the SS for V_3Si. (a) SOEC's following Table VIII. (b) TOEC's following Eq. (17). (c) Degree of nonlinearity L_1 and stress conjugate to e_{s2} (see text).

ment with the experimental data of Testardi *et al.*[60] in the paraelastic phase, they differ on an important point in the ferroelastic phase. As shown in Fig. 4(a) and Table V, they predict a discontinuous change of sign at T_c, *the rigidity becoming negative under the transition point.* In our calculations, the origin of such a physically unrealistic situation lies in the fact that the expression for the stiffness is

$$C_{11}-C_{12}=C_{11}^0-C_{12}^0-\beta_1 e_{s2}+\beta_2 e_{s2}^2 ,$$

so that its negative sign comes from the smallness of β_1 and β_2 [the coefficients of the third and fourth powers of the OP in (15)], which cannot compensate for the negative sign of $C_{11}^0-C_{12}^0$ below T_c. *Such a feature indicates that within a model based on (15) the tetragonal phase is unstable below* T_c.

Actually, Testardi and Bateman[71] have shown that below T_c, $C_{11}-C_{12}$ remains surprisingly close to its lower value, while in the isomorphous compound Nb_3Sn, the rigidity is normally restored in the tetragonal phase. An interpretation of the preceding facts can be given, following a suggestion by Sakhnenko and Talanov,[51] i.e., *near* T_c *the material is close to a second transition to an orthorhombic phase predicted by the Landau theory and corresponding to the onset of the strain component* e_{s1}. The small value of $C_{11}-C_{12}$ in the ferroelastic phase should thus be associated with a *softening* of this constant. If an orthorhombic structure has not escaped detection under T_c, one cannot use model (15) in its simplest form (which assumes no secondary OP) and one has to introduce a *coupling* to some other effect (possibly related to the superconducting transition at 17 K) *which has the result of stabilizing the tetragonal structure.*

(3) The theoretical values of C_{33}, C_{44}, and C_{66} reveal (as for $C_{11}-C_{12}$) a weak discontinuity at T_c, consistent with the first-order character of the transition. As is observed experimentally,[71] C_{44} is theoretically predicted to increase in the ferroelastic phase. However, the experimental data show also a slow decrease of about 5% in C_{44} from 300 K to T_c, not assumed in our model. In Fig. 4(a) are also shown the variations of C_{13}, C_{33}, and C_{66}, for which no measurements are available.

To estimate the elastic nonlinearity of V_3Si, we can derive from (15) some combinations of TOEC's vanishing in the paraelastic phase:

$$\begin{aligned} C_{333}-C_{111}&=4\beta_2 e_{s2} , \\ C_{113}-C_{112}&=\tfrac{4}{3}\beta_2 e_{s2} , \qquad (17) \\ C_{113}-C_{133}&=\tfrac{8}{3}\beta_2 e_{s2} . \end{aligned}$$

The curves corresponding to (17) are given in Fig.

4(b) and some characteristic numbers are given in Table V. The common feature of the curves is a drastic jump at T_c followed by a substantial increase as the temperature is lowered. One can also observe, as for TeO_2, that while the individual values of the TOEC's are negative, it is their positive combinations which express the elastic nonlinearity of the material. For an estimation of the degree of nonlinearity L_1 of V_3Si in the ferroelastic phase, we need to know the TOEC and FOEC combinations C_{3s} and C_{4s}. We have

$$\frac{C_{3s}}{6}=\tfrac{1}{6}[6(C_{123}+C_{113}-C_{133})+9C_{112}+4C_{333}-C_{111}]=\beta_1+\tfrac{14}{3}\beta_2 e_{s2}\,,$$

$$\frac{C_{4s}}{72}=\tfrac{1}{72}[C_{1111}+3C_{1122}+4C_{1112}-32C_{1333}+8(C_{3333}-C_{1113})]+3(C_{1133}-C_{1123}+C_{1233})=\beta_2\,.$$

Thus

$$L_1=\frac{\tfrac{1}{6}C_{3s}e_{s2}+\tfrac{1}{24}C_{s4}e_{s2}^2}{\tfrac{1}{2}C_{2s}}\simeq\begin{cases}3.5\\1.9\end{cases}$$

at $T=20$ and 4.6 K, respectively, using the calculated values of C_{3s} and C_{4s} given in Table V, and for $C_{2s}\simeq C_{11}-C_{12}$ the experimental numbers $C_{2s}(4.6\ \mathrm{K})=0.30\times10^{10}\ \mathrm{N/m^2}$ and $C_{2s}(20\ \mathrm{K})=0.07\times10^{10}\ \mathrm{N/m^2}$ deduced from Ref. 71. The values of L_1 and the shape of the curve $L_1(T)$ [Fig. 4(c)] are in good agreement with the qualitative results based on (15) and illustrated on Fig. 3. These results predict a high degree of nonlinearity as can be seen by noting the dependence on temperature of the stress

$$\sigma(e_{s2})=\tfrac{1}{2}C_{s2}e_{s2}+\frac{C_{s3}}{6}e_{s2}^2+\frac{C_{4s}}{24}e_{s2}^3\,.$$

From the $\sigma(T)$ curve plotted on Fig. 4(c), we can deduce the characteristic values of $\sigma(20K)=0.447\times10^6\ \mathrm{N/m^2}$ and $\sigma(4.2\ \mathrm{K})=2.142\times10^6\ \mathrm{N/m^2}$ which are consistent with the stress values $\sigma_3(e_2)$ determined by Batel and Batterman.[59]

The preceding description is also possibly appropriate to other materials undergoing a $m3m$-to-$4/mmm$ structural change. This is the case in particular for the indium-thallium alloys for which a softening of the acoustic mode has been observed[75] and the variation of the SOEC's measured as a function of temperature.[76] For another $A15$ compound, Nb_3Sn, it is not clear that the SS is the primary OP, as an optic mode (corresponding to internal displacement of the Nb atoms) which couples linearly to the soft shear acoustic mode has been observed.[77] For these materials the determination of the TOEC values should allow a numerical model based on (15) and help the understanding of their transition mechanisms.

C. Type-III and -IV ferroelastics

Type-III and -IV ferroelastics are characterized by the fact that the same IR induces two independent components e_{s1} and e_{s2} of the strain tensor so that the primary OP of the transition corresponds to one of these components and couples linearly to the other (the secondary OP).

In Table I we see that IR's are one-dimensional (and consequently satisfy the Landau-Lifshitz criteria), for the three species of type III, whereas the IR's are two-dimensional (and violate the Landau condition) for species of type IV. Accordingly, the LFE of type-III and -IV ferroelastics will differ, respectively, from the LFE of types I and II mainly by a bilinear term $Ce_{s1}e_{s2}$, where C is a combination of SOEC's expressing the coupling between e_{s1} and e_{s2}. As this coupling does not modify in an essential manner the features described in Secs. II A and II B, we will limit the discussion to an illustrative example of these categories of materials. From column 11 of Table I, it can be seen that $LaNbO_4$ is the only known potential example of a proper ferroelastic belonging to types III and IV. This material undergoes a $4/m$-to-$2/m$ continuous structural change at $T_c=495\,^\circ\mathrm{C}$,[78] accompanied by the onset of two independent spontaneous-strain components (e_6 and e_1-e_2) which transform as the same Brillouin-zone-center IR of the $I4_1/a$ space group. Although no experimental data are available for the SOEC's and TOEC's, the observation of a domain structure,[79,80] the softening of an acoustic mode, and the absence of optical-mode softening[81] strongly suggests a proper ferroelastic character. The primary OP of the transition seems to be the spontaneous shear strain e_6, as this component is larger than e_1-e_2.[81] However, this choice must be confirmed by checking the vanishing of C_{66} and a nonzero value of $C_{11}-C_{12}$ (corresponding to the secondary OP e_1-e_2) at T_c. The absence of elastic constant data for lanthanum niobate, besides leaving doubts about the transition mechanism, allows only a qualitative description of its elastic properties.

