The Elastic Constants of Crystals

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I. General Considerations

1. INTRODUCTION

The elastic properties of solid matter hold interest for both technology and basic research. In the first field applied elasticity is an important discipline for those fundamental considerations of engineering design which are usually included under the designation "strength of materials." The treatment of structural materials requires semiempirical methods, because their compositions are complex and prior treatment has a pronounced effect. On the other hand, basic research into elastic properties is usually concerned with work on specimens in the simplest state which can be obtained reproducibly, e.g., annealed single crystals. The complete tabulation of elastic constants for such specimens is valuable, not only for itself, but also because the data can be correlated with other physical measurements and thereby provide possible insight into the nature of the atomic forces in solid matter.

The research aspect of elastic studies will be of primary interest for this review. In general, consideration will be limited to inorganic, crystalline materials. For the most part, interest has been focused on the properties of single crystals. Even with these limitations, the amount of material to be covered is very large. To maintain a reasonable length and enhance readability, the detailed analysis has been restricted. Bulky expressions for the transformation of coordinates and similar relations have been curtailed. The character of the tables has been designed to be more representative than comprehensive.

A brief description of the various parts of the article follows. Part I deals with general considerations. Here the formalism of elasticity and the associated definitions appear. The stresses, strains and elastic constants are introduced in the notation of Voigt and Love. The alternative representation of the tensor notation is also stressed. The simplifications which result from the various crystal symmetries and from isotropy are then pointed out. The current theoretical approaches to elastic constants are considered from two different points of attack, one based on a generalized force model as propounded by Born and co-workers, and the other based on attempts to evaluate elastic constants directly from the fundamental considerations of quantum mechanics. The first approach offers a convenient opportunity to discuss the Cauchy relations and the conditions for their validity. The question of whether local rotations and torques

should appear in the elastic matrix is also considered at length in this section. Brief mention is made of tensor properties other than the elastic constants which may enter in the complete formulation of the thermodynamic potentials of various materials. The third-order elastic constants receive special consideration. The final section of Part I deals with the interrelationship of the elastic constants and other physical quantities.

Part II treats methods of measurement and is necessarily cursory rather than complete. The various techniques are indentified and described briefly with concern for general principles only.

In Part III representative elastic data are presented for various pure substances, organized into tables according to crystal symmetry. An effort has been made to keep the tables concise even at the cost of some arbitrariness in the selection of material. For example where two or more experimenters are in reasonable accord only one set of data is given. Also the tables include for the most part only the results for the elements and reasonably well-known compounds. For a more comprehensive compilation of elastic data the reader is referred to two excellent review articles by R. F. S. Hearmon.[1]

The various sections of Part III treat with different types of materials —their elastic properties, and particularly the theoretical interpretation of these properties in terms of basic atomic models. In the last section of Part III a brief account is included of results for polycrystalline materials, particularly some which have not yet been studied in single crystal form. The problem of predicting the elastic properties of polycrystalline aggregates from the elastic constants of single crystals is also discussed.

In Part IV the dependence of the elastic constants on temperature and pressure is presented for a variety of materials. The theory of the thermal variation of the elastic constants is developed from the standpoint of the idealized equation of state. Particular application is made to a central force model for the alkali halides.

Many factors which influence elastic behavior are not treated in an idealized equation of state. In Part V the presence of unwanted impurities, intentional alloying, phase transitions, dislocation motion, and radiation damage are considered for their effects on the elastic parameters. The action of each of them involves to a greater or less degree the relaxation of some element. A short section on relaxation phenomena serves as an introduction to Part V. In the final sections two particular low-temperature effects are discussed, one associated with the superconducting transition and the other with electron damping.

[1] R. F. S. Hearmon, *Revs. Modern Phys.* **18**, 409 (1946), and R. F. S. Hearmon, *Advances in Phys.* **5**, 323 (1956); referred to hereafter as Hearmon I and Hearmon II, respectively.