Considering the various terms which couple to e_6 and e_1-e_2 in the linear and nonlinear elastic energies, we can write the LFE and $LaNbO_4$ in the form

$$
\begin{aligned}
F(T,e_6)={}&F(T,0)+\frac{C^0_{66}}{2}e_6^2+\frac{C^0_{6666}}{24}e_6^4+C^0_{16}e_6(e_1-e_2)\\
&+\tfrac{1}{4}(C^0_{11}-C^0_{12})(e_1-e_2)^2+\tfrac{1}{4}(C^0_{11}+C^0_{12})(e_1+e_2)^2\\
&+\tfrac{1}{2}(C^0_{33}e_3^2+C^0_{44}e_4^2+C^0_{55}e_5^2)+C^0_{13}e_3(e_1+e_2)\\
&+\frac{(C^0_{111}-C^0_{112})}{3}(e_1-e_2)^2(e_1+e_2)+\frac{(C^0_{113}-C^0_{123})}{6}(e_1-e_2)^2e_3\\
&+\tfrac{1}{12}(C^0_{1166}-C^0_{1266})(e_1-e_2)^2e_6^2\ . \qquad (18)
\end{aligned}
$$

In a first approximation we can neglect in (18) the quadratic coupling between e_1-e_2 and e_6. Similarly, in the determination of the equilibrium values of the strain components, the cubic contributions of (e_1-e_2) can be considered small with respect to the linear ones. Accordingly, we obtain expressions for the strains in the ferroelastic phase (Table VIII) which reveal that the coupling term results in a shift upward of the transition temperature T_c, the magnitude of the shift depending both on the intensity of the coupling coefficient C^0_{16} and of the softening of the secondary OP (e_1-e_2) (i.e., of the magnitude of $C_{11}-C^0_{12}$ at T_c). The same ratio A_0 expresses the linear dependence of e_1-e_2 on e_6. Since e_1-e_2 depends quadratically on e_6, e_1, and e_2 can be written as the sum of linear and quadratic contributions whose respective importance depends on the SOEC and TOEC combination A_0A_1. As for type-I ferroelastics, the nonzero non-symmetry-breaking strain components (e_3 and e_1+e_2) vary quadratically with e_6 (i.e., linearly with temperature). The algebraic expressions of e_1, e_2, and e_6 in Table VIII are qualitatively verified by the experimental curves given by Tsunekawa and Tanaka[8] and Wada *et al.*[81] From the observed increase of e_1 (and decrease of e_2) we can deduce that $C^0_{16}<0$. Moreover, the slope of e_6^2 given in Ref. 79 leads to $6a/C^0_{6666}\simeq 4.45\times 10^{-6}$. From the values of $(e_1-e_2)/2$ at $T=20\,^\circ\mathrm{C}$ and $T=490\,^\circ\mathrm{C}$ (-340×10^{-4} and -40×10^{-4}, respectively) we obtain

$$\frac{C^0_{16}}{C^0_{11}-C^0_{12}}=-0.743$$

at 20 °C and

$$\frac{C^0_{16}}{C^0_{11}-C^0_{12}}=-0.781$$

at 490 °C. Assuming that C^0_{16} is constant in the low-temperature phase, we can deduce that $C^0_{11}-C^0_{12}$ decreases only weakly as T_c is approached. This justifies, after the fact, the choice of e_6 as the primary OP of the transition in $\mathrm{LaNBO_4}$. From (18) we obtain expressions for the SOEC's in the ferroelastic phase (Table VIII). We can see that, due to the existence of a secondary OP, a larger number of SOEC's (than for type-I ferroelastics) vary with temperature in the ferroelastic phase. For C_{16}, C_{26}, C_{66}, and $C_{11}-C_{12}$, this variation is linear with T_c-T. The constants which couple each of the two OP to non-symmetry-breaking components of the strain tensor contain also terms in $(T_c-T)^{1/2}$. On the other hand, while e_6 vanishes linearly at T_c, neither $C_{11}-C_{12}$ nor $(C_{11}+C_{22}-2C_{12})/2=C_{2s}$ go to zero at the transition temperature. Thus, for continuous transitions, the primary OP can be identified by considering temperature dependence of the elastic constants. The preceding remarks do not hold for higher-order constants as one finds that, similarly to type-I ferroelastics, only those constants related to the primary OP vary with temperature in the ferroelastic phase, with C_{666} vanishing at T_c. The other TOEC's (as well as the FOEC's) remain constant at their high-temperature value. In particular $C_{3s}=C_{111}-C_{222}-3(C_{112}-C_{122})$ is zero in both phases.

In summary, type-III and -IV ferroelastics are distinguishable from type-I and -II ferroelastics by the existence of a secondary OP which couples linearly to the transition OP. This linear coupling shifts the transition temperature upward and increases the number of temperature-dependent SOEC's. However, it does not modify the qualitative features obtained for the second-order elastic constants, as well as for higher-order constants. We have excluded

TABLE VIII. Temperature dependence of strain components and temperature dependence of SOEC's [derived from (18)] for LaNbO$_4$.

Temperature dependence of strain components	Temperature dependence of SOEC's in the ferroelastic phase
$e_6=\left[\frac{6a(T_c-T)}{C^0_{6666}}\right]^{1/2}$	$C_{44}=C^0_{44};\ C_{55}=C^0_{55};\ C_{13}=C^0_{13}-\frac{C^0_{113}-C^0_{123}}{3}A_0e_6$
$e_1=-\frac{A_0}{2}e_6+\frac{A_1A_0^2}{2}e_0^2$	$C_{22}=C^0_{13}+\frac{C^0_{113}-C^0_{123}}{3}A_0e_6$
$e_2=\frac{A_0}{2}e_6+\frac{A_1A_0^2}{2}e_6^2$	$C_{66}=C^0_{66}+\left[C^0_{6666}+\frac{A_0^2}{3}\right]\frac{e_6^2}{2}$
$e_3=-A_2A_0e_6^2$	$C_{16}=C^0_{16}-\frac{A_0}{3}(C^0_{1166}-C^0_{1266})e_6^2$ $C_{26}=C^0_{16}+\frac{A_0}{3}(C^0_{1166}-C^0_{1266})e_6^2$
$T_c=T_0+\frac{2C^{02}_{16}}{a(C^0_{11}-C^0_{12})}$	$C_{11}=\frac{1}{2}[(C^0_{11}-C^0_{12})+(C^0_{11}+C^0_{12})]-B_1e_6+B_3e_6^2$
$A_0=\frac{2C^0_{16}}{C^0_{11}-C^0_{12}}$	$C_{22}=\frac{1}{2}[(C^0_{11}-C^0_{12})+(C^0_{11}+C^0_{12})]+2B_1e_6+B_4e_6^2$
$A_1=\frac{1}{3}\left[\frac{C^0_{13}(C^0_{113}-C^0_{123})-2C^0_{33}(C^0_{111}-C^0_{112})}{C^0_{33}(C^0_{11}+C^0_{12})-2C^{02}_{13}}\right]$	$C_{12}=\frac{1}{2}[(C^0_{11}+C^0_{12})-(C^0_{11}-C^0_{12})]-B_1e_6+B_2e_6^2$
$A_2=\frac{1}{6}\left[\frac{6C^0_{13}A_1+(C^0_{113}-C^0_{123})}{C^0_{33}}\right]$	$B_1=\frac{2A_0}{3}(C^0_{111}-C^0_{112})$ $B_2=\frac{1}{3}[(C^0_{112}-C^0_{123})A_0A_2-\frac{1}{2}(C^0_{1166}-C^0_{1266})]$ $B_3=\frac{4A_0^2A_1}{3}(C^0_{111}-C^0_{112})-B_2$ $B_4=\frac{B_3-B_2}{2}$

from the above description the case where, due to a strong coupling between two components of similar magnitude, the transition is induced by two simultaneous OP's. This limit situation will be discussed in a further study.[36]

III. PSEUDOPROPER FERROELASTIC TRANSITIONS

In the PFT considered in Sec. II, the spontaneous strain has been assumed to be the only OP and the acoustic mode the only strongly temperature-dependent excitation. A model based on these assumptions may give, for some strain-induced PFT, a rather accurate description of their elastic properties. For other PFT, it can be only a first approximation, as other secondary OP and excitations must be introduced into the model to account for the entire set of experimental facts. In V$_3$Si, for instance, we have seen that a coupling to some parameter was necessary to explain the persistent stability of the tetragonal structure at low temperature. Nevertheless it appears that *most of the elastic properties* of strain-induced transitions can be described ignoring the secondary parameters involved in the transition and considering exclusively the spontaneous and nonspontaneous components of the strain tensor.