2. Stresses and Strains

The formal concepts of elasticity theory will next be introduced. In the unstrained medium one may establish a Cartesian coordinate system with coordinates x_1, x_2, and x_3. If the material is homogeneously stressed, then every volume element is subject to a force acting at the bounding surface. Let the force acting on the element of surface ΔA_j (perpendicular
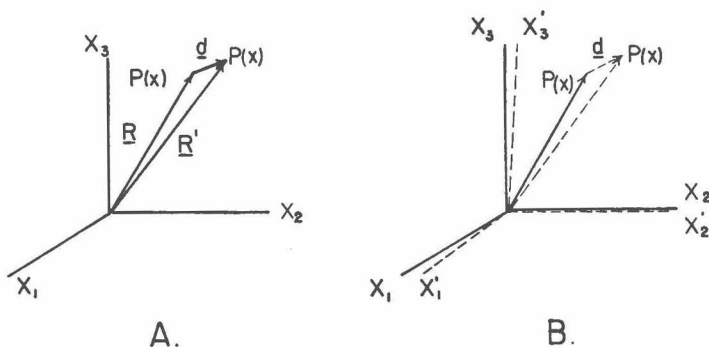
Fig. 1. Elastic displacement in medium. A. Coordinate system fixed in space. B. Coordinate system fixed in medium.

to the j axis) have components ΔF_i. The tensor T_{ij} is then defined as the limit approached by the ratio of ΔF_i to ΔA_j as ΔA_j goes to zero,

$$T_{ij} = \lim_{\Delta A_j \to 0} \frac{\Delta F_i}{\Delta A_j}. \tag{2.1}$$

The symmetric part of T_{ij} is the stress tensor, whereas the antisymmetric part is the density of the resultant torque. The latter is generally neglected by elastic theory. According to the usual sign convention the normal stresses, or T_{ii}, are tensions when positive. The T_{ij}, for $i \neq j$, are the shear stresses.

When the material is strained, each point moves to a new position. For a general point with initial position vector $\mathbf{r}$, the position vector $\mathbf{r}'$ after deformation is given by

$$\mathbf{r}' = \mathbf{r} + \mathbf{d} \tag{2.2}$$

where $\mathbf{d}$ is the vector displacement, having components u, v, w (see Fig. 1A). The explicit dependence of $\mathbf{d}$ on the original x_i is apparent. From derivatives of its components (u, v, w) with respect to the x_i coordinates

(x, y, z) one defines the strains in the traditional manner:[2]

$$e_{11} = \frac{\partial u}{\partial x}; \qquad e_{22} = \frac{\partial v}{\partial y}; \qquad e_{33} = \frac{\partial w}{\partial z};$$
$$e_{23} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}; \qquad e_{13} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}; \qquad e_{12} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}. \qquad (2.3)$$

The e_{ii} are the normal strains and are positive when the medium is extended. The dilation, or fractional change in volume, is given by their sum,

$$\delta = \frac{\Delta V}{V} = e_{11} + e_{22} + e_{33}. \qquad (2.4)$$

The nondiagonal components of e_{ij}, for which i is not equal to j, are the shear strains. If the medium is homogeneously strained, it is
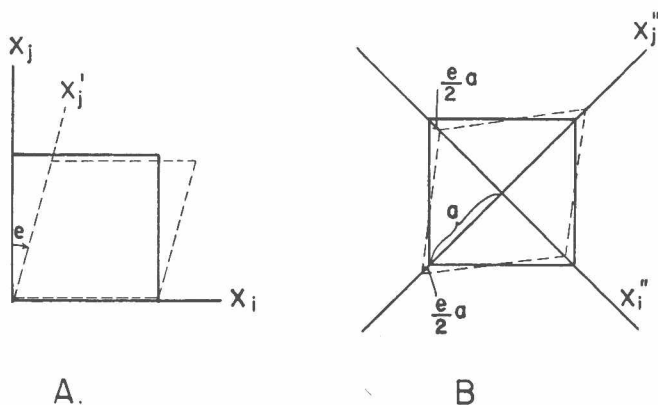
Fig. 2. Transformation of shear strain to normal axes. Rotation of axes by 45° makes shear strain in A appear as compression and expansion along the new axes in B.

possible to establish a new, non-Cartesian coordinate system in which the points of the strained medium retain their old coordinates in their new locations (see Fig. 1B). Small changes in angles between the new axes (which were formerly 90° in the Cartesian system) are given by the nondiagonal e_{ij}. It is of interest to observe that, if a single shear strain $e_{ij} = e$ is present, a rotation of 45° of the i, j axes in their common plane changes the form of the strain into an extension $\frac{1}{2}e$ along one of the transformed axes and a compression $\frac{1}{2}e$ along the other (see Fig. 2). We shall have occasion to make use of this relation later in discussing the condition for isotropy.