However, the preceding situation is not the most frequently encountered among materials undergoing a PFT. In column 11 of Table I we can see that a majority of materials in which a PFT has been observed have been labeled as pseudoproper. This means that the strain cannot be considered as the primary OP and results only from a bilinear coupling to a primary OP having the same symmetry (i.e., transforming as the same IR). In materials such as LaP$_5$O$_{14}$ or BiVO$_4$ the primary OP expresses an atomic displacement within the unit cell which is distinct from the motion resulting in the symmetry-breaking strain. It can be identified as the eigenvector of a condensed optic mode which becomes unstable primarily with respect to the acoustic mode, both modes being proportional to each other in the low-symmetry phase. In rare-earth vanadates or spinels there are no soft optic modes but the acoustic instability arises from a coupling of strain to electronic energy levels in a cooperative Jahn-Teller effect. In some cases, such as $K_2Mn_2(SO_4)_3$ or *s*-triazine the experimental data are insufficient or controversial so that it is not clear which is the primary instability responsible for the transition.

In this section we describe the elastic (linear and nonlinear) properties of pseudoproper PFT emphasizing their differences with respect to proper PFT. As the coefficients of the OP expansion are not expressed directly through SOEC's, TOEC's, and FOEC's, the entire set of second- and higher-order constants have to be introduced in the complete LFE via elastic energies of various orders. Furthermore, to perform a numerical model for a given material, one needs to know, in addition to the values of the elastic constants in the HT phase, the experimental parameters corresponding to the coefficients of the OP invariants and to the coefficients which couple the strains to the primary OP (Q). For none of the pseudoproper materials listed in Table I is the entire set of numbers available. However, for some of them [LaP_5O_{14}, $KH_3(SeO_3)_2$, $RbAg_4I_5$], the experimental results allow a semiquantitative description. We shall first discuss the case of lanthanum pentaphosphate, then we will briefly review the distinctive features of the other pseudoproper materials.

A. LaP_5O_{14}

Lanthanum pentaphosphate undergoes a continuous transition at $T_c = 125\,^\circ\mathrm{C}$ from an orthorhombic *mmm* paraelastic phase to a monoclinic $2/m$ ferroelastic phase.[82,83] Below T_c, a spontaneous monoclinic shear e_5 in the *xz* plane has a temperature dependence determined by Weber *et al.*,[83] revealing a magnitude of approximately 10^{-2} rad at room temperature. Several soft modes have been observed in this material, namely a transverse-acoustic mode detected by Brillouin scattering measurements[84] and two strongly softening optic modes revealed by Raman scattering.[85,86] The softer of these optic modes has the same symmetry as the monoclinic shear, and its associated normal coordinate Q has been proposed as the actual OP of the transition.[87] This choice is suggested by the fact that the corresponding frequency ω_Q is considerably larger than that of the bare acoustic mode, and has a strong temperature dependence. Accordingly, a phenomenological theory taking Q as the primary OP has been proposed by Errandonea,[87] which describes accurately the temperature dependence of the strains and of most of the SOEC's. Errandonea suggests also that the experimental features which are not accounted for by his model, namely the slope of the C_{55} coefficient and the slight anomaly observed at T_c for C_{44}, may be explained by the introduction of a quadratic coupling between Q and e_s.[88]

In order to describe the nonlinear elastic properties of LaP_5O_4, we add to the LFE, which is given in Ref. 87, terms expressing the third-order elastic energy in the paraelastic phase. We thus have

$$F(T,e_i,Q)=\frac{\alpha}{2}Q^2+\frac{\beta}{4}Q^4+\frac{1}{2}\sum_{i,j=1,3}C^0_{ij}e_ie_j+\frac{1}{2}\sum_{k=4,6}C^0_{kk}e_k^2$$

$$+\frac{1}{2}\sum_{i,j=1,3}C^0_{iij}e_i^2e_j+\frac{1}{2}\sum_{\substack{i=1,3\\ j=4,6}}C^0_{ijj}e_j^2e_i+C^0_{123}e_1e_2e_3+C^0_{456}e_4e_5e_6+\gamma e_5Q+\sum_{i=1,3}\delta_ie_iQ^2\,, \qquad (19)$$

in which we assume $\alpha = a(T-T_0)$ and $\beta > 0$. Here γ and δ_i ($i=1,3$) are coefficients coupling Q to the various components of the strain tensor. (Only the lowest-order coupling has been considered, as in Ref. 87.) Constants C^0_{ij} and C^0_{ijk} are, respectively, the values of the SOEC's and TOEC's in the paraelastic phase. We can verify that there are nine independent SOEC's and 20 TOEC's. It must be stressed that, in contrast with proper PFT, description of the elastic nonlinear properties of pseudoproper PFT requires terms of the form $e_i^2e_j$ ($i,j \neq 5$) proportional to Q^6, whereas we have limited the OP expansion to the fourth degree. By contrast, in order to obtain a numerical estimate of some TOEC's, the fourth-order elastic energy has been neglected, so that the FOEC's are explicitly absent from (19). This approximation is justified by the fact that most of the contributions to fourth-order elastic energy (except terms containing e_5) correspond to powers Q^8.

Let us first summarize the results obtained in Ref. 87 for the equilibrium values of the strains and SOEC's in LaP_5O_{14}, and compare them to those obtained for proper ferroelastics.

TABLE IX. Temperature dependence of SOEC's and TOEC's for LaP_5O_{14}; $t=T-T_c=-t'$; $\beta'=\beta-2\sum_{i,j=1,3}S_{ij}^0\delta_i\delta_j$; $g=aC_{55}^0/\gamma=1/(T_c-T_0)$; $g'=(2\beta/\beta')g$.

	(Ref. 87)			TOEC	
	Orthorhombic phase	Monoclinic phase		Orthorhombic phase	Monoclinic phase
Q	0	$\pm\left[\frac{at'}{\beta'}\right]^{1/2}$	C_{ijk} $(i,j,k=1,2,3)$	C_{ijk}^0	$C_{ijk}^0+8\delta_i\delta_j\delta_k\frac{g't'}{a\beta'}\frac{(2-g't')}{(1+g't')^3}$
e_5	0	$\mp\frac{\gamma}{C_{55}^0}\left[\frac{at'}{\beta'}\right]^{1/2}$	C_{ij5} $(i,j=1,2,3)$	0	$4\delta_i\delta_j\frac{\gamma g'}{a^2}\frac{(2-g't')}{(1+g't')^3}$
e_i $(i=1,2,3)$	0	$-\left[\sum_{j=1}^{3}S_{ij}^0\delta_j\right]\frac{at'}{\beta'}$	C_{555}	0	$\mp 6\beta\left[\frac{\gamma g}{a}\right]^3\frac{(at'/\beta')^{1/2}}{(1+g't')^3}$
e_4,e_6	0	0	C_{i55} $(i=1,3)$	$C_{i55}^0+\frac{2\delta_i\gamma^2g^2/a^2}{1+gt}$	$C_{i55}^0+\frac{2\delta_i\gamma^2g^2}{a^2}\ \frac{1-2g't'}{(1+g't')^3}$
C_{55}	$C_{55}^0\frac{gt}{1+gt}$	$C_{55}^0\frac{g't'}{1+g't'}$	C_{ijj} $(i=1,2,3)$ $(j=4,6)$	C_{ijj}^0	C_{ijj}^0
C_{i5} $(i=1,2,3)$	0	$\mp\delta_i\left[\frac{2C_{55}^0}{\beta}\right]^{1/2}\frac{(g't')^{1/2}}{1+g't'}$	C_{456}	C_{456}^0	C_{456}^0
C_{ij} $(i,j=1,2,3)$	C_{ij}^0	$C_{ij}^0-\frac{2\delta_i\delta_j}{\beta}\ \frac{g't'}{1+g't'}$			

(1) The coupling between Q and e_5 produces an upward shift of the transition temperature T_c in a mechanically free crystal (i.e., when e_5 is the unique OP). The transition takes place at $T_c=T_0+\gamma^2/aC_{55}^0$. Using experimental values of $\gamma^2/a=1070$ and $C_{55}^0=6.62\times10^{10}$ N/m^2, Errandonea found a shift $T_c-T_0=161$ °C indicating a strong coupling.

(2) The spontaneous strain e_5 is found to vary as $(T_c-T)^{1/2}$ while the e_i $(i=1,2,3)$ vary as (T_c-T). The same results have been obtained for proper ferroelastics (see Sec. II A). However, as shown in Table IX, the slopes of e_5^2 and e_i, are modified by coupling between Q^2 and e_i, via the δ_i coefficients.

(3) The coefficients C_{55} and C_{i5} $(i=1,2,3)$ are found to be temperature dependent, whereas for a proper ferroelastic C_{ij} would be temperature independent. Moreover, one can see in Table IX that the laws of temperature variation are different than in the proper ferroelastic case. Here C_{55} varies as

$$\frac{g'(T_c-T)}{1+g'(T_c-T)}$$

and C_{i5} as

$$\frac{[g'(T_c-T)]^{1/2}}{1+g'(T_c-T)}$$

(where g' depends on the coupling coefficients). By contrast, if e_5 were the primary OP, these coefficients would be proportional to (T_c-T) and $(T_c-T)^{1/2}$.

Using the notation of Ref. 87 (see Table IX) we have calculated from (19) the variation of the TOEC's as a function of temperature. The nonzero constants are given in Table IX where one can note a number of differences with the results for proper ferroelastics. Actually 19 TOEC's are found to be temperature dependent in the ferroelastic phase of which three (C_{i55}, $i=1,2,3$) vary also in the paraelastic phase. This is in striking contrast with the proper ferroelastic case, where only one constant (C_{555}) varies with temperature and only in the ferroelastic phase. Moreover, the laws of temperature variation differ considerably from the simple law $(T_c-T)^{1/2}$ obtained in Sec. II A. Curves of some representative TOEC's are given in Fig. 5. Since the high-temperature values C_{ijk}^0 and C_{i55}^0 are unknown, we show only the differences $(C_{ijk}-C_{ijk}^0)$ and $(C_{i55}-C_{i55}^0)$. For C_{555} and C_{ij5} $(i,j=1,2,3)$, we obtain explicit expressions, as these constants vanish by symmetry above T_c.

Apart from $|C_{i55}-C_{i55}^0|$, which exhibits a maximum at T_c and decreases in both phases, all constants exhibit a sharp variation at T_c and a slow increase as the temperature is lowered.

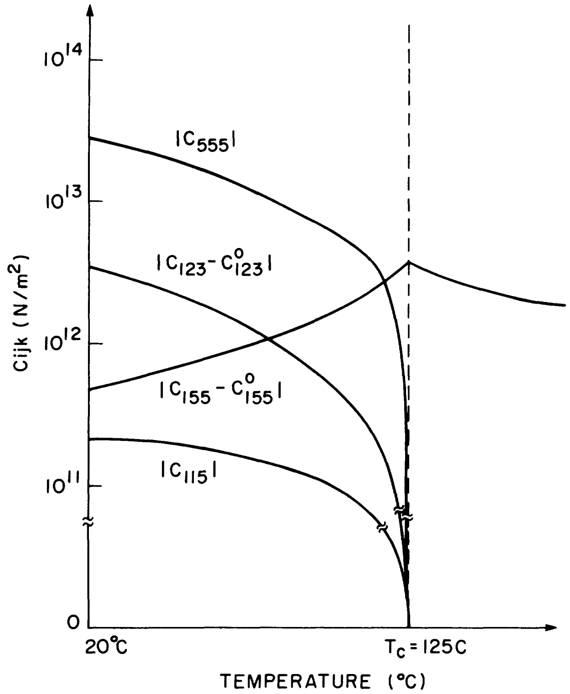

FIG. 5. Temperature dependence of some representative TOEC modulus for LaP_5O_{14}, following the calculated expressions in Table IX.

Calculated numerical values of the TOEC's at 20 °C are given in Table X. We see that C_{i55} ($i=1,3$) and C_{555} are, respectively, about 1 and 3 orders of magnitude larger than C_{i5} and C_{55}. The differences $C_{ijk}-C^0_{ijk}$ ($i,j=1,2,3$) and $C_{i55}=C^0_{i55}$ ($i=1,2,3$) indicate that the C_{ijk} and C_{i55} should be about 2 orders of magnitude larger than the corresponding SOEC's. Using expressions (9) (in which the FOEC contribution is neglected), we can calculate the degree of nonlinearity in lanthanum pentaphosphate. We have here

$$L_1=\frac{1}{3}\frac{C_{555}e_5}{C_{55}}=2.96\ ,$$

in which $C_{55}(20\,^\circ\mathrm{C})=4.14\times10^{10}$ N/m² (see Ref. 87) and $e_5(20\,^\circ\mathrm{C})\simeq 8\times10^{-3}$ rad. The large value found for L_1 indicates that elastic nonlinearity in pseudoproper ferroelastics, in which a strong coupling exists between the OP and the symmetry-breaking strain, can be even larger than for proper ferroelastics.

B. Other pseudoproper ferroelastics

In addition to LaP_5O_{14}, three other materials are given in Table I as examples of pseudoproper ferroelastics of type I, namely $KH_3(SeO_3)_2$, $DyVO_4$, and $TbVO_4$. Some features of potassium trihydrogen selenite are very similar to those of lanthanum pentaphosphate: the same symmetry change $mmm \rightarrow 2/m$ (accompanied by the onset of a spontaneous shear strain[89] e_5) continuous character reported for the $-62\,^\circ$C transition,[90] and a large shift of the transition temperature, with $T_c-T_0=137\,^\circ$C.[91] Accordingly, a microscopic mechanism which does not result in macroscopic components (a rearrangement of the proton system) has been invoked to play the role of the OP of the transition. The corresponding phenomenological theory has been discussed by Makita *et al.*[91] and Kessenikh *et al.*[92] based on a LFE containing a linear proton-phonon coupling. However, the dependence of the SOEC's with temperature[91] displays two important features which differentiate $KH_3(SeO_3)_2$ from LaP_5O_{14}. At first, it appears that while C_{55} (C_{44} with the convention of Makita *et al.*[91]) softens similarly for both materials, the other elastic constants are nearly temperature independent in the ferroelastic phase. Moreover, discontinuities which are characteristic of a slightly first-order transition are observed for C_{11}, C_{22} and C_{12}, and C_{13}.[91] These facts can be indicative of a weak coupling between the OP Q and the strain components other than e_5. One can also assume that the linear coupling between Q and e_5 is not as strong as suggested by the shift of T_c, as this shift can be partially attributed to the first-order character of the transition. It thus leaves open the possibility of interpreting the transition in $KH_3(SeO_3)_2$ as a first-order *proper* transition.