[2] A. E. H. Love, "Mathematical Theory of Elasticity," p. 38. Dover, New York, 1944.

We have seen that the descriptions of both stress and strain involve six quantities identifiable by a double subscript notation. Both quantities are symmetric with respect to an interchange of the subscripts. It will be convenient in many situations to abbreviate the double subscript notation to a single subscript, running from 1 to 6, according to the following scheme:

$$11 \rightarrow 1, \ 22 \rightarrow 2, \ 33 \rightarrow 3, \ 23 \rightarrow 4, \ 13 \rightarrow 5, \text{ and } 12 \rightarrow 6.$$

For example, $e_{33} = e_3$ and $T_{13} = T_5$.

A complete description of the displacement vector requires also the specification of the three components of infinitesimal rotation, ω_{ij}. The ω_{ij} constitute an axial vector which is the antisymmetric part of the $\partial u_i / \partial x_j$ tensor. The complete expression for the variation of the displacement with position can accordingly be written:

$$du_i = \tfrac{1}{2} \sum_j \{(e_{ii}\delta_{ij} + e_{ij}) + 2\omega_{ij}\}dx_j. \tag{2.5}$$

The function representing the stored elastic energy occupies a fundamental position in the theory of the elastic constants. Its existence was first postulated by Green and was later firmly established by Lord Kelvin.[3] Let us introduce a Cartesian coordinate system x_i in a volume V, which is initially stress-free. After a displacement with components u_i has occurred, one can write the First Law of Thermodynamics for the volume V under stress in the form

$$
\begin{aligned}
\delta U &= \delta Q + \int \mathbf{F_b} \cdot \delta \mathbf{u} \rho dV + \int \mathbf{F_s} \cdot \delta \mathbf{u} dS \\
&= \delta Q + \int \sum_i F_i \delta u_i \rho dV + \int \sum_{ij} T_{ij} \delta u_i dS_j
\end{aligned}
\tag{2.6}
$$

where δU and δQ are respectively the change in internal energy and the heat flow accompanying the displacement $\delta \mathbf{u}$. The second and third terms on the right-hand side give respectively the work done by the body forces per unit mass, F_b (having components F_i), and that done by the surface forces, F_s which give rise to the stresses T_{ij}.

For an adiabatic process $\delta Q = 0$. An application of Green's theorem to the surface integral leads to the relation

$$\delta U = \int \sum_i \left(F_i \rho + \sum_j \frac{\partial T_{ij}}{\partial x_j} \right) \delta u_i dV + \int \sum_{ij} T_{ij} \frac{\partial (\partial u_i)}{\partial x_j} dV. \tag{2.7}$$

[3] "Mathematical and Physical Papers by Sir William Thomson," Vol. 1, p. 291. Cambridge, 1882. The treatment shown here is taken from pp. 92–99 in ref. 2.

The first term on the right gives the work done by the unbalanced force on the center of mass of the volume V, or the change in kinetic energy of the system. If one regards δU as the sum of the change in kinetic energy and the strain energy δW stored by elastic deformation during the displacement $\delta \mathbf{u}$ and takes $\partial(\delta \mathbf{u}_i)/\partial x_j$ from (2.5), one obtains

$$\delta W = \tfrac{1}{2} \int \sum_{ij} T_{ij}[\delta e_{ij}(1 + \delta_{ij}) + 2\omega_{ij}]dV. \tag{2.8}$$

If there is no torque density in V, then the part involving the ω's vanishes from symmetry. We may introduce a stored energy density function w

$$\delta w = \sum_{i \geq j} T_{ij}\delta e_{ij}. \tag{2.9}$$

Since δw is a perfect differential, it follows that

$$T_{ij} = \frac{\partial w}{\partial e_{ij}}. \tag{2.10}$$

A similar result is also valid for an isothermal process, although δQ does not vanish in this case. By an application of the Second Law of Thermodynamics δQ can be shown to be a state function, i.e., independent of the isothermal process by which the final state is attained. For the isothermal case δW is a state function and is equal to δU minus the sum of δQ and the change in kinetic energy. The properties of δw follow as before.