TABLE X. Calculated values of the moduli of TOEC's for LaP_5O_{14}.

TOEC's at $T=20\,^\circ$C (10^{12} N/m²)	
$\lvert C_{123}-C^0_{123}\rvert$	5.0
$\lvert C_{111}-C^0_{111}\rvert$	6.1
$\lvert C_{222}-C^0_{222}\rvert$	2.1
$\lvert C_{333}-C^0_{333}\rvert$	10.5
$\lvert C_{155}-C^0_{155}\rvert$	0.68
$\lvert C_{255}-C^0_{255}\rvert$	0.49
$\lvert C_{355}-C^0_{355}\rvert$	0.83
$\lvert C_{555}\rvert$	46.0
$\lvert C_{115}\rvert$	0.34
$\lvert C_{255}\rvert$	0.17
$\lvert C_{335}\rvert$	0.46

The nonlinear properties of potassium trihydrogen selenite, in the vicinity of the transition temperature have been investigated by Zagrai *et al.*[14] These authors estimate the value of C_{222} of 0.9×10^{12} N/m²,which is 1 order of magnitude smaller than the same constant in LaP_5O_{14} (Table V). But as C_{22} in $KH_3(SeO_3)_2$ is also 1 order of magnitude smaller than in LaP_4O_{14} the ratio C_{222}/C_{22} is similar for both materials. However, it is the value of C_{555} that would give more valuable information on elastic nonlinearity in $KH_3(SeO_3)_2$ and incidently, on the magnitude of the coupling between Q and e_5.

The pseudoproper character of the rare-earth vanadates RVO_4 ($R=$Dy,Tb,Tm) is more certain as several studies[93–95] have shown that the distortion of the lattice at low temperature in this family of materials results from a coupling between the low-lying electronic energy levels of the rare-earth ions and the lattice phonons (i.e., a Jahn-Teller-type effect). However, the situation is not consistent among the various members of this family of compounds. In $DyVO_4$ the 14-K $I4_1/amd \rightarrow Imma$ transition is associated with the IR τ_3 of the $I4_1/amd$ group at Brillouin-zone center while it is the IR τ_4 of the same space group which induces the $I4_1/amd \rightarrow Fddd$ space-group change in $TbVO_4$.[96] In the former case, it is the constant $C_{11}-C_{12}$ which vanishes at τ_c whereas in the latter it is the constant C_{66} which softens. In $TmVO_4$,[97] both constants undergo a large softening but only C_{66} goes to zero at 2.15 K denoting a strong coupling between the two corresponding modes. However, the elastic data are still insufficient to provide indirect indications of the nonlinear properties of rare-earth vanadates and also to confirm the mechanism currently assumed for their transition

There also exists a Jahn-Teller-type effect proposed as an explanation of the transitions taking place in $RbAg_4I_5$ and $NiCr_2O_4$, two type-II pseudoproper ferroelastics. The 64.3 °C transition in rubidium silver pentaiodide $RbAg_4I_5$ (Ref. 98) has the peculiarity of being induced by a three-dimensional IR(τ_5) of the space group $P4_132$, which violates simultaneously the Landau-Lifshitz criteria. One should thus expect a strong first-order character for the transition and the possible occurrence of a structural incommensuration in the LT phase. Nevertheless, due to the absence of thermal hysteresis and specific-heat anomalies[99,100] the transition has been claimed to be continuous and the low-temperature phase to be of definite rhombohedral $R32$ symmetry.[100] However, when examining the elastic data given by Graham and Chang,[101] a non-negligible discontinuity of C_{11} and C_{12} is apparent. Moreover, this first-order character is confirmed by a slight jump observed in the temperature dependence of the birefringence.[100] From the pressure derivatives of the acoustic velocity some combinations of TOEC's have been estimated in the paraelastic phase.[101] . Though an evaluation of the importance of the elastic nonlinearity necessitates data for the ferroelastic phase (and especially the value of C_{456}), the numbers given in Ref. 101 for the TOEC's reflect a small amount of nonlinearity as they are less than 10 times larger than the corresponding SOEC values.

The crystal $NiCr_2O_4$ is one of the members of the large family of spinels undergoing a $Fd3m \rightarrow I4_1/amd$ Jahn-Teller-induced transition. Their behavior should be compared to that of the $A15$ compounds, as (similarly to V_3Si and Nb_3Sn) some members, such as $CuCr_2O_4$,[102] exhibit $c/a > 1$ distortion (so that the C_{3s}^0 coefficient is negative) while others, such as $NiCr_2O_4$,[103] have $c/a < 1$ ($C_{3s}^0 > 0$). However, the elastic constant data given for $NiCr_2O_4$ (Ref. 104) are incomplete and do not allow a detailed phenomenological model for this material. Adequate comparison of the temperature dependence of strains and SOEC obtained for $NiCr_2O_4$ and V_3Si, allows one, however, to see that differences are found between pseudoproper and proper type-II ferroelastics which are similar to that found for type-I ferroelastics. In particular, it appears that a larger number of SOEC's are temperature dependent and their variation laws are sensibly distinct.

Finally, let us briefly review the two examples of pseudoproper materials given in Table I for type-III and -IV ferroelastics. The 255 °C ferroelastic change in $BiVO_4$ has been reported by Bierlein and Sleight,[105] and a zone-center soft-optic mode was observed in this material by Pinczuk *et al.*,[106] who subsequently gave a phenomenological model in which the optical mode was assumed to drive the transition.[107] However, another model by Dudnik *et al.*,[1–8] was based on the assumption that $BiVO_4$ is an improper ferroelastic. The recent observation of a soft acoustic mode[103] is in favor of the first assumption. The linear coupling between the OP and the strain components, in the model of Pinczuk *et al.*,[107] appears to be extremely large as it produces a shift of the transition temperature of $T_c - T_0 = 228$ °C. However, no mention is made in Ref. 107 of a linear coupling with the two independent components e_6 and (e_1-e_2) which characterize type-III pseudoproper ferroelastics. More complete data on the elastic constants of $BiVO_4$ (in particular, the confirmation of a softening of both C_{66} and $C_{11}-C_{12}$) should allow the verification of the pseudoproper character of this compound.

In sodium azide, NaN_3, a coupling between the orientational motion of the azide ions and the lattice strains (e_4 and e_1-e_2) has been suggested[110] as a mechanism for the room-temperature transition. Though the softening of C_{44} and $C_{11}-C_{12}$ has been observed,[111] no other elastic data exist for verifying the pseudoproper character of the transition. Such additional data should also allow a check of the continuous nature of the 20 °C transition claimed by Simonis and Hathaway[112] which is in contradiction with the existence of a cubic invariant in the LFE.

To conclude this section let us note that some materials listed in Table I have not been classified among proper or pseudoproper ferroelastics as too much uncertainty remains about the mechanism of their transition. This is the case for *s*-triazine,[113] KNO_2,[114] and $K_2Mn_2(SO_4)_3$. For this last material, a member of the langbeinite family, there exists strong controversy concerning the symmetry of the OP,[115–117] and elastic data would allow the determination of which IR induces the observed cubic to orthorhombic transition.

IV. SUMMARY AND CONCLUSION

In this paper nonlinear elasticity in proper ferroelastics (nonsimultaneously ferroelectrics) has been investigated, using the Landau theory of phase transitions. Thus, the basis for the determination of third- and higher-order elastic constants was provided by truncated expansions in the OP and strain-tensor components (i.e., the LFE). For a given real transition, the detailed expression of the corresponding LFE is deduced from a set of symmetry restrictions, such as the IR inducing the transition and the possible couplings of the OP to some other physical quantities, from nonsymmetry properties, namely the nature of the OP and the thermal expansion of lattice parameters in the paraelastic phase, and also from considerations where symmetry may possibly be involved, such as the order of the transition.

In ferroelastics where certain strain components correspond to the OP, coefficients in the LFE coincide with special combinations of elastic constants of second and higher order, so that linear and nonlinear elasticity are directly accounted for by the Landau theory. Accordingly, the elastic behavior of four classes of strain-induced ferroelastics have been distinguished (Sec. II). Let us first summarize their general properties.

(1) Type-I ferroelastics correspond to a tetragonal-orthorhombic or an orthorhombic-monoclinic structural change. The transition, induced by a one-dimensional "active"[118] IR can be of the second or the first order, depending on the sign of the paraelastic combinations of the FOEC's C_{4s}^0. Values for C_{4s}^0 and C_{3is}^0 can be deduced from the temperature variation of strain components and SOEC's in the ferroelastic phase. When only nonlinear couplings between (spontaneous and nonspontaneous) strain components influence the transition (i.e., no secondary OP is involved) all the TOEC's and FOEC's remain constant across the transition temperature T_c, except for the TOEC's composing C_{3s}, and eventually (for a first-order transition) those FOEC's which appear in the combination C_{4s}. For a second-order transition ($C_{4s}^0>0$) C_{2s} and C_{3s} vanish at T_c, while for a first-order transition C_{2s} remains nonzero at the Curie point. First-order transitions, which require for their description introduction of elastic constants of the sixth order (at least), can also be distinguished by a jump at T_c of the strain components and elastic constants C_{2s}, C_{3s}, and C_{4s}. The magnitude of these jumps depends (and provides information) on the values of the paraelastic constants C_{3is}^0, C_{4s}^0, and C_{6s}^0.

(2) The paraelastic phase of type-II ferroelastics belongs to the cubic or hexagonal systems. A transition of this class is associated with an IR violating the Landau condition. Accordingly, the LFE possess cubic invariant(s) and the transition should be of the first order. Its elastic behavior resembles qualitatively that of first-order transitions of type-I ferroelastics, but with the noteworthy difference of the nonvanishing of C_{3s} in the paraelastic phase.

(3) Type-III and -IV ferroelastics are, respectively, distinguished from ferroelastics of type I and II by the existence of a secondary OP coupling linearly to the transition OP. This coupling shifts the transition temperature and increases the number of temperature-dependent SOEC's, but does not modify the behavior of higher-order constants as described for ferroelastics of types I and II.

As a quantitative estimate of the nonlinear elasticity stored at a ferroelastic transition, a coefficient L_1 was defined (the degree of nonlinearity). For a second-order type-I (or -III) ferroelastic, the value $L_1=\frac{5}{4}$ is found, and $L_1>\frac{5}{4}$ for a first-order transition of the same class. For type-II (or -IV) ferroelastics, L_1 is a slowly decreasing function of temperature, with a sharp peak ($L_1 \gtrsim 3$) at the transition temperature T_1. One must note the qualitative resemblance of $L_1(T)$ with the specific heat predicted theoretically by the Landau theory for second- and first-order transitions.

As an illustration of the preceding results, numerical models were established for ferroelastics of type I (TeO_2) and of type II (V_3Si). The discussion of these models demonstrated that nonlinear elasticity in ferroelastics cannot be estimated by the mere values of individual higher-order constants, but only from particular combinations (as C_{3s}) of TOEC's and FOEC's. In TeO_2, as well as in V_3Si, while most of the individual TOEC's are small and negative in the paraelastic phase, they combine in such a way that C_{3s} is positive and increases rapidly below the Curie point. Thus the ratio L_2 ($=C_{3s}/C_{2s}$) provides, complementarily to L_1, a suitable indication of nonlinear elasticity. The corresponding values for TeO_2 and V_3Si are, respectively, L_2 (20 kbar)$\simeq$50 and L_2(4.6 K)$\simeq$450, which is between 1 and 2 orders of magnitude larger than the values usually obtained for ratios of TOEC's and SOEC's in nonferroelastic materials.[5] Therefore, for an experimental estimate of nonlinear elasticity in a ferroelastic material, the measurement of C_{3s} (and C_{2s}) provides important basic information.

As shown in Sec. II, a theoretical determination of the relevant TOEC's and FOEC's at any temperature for a given ferroelastic material is possible if one knows the following: (a) numerical values, in the paraelastic phase, for the SOEC's, TOEC's, and FOEC's involved in the LFE; (b) the temperature variation of the SS in the ferroelastic phase. However, although complete sets of values for the preceding FOEC's and TOEC's are not generally available from experiments, they can be deduced from the temperature variation of strains and SOEC's. Accordingly, for the materials examined in Sec. II, a preliminary discussion was based on these latter quantities, comparing their theoretical behavior as predicted by the LFE, and the corresponding experimental data. For TeO_2, C^0_{4s} was deduced from the slope of $C_{11}-C_{12}$, whereas for V_3Si it was approximated from the jump of e_s at the transition point.

Such a comparison between theoretical predictions and experimental data is also necessary for testing the LFE assumed as a first approximation. Thus, a temperature variation for $C^0_{11}+C^0_{12}$ and two higher-degree coupling terms were introduced in a refined model for TeO_2, while for V_3Si it was shown that a coupling to some secondary parameter was indeed necessary in order to explain the anomalous resoftening of the rigidity in the ferroelastic phase. These adjustments, though modifying the simplest model derived from the Landau theory, do not contradict the choice of the SS as a primary OP for the two preceding materials. Such a choice is suggested by the observed symmetry change and by the lack of clear experimental data relating the transition to some physical mechanism distinct from the one resulting in the onset of spontaneous strains. The accurate fit with experimental data, largely verified for the theoretical behavior of strain components and TOEC's (Figs. 2 and 4), strongly confirms the strain-induced character assumed for the transitions in TeO_2 and V_3Si.[119]

Among real examples of PFT, strain-induced transitions are at present in the minority, as most known cell-preserving ferroelastic transitions have been described with an OP distinct from the SS. For pseudoproper transitions, elastic properties are accounted for in the LFE, via elastic energies of second and higher orders. In Sec. III the elastic features of pseudoproper ferroelastics were examined through the specific case of LaP_5O_{14}. In this material it has been established experimentally[87] that SOEC's varying with temperature in the ferroelastic phase, are more numerous, and follow different variation laws than for a strain-induced transition undergoing the same symmetry change. We have shown that similar conclusions hold for TOEC's. Numerical values obtained for these latter constants reveal that elastic nonlinearity (characterized by the numbers $L_1\simeq3$ and $L_2\simeq10^3$ at $T=20\,^\circ\mathrm{C}$) can be large in pseudoproper ferroelastics such as LaP_5O_{14} in which a strong coupling exists between the OP and the SS. The different behavior obtained for SOEC's and TOEC's in proper and pseudoproper ferroelastics, respectively, confirms that the distinction between these two concepts is not a purely formal one, but has a strong physical basis. However, the classification of a particular ferroelastic in one of the two categories is never obvious and may in some cases require consideration of a whole set of physical properties, including elastic constants of second and higher orders.

Most studies devoted to ferroelastics have stressed the analogy of this class of materials with ferroelectrics or ferromagnets. In this paper nonlinear elasticity has been shown to be a remarkable feature of proper ferroelastic transitions. A study of nonlinear elasticity in other categories of ferroelastics (improper ones or simultaneously ferroelectrics) as well as in nonferroelastic materials, should be of interest, as it would give a more general picture of the respective importance of this phenomenon among the various categories of solids. It would also indicate to what extent a high degree of elastic nonlinearity is related to the onset of large strains, or to lattice instabilities taking place at any phase transition.