3. THE MODULI OF ELASTICITY AND COMPLIANCE

a. *Traditional Elasticity*

The usual starting point for elasticity theory is the postulation of Hooke's law, which states that stress is proportional to strain for sufficiently small strains. Its generalized statement for an anisotropic medium may be taken as

$$T_i = \sum_{j=1}^{6} c_{ij}e_j. \tag{3.1}$$

The constants of proportionality introduced hereby (c_{ij}) are called the elastic constants, stiffness constants, or the moduli of elasticity. The set of linear, homogenous, independent equations represented by (3.1) can be solved for the e's in terms of the T's and leads to the relations

$$e_i = \sum_{j=1}^{6} s_{ij}T_j. \tag{3.2}$$

The components of the inverse matrix s_{ij} are called the moduli of compliance. The c's have the dimensions of force per unit area, or energy per unit volume, and will be expressed throughout this paper in units of 10^{11} dynes/cm². The s_{ij} have reciprocal dimensions and will be given in units of 10^{-12} cm²/dyne.

It would appear that the 6 by 6 array of constants of either type would contain 36 independent quantities in the most general case. This number is, however, reduced to 21 by the requirement that the matrices be symmetric on interchange of the double indices. This condition follows from the existence of the strain-energy density w. The symmetry of the c_{ij} with respect to interchange of the subscripts is proved by applying the conditions of compatibility, Eq. (2.10) and Eq. (3.1):

$$c_{ij} = \frac{\partial T_i}{\partial e_j} = \frac{\partial^2 w}{\partial e_j \partial e_i} = \frac{\partial^2 w}{\partial e_i \partial e_j} = \frac{\partial T_j}{\partial e_i} = c_{ji}. \tag{3.3}$$

Moreover the assumption of linearity between stress and strain allows (2.9) to be integrated directly giving

$$w = \tfrac{1}{2} \sum_{j \geq 1} T_{ij} e_{ij}. \tag{3.4}$$

The number of independent elastic constants will be further reduced by the symmetry operations of the respective crystal classes. For example there are only 9 independent constants for the orthorhombic classes, 5 for the hexagonal classes, and 3 for the cubic classes (see Fig. 5 described in Section 5). In all but the triclinic classes the effect of crystal symmetry is revealed by the presence of zeros and repeated elements among the matrix components. To investigate the effect of a particular symmetry operation on the elastic matrix one develops expressions for the strains in a transformed coordinate system obtained from the original by the symmetry operation. The expression for the elastic energy w (3.4) in terms of the transformed strains is then equated identically to the original w. The resulting equations between the coefficients of corresponding strain products give the relations which reduce the number of independent elastic constants. As an example of how such relations are derived, we consider a plane which is known to be elastically isotropic and develop the expression for the strain energy density arising from a pure shear strain in this plane, say $e_{12} = e$. We equate this expression for w to that obtained from a comparable strain rotated through 45°. It has been pointed out earlier that the comparable strain consists of a compression $-e/2$ along one axis and an expansion $+e/2$ along the other. As a result

we obtain

$$w(e) = \tfrac{1}{2}c_{66}e^2 = \tfrac{1}{2}(c_{11} - 2c_{12} + c_{22})e^2/4$$

or

$$c_{66} = \tfrac{1}{2}(c_{11} - c_{12}). \tag{3.5}$$

This relation between the elastic constants is typical of isotropic conditions. For example, inspection of the hexagonal classes in Fig. 5 shows that c_{66} is replaced by $\tfrac{1}{2}(c_{11} - c_{12})$—a consequence of the elastic isotropy in the basal plane. For the isotropic medium there are only two independent elastic moduli as one can show by requiring that the constants for cubic symmetry satisfy the condition of (3.5).