Nonlinear elasticity in solids has been, in recent years, the subject of an increasing number of studies.[1-11] However, because of intrinsic difficulties, experimental data on elastic constants of higher order remain scarce and uncertain.[5] A theoretical understanding of the microscopic mechanism of nonlinear elasticity,[120] and of its phenomenological aspects for various classes of materials, should stimulate the improvement of experimental methods of measurements of elastic constants of third and higher orders.

ACKNOWLEDGMENTS

We are grateful to Dr. J. C. Toledano for several very helpful discussions and a careful reading of the manuscript. We are indebted to Dr. G. Errandonea for his clarifying remarks about pseudoproper ferroelastics. It is a pleasure to thank Professor H. Z. Cummins for sending us his very useful review paper (Ref. 33) before publication.

[*] On leave from the Université de Picardie rue Saint-Leu 33, F-80039 Amiens Cedex, France.

[1] A. Seeger and O. Buck, Z. Naturforsch. 15a, 1056 (1960).

[2] A. A. Gedroits and V. A. Krasil'nikov, Zh. Eksp. Teor. Fiz. 43, 1592 (1962) [Sov. Phys.—JETP 16, 1122 (1963)].

[3] R. N. Thurston and K. Brugger, Phys. Rev. 133, A1064 (1964).

[4] F. Birch, Phys. Rev. 71, 809 (1974); K. Brugger, *ibid.* 133A, 1611 (1964).

[5] R. S. F. Hearmon, in *Elastic Piezoelectric and Related Constants of Crystals,* Vol. III of *Landolt-Bornstein* (Springer, Berlin, 1979), p. 11.

[6] G. R. Barsch, J. Appl. Phys. 39, 3780 (1968).

[7] Y. Hiki, Annu. Rev. Mater. Sci. 11, 51 (1981).

[8] Y. Hiki, J. R. Thomas, and A. V. Granato, Phys. Rev. 153, 764 (1967).

[9] Z. P. Chang and G. R. Barsch, Phys. Rev. Lett. 19, 1381 (1967).

[10] D. E. Khmel'nitskii, Fiz. Tverd. Tela (Leningrad) 16, 3188 (1974) [Sov. Phys.—Solid State, 16, 2079 (1975)].

[11] L. K. Zarembo, V. A. Krasil'nikov, O. Yu. Serdobol'skaya, and V. I. Serikov, Fiz. Tverd. Tela (Leningrad) 16, 3578 (1974) [Sov. Phys.—Solid State, 16, 2327 (1975)].

[12] K. Aizu, J. Phys. Soc. Jpn. 27, 387 (1969).

[13] J. C. Toledano, Ann. Telecommun. 29, 243 (1974).

[14] N. P. Zagrai, K. K. Zarembo, N. R. Ivanov, O. Yu. Serdobol'skaya, and L. A. Shuvalov, Kristallografiya 25, 787 (1980) [Sov. Phys.—Crystallogr. 25, 451 (1980)].

[15] A. M. Antonenko, D. D. Volnyanskii, and A. Yu Kudsin, Kristallografiya 24, 1071 (1980) [Sov. Phys.—Crystallogr. 24, 613 (1979)].

[16] C. S. Menon and J. Philip, Solid State Commun. 26, 897 (1978).

[17] E. L. Meeks and R. T. Arnold, Phys. Rev. B 1, 982 (1970).

[18] A. I. Korobov, V. M. Prokhorov, O. Yu. Serdobol'skaya, and P. Hegedush, Kristallografiya 23, 566 (1979) [Sov. Phys.—Crystallogr. 23, 314 (1978)].

[19] H. Beige and G. Schmidt, Izv. Akad. Nauk SSSR, Ser. Fiz. 39, 970 (1975) [Bull. Acad. Sci. USSR Phys. Ser. 39, 65 (1975)].

[20] B. E. Powell and M. J. Skove, Phys. Rev. 174, 977 (1968).

[21] O. Buck and D. O. Thompson, Mater. Sci. Eng. 1, 117 (1966).

[22] See, for example, the discussion performed in Sec. II about the choice of the OP and Landau free energy in the case of V_3Si.

[23] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958).

[24] J. C. Toledano and P. Toledano, Phys. Rev. B 21, 1139 (1980).

[25] G. Pascoli, Thèse de troisième cycle, Université de Lille I, 1981 (unpublished); P. Toledano and G. Pascoli, Ferroelectrics 25, 427 (1980).

[26] J. C. Toledano, Ferroelectrics 35, 31 (1981).

[27] K. Aizu, J. Phys. Soc. Jpn. 28, 706 (1970).

[28] N. Boccara, Ann. Phys. (N.Y.) 47, 40 (1968).

[29] V. Janovec, V. Dvorak, and J. Petzelt, Czech. J. Phys. B 25, 1362 (1975).

[30] S. Aubry and R. Pick, J. Phys. (Paris) 32, 657 (1971).

[31] K. Aizu, J. Phys. Chem. Solids 32, 1959 (1971).

[32] V. Dvorak, Ferroelectrics 7, 1 (1974).

[33] H. Z. Cummins, in Light Scattering Near Phase Transitions, edited by A. P. Levanyuk and H. Z. Cummins (North-Holland, Amsterdam, in press).

[34] A. P. Levanyuk and D. G. Sannikov, Usp. Fiz. Nauk 112, 561 (1974) [Sov. Phys.—Usp. 17, 199 (1974)].

[35] A. P. Levanyuk and D. G. Sannikov, Fiz. Tverd. Tela (Leningrad) 17, 526 (1975) [Sov. Phys.—Solid State 17, 327 (1975)].

[36] P. Toledano, M. M. Fejer, and B. A. Auld (unpublished).

[37] K. Brugger, J. Appl. Phys. 36, 759 (1965).

[38] R. A. Cowley, Phys. Rev. B 13, 4877 (1976).

[39] P. B. Ghate, Indian J. Phys. 39, 257 (1965).

[40] D. Y. Chung and Y. Li, Acta Crystallogr. A 30, 1 (1979).

[41] P. S. Peercy and I. J. Fritz, Phys. Rev. Lett. 32, 466 (1979).

[42] P. S. Peercy, I. J. Fritz, and G. A. Samara, J. Phys. Chem. Solids 36, 1105 (1975).

[43] T. G. Worlton and R. A. Beyerlein, Phys. Rev. B 12, 1899 (1975).

[44] D. B. McWhan, R. J. Birgeneau, W. A. Bonner, H. Taub, and J. D. Axe, J. Phys. C 8, L81 (1975).

[45] I. J. Fritz and P. S. Peercy, Solid State Commun. 16, 1197 (1975).

[46] G. Arlt and H. Schweppe, Solid State Commun. 6, 4692 (1969).

[47] N. Uchida and Y. Ohmachi, J. Appl. Phys. 40, 4692 (1969).

[48] E. F. Skelton, J. L. Feldman, C. Y. Liu, and I. L. Spain, Phys. Rev. B 13, 2605 (1976).

[49] H. Uwe and H. Tokumoto, Phys. Rev. B 19, 3700 (1979).

[50] P. Toledano and G. Pascoli, in *Symmetries and Broken Symmetries in Condensed Matter Physics,* edited by N. Boccara (IDSET, Paris, 1981), p. 231.

[51] V. P. Sakhnenko and V. M. Talanov, Fiz. Tverd. Tela (Leningrad) 22, 785 (1980) [Sov. Phys.—Solid State 21, 1401 (1980)].

[52] P. W. Anderson and E. I. Blount, Phys. Rev. Lett. 14, 217 (1965).

[53] Yu. M. Gufan and V. P. Sakhnenko, Fiz. Tverd. Tela (Leningrad) 14, 1915 (1972) [Sov. Phys.—Solid State 14, 1660 (1973)].

[54] J. D. Axe and Y. Yamada, Phys. Rev. B 24, 2567 (1981).

[55] B. W. Batterman and C. S. Barrett, Phys. Rev. Lett. 13, 390 (1964).

[56] B. W. Batterman and C. S. Barrett, Phys. Rev. 145, 296 (1966).

[57] G. Bilbro and W. L. McMillan, Phys. Rev. B 14, 1887

(1976).

[58] For a general review, see L. R. Testardi, *Physical Acoustics* 10, 193 (1973).

[59] J. R. Batel and B. W. Batterman, Phys. Rev. 148, 662 (1966).

[60] L. R. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Lett. 15, 280 (1965).

[61] R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Status Solidi 32, K67 (1969).

[62] L. R. Testardi, Phys. Rev. Lett. 31, 37 (1973).

[63] B. N. N. Achar and G. R. Barsch, Phys. Rev. B 19, 3761 (1979).

[64] G. R. Barsch, Solid State Commun. 14, 983 (1979).

[65] L. R. Testardi, Phys. Rev. B 5, 4342 (1972).

[66] G. Shirane, J. D. Axe, and R. J. Birgeneau, Solid State Commun. 9, 397 (1971).

[67] L. R. Testardi, Rev. Mod. Phys. 47, 637 (1975).

[68] J. Noolandi and L. J. Sham, Phys. Rev. B 8, 2468 (1973).

[69] R. N. Bhatt and W. L. McMillan, Phys. Rev. B 14, 1007 (1976).

[70] J. Wanagel and B. W. Batterman, J. Appl. Phys. 41, 3610 (1970).

[71] L. R. Testardi and T. B. Bateman, Phys. Rev. 154, 402 (1966).

[72] B. S. Chandrasekhar, H. R. Ott, and B. Seeker, Solid State Commun. 39, 1265 (1981).

[73] L. J. Vieland, R. W. Cohen, and W. Rehwald, Phys. Rev. Lett. 26, 273 (1971).

[74] J. Zak, A. Casher, H. Gluck, and Y. Gur, *The Irreducible Representations of Space Groups* (Benjamin, New York, 1969).

[75] D. J. Gunton and G. A. Saunders, Solid State Commun. 12, 569 (1973).

[76] M. R. Madhava and G. A. Saunders, Phys. Rev. B 4, 2957 (1971).

[77] G. Shirane and J. D. Axe, Phys. Rev. B 4, 2957 (1971).

[78] L. H. Brixner, J. F. Whitney, F. G. Zumsteg, and G. A. Jones, Mater. Res. Bull. 12, 17 (1977).

[79] S. Tsunekawa and H. Takei, J. Phys. Soc. Jpn. 40, 1523 (1976).

[80] S. Tsunekawa and M. Tanaka, Phys. Status Solidi (A) 55, K1 (1979).

[81] M. Wada, Y. Nakayama, A. Sawada, S. Tsunekawa, and Y. Ishibashi, J. Phys. Soc. Jpn. 47, 1575 (1979).

[82] H. Schulz, K. H. Thiemann, and J. Fenner, Mater. Res. Bull. 9, 1525 (1974).

[83] H. R. Weber, B. C. Tofield, and P. F. Liao, Phys. Rev. B 11, 1152 (1975).

[84] J. C. Toledano, G. Errandonea, and J. P. Jaguin, Solid State Commun. 20, 905 (1976).

[85] D. L. Fox, J. F. Scott, and P. M. Bridenbaugh, Solid State Commun. 18, 111 (1976).

[86] G. Errandonea and J. Sapriel, Solid State Commun. 32, 391 (1979).

[87] G. Errandonea, Phys. Rev. B 21, 5221 (1980).

[88] G. Errandonea, Ferroelectrics 26, 673 (1980).

[89] N. R. Ivanov, L. A. Shuvalov, H. Schmidt, and E. Stolp, Izv. Akad. Nauk. SSSR 39, 933 (1975).

[90] L. A. Shuvalov, N. R. Ivanov, and T. K. Sitnik, Kristallografiya 12, 366 (1967) [Sov. Phys.—Crystallogr. 12, 315 (1967)].

[91] Y. Makita, F. Sakurai, T. Osaka, and I. Tatsuzaki, J. Phys. Soc. Jpn. 42, 518 (1977).

[92] G. G. Kessenikh, C. VanKuin, and G. Schmidt, Izv. Akad. Nauk SSSR 43, 1701 (1979) [Bull. Acad. Sci. USSR Phys. Ser. 43, 130 (1979)].

[93] R. J. Elliott, A. P. Young and S. R. P. Smith, J. Phys. C 4, L317 (1971).

[94] R. J. Elliott, R. T. Harley, W. Hayes and S. R. P. Smith, Proc. R. Soc. London Ser. A 138, 217 (1972).

[95] J. Sivardiere, Phys. Rev. B 6, 4284 (1972).

[96] J. R. Sandercock, Solid State Commun. 11, 729 (1972).

[97] R. L. Melcher, E. Pytte, and B. A. Scott, Phys. Rev. Lett. 31, 307 (1973).

[98] B. B. Owens and O. R. Argne, Science 157, 308 (1967).

[99] S. Geller, Science 157, 310 (1967).

[100] F. L. Lederman, M. B. Salamon, and H. Peisl, Solid State Commun. 19, 147 (1976).

[101] L. J. Graham and R. Chang, J. Appl. Phys. 46, 2433 (1975).

[102] J. B. Godenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).

[103] J. Kanamori, M. Kataoka, and Y. Itoh, J. Appl. Phys. 30, 688 (1968).

[104] M. Kataoka and J. Kanamori, J. Phys. Soc. Jpn. 32, 113 (1972).

[105] J. D. Bierlein and A. W. Sleight, Solid State Commun. 16, 69 (1975).

[106] A. Pinczuk, G. Burns, and F. H. Dacol, Solid State Commun. 24, 163 (1977).

[107] A. Pinczuk, B. Welber, and F. H. Dacol. Solid State Commun. 29, 515 (1979).

[108] E. F. Dudnik, V. V. Gene, and I. E. Mnushkina, Izv. Akad. Nauk SSSR 43, 149 (1979) [Bull. Acad. Sci. USSR Phys. Ser. 43, 1723 (1979)].

[109] Gu Benyuan, M. Copic, and H. Z. Cummins, Phys. Rev. B 24, 4098 (1981).

[110] J. C. Raich, Solid State Commun. 29, 335 (1979).

[111] J. C. Raich and A. Huller, J. Chem. Phys. 70, 3669 (1979).

[112] G. J. Simonis and C. E. Hathaway, Phys. Rev. B 10, 4419 (1979).

[113] J. H. Smith and A. I. M. Rae, J. Phys. C 11, 1761 (1978).

[114] J. K. Solbakk and K. O. Stromme, Acta Chem. Scand. 23, 300 (1969).

[115] B. Dvorak, Phys. Status Solidi B 52, 93 (1972).

[116] D. G. Sannikov, Fiz. Tverd. Tela (Leningrad) 20, 837 (1978) [Sov. Phys.—Solid State 20, 485 (1978)].

[117] Yu. M. Gufan and G. M. Chechin, Kristallografiya 25, 453 (1980) [Sov. Phys.—Crystallogr. 25, 261 (1980)].

[118] G. Ya. Lyubarskii, *The Application of Group Theory in Physics* (Pergamon, New York, 1960).

[119] Recently published results [M. P. Brassington and G. A. Saunders, Phys. Rev. Lett. 48, 159 (1982)] reveal that the situation in In-Tl alloys is indeed similar to the one described in this paper for V_3Si. In particular, the

smallness of the cubic invariant (i.e., the very weak first-order character of the corresponding ferroelastic transition) appears to be a common property among metallic alloys undergoing a fcc-to-fct transition.

[120] F. Milstein and D. Rasky, Philos. Mag. A 45, 49 (1982).

[121] J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1960).