The case of the isotropic medium is important both for the chronological development of the subject of elasticity and also for its applicability to polycrystals and glasses. At this point we digress briefly to define the terms which appear most frequently in its description.

The Lamé constants, λ and μ, are the pair most usually chosen to appear in the matrix of the elastic moduli. The shear constant μ replaces c_{44}, c_{55}, and c_{66} while the other λ replaces c_{12}, c_{23}, and c_{13} to give the following matrix:

$$
\begin{array}{cccccc}
\lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu
\end{array}
$$

Equation (3.5) has been used to obtain the quantity $(\lambda + 2\mu)$ which replaces c_{11}, etc.

Another important constant is Young's modulus which is defined as the ratio of the uniaxial stress exerted on a thin rod to the resulting normal strain in the same direction. Since all other stresses vanish, the equations for the strains are:

$$
\begin{aligned}
T &= (\lambda + 2\mu)e_1 + \lambda e_2 + \lambda e_3 \\
0 &= \lambda e_1 + (\lambda + 2\mu)e_2 + \lambda e_3 \\
0 &= \lambda e_1 + \lambda e_2 + (\lambda + 2\mu)e_3.
\end{aligned} \tag{3.6}
$$

It is apparent that $e_2 = e_3$ and that

$$\sigma = -e_2/e_1 = \frac{\lambda}{2(\lambda + \mu)}. \tag{3.7}$$

Here the quantity σ is called Poisson's ratio and is defined as the negative of the ratio of the strains perpendicular and parallel to the uniaxial stress

on a thin rod. The expression for the Young's modulus can now be written

$$E = \mu(2\mu + 3\lambda)/(\lambda + \mu). \tag{3.8}$$

The bulk modulus B is defined for materials under hydrostatic pressure as the ratio of the applied pressure to the negative dilatation. For the isotropic case one obtains

$$B = V\frac{\partial P}{\partial V} = (3\lambda + 2\mu)/3. \tag{3.9}$$

For anisotropic materials the normal strains may not all be equal even under hydrostatic loading. The reciprocal of the bulk modulus is called the compressibility and will be denoted by β.

Although these quantities have been introduced primarily with reference to isotropic materials, they appear in the literature in more general connections. For example one finds frequent use of such symbols as E_{111} meaning the ratio of stress to parallel strain for a uniaxially thin rod oriented in the [111] direction. Similarly a quantity σ_{12} is frequently used to denote the ratio of the strains along two orthogonal axes 1 and 2 when the specimen is loaded uniaxially along the 1 axis. Similarly the quantity β_i is used to denote the ratio of the strain along the ith axis to the hydrostatic pressure.

b. *Tensor Notation and Equations of Motion*

The conventional formulation of classical elasticity suffers from the disadvantage that the strains are not presented in tensor form. As a result any transformation of coordinates requires an involved treatment. An alternate formulation which utilizes the conciseness and economy of the tensor presentation has been developed by Sokolnikoff and others.[4] Their alternate expression for the strains is:

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \tag{3.10}$$

The ϵ_{ij} so defined show their tensor properties in the manner of their transformation under a change of coordinates. Contravariant tensors of the first order transform like Cartesian coordinates

$$\bar{x}^i = \alpha_j{}^i x^j \tag{3.11}$$

where $\alpha_j{}^i = (\partial \bar{x}^i/\partial x^j)$. The use of repeated indices (j in this case) indi-

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[4] I. S. Sokolnikoff, "Mathematical Theory of Elasticity." McGraw-Hill, New York, 1946; W. A. Wooster, "Crystal Physics." Cambridge Univ. Press, London and New York, 1938; also J. F. Nye, "Physical Properties of Crystals." Clarendon Press, Oxford, 1957,

cates summation according to the tensor convention. For general coordinate transformations the distinction between upper (contravariant) and lower (covariant) indices must be preserved. The distinction can be dispensed with, however, when the transformation involves only Cartesian coordinate systems under infinitesimal distortion, as is the case in linear elasticity. With this simplification the transformation of the strain tensor has the general form

$$\bar{\epsilon}_{ij} = \alpha_{ik}\alpha_{jl}\epsilon_{kl}. \tag{3.12}$$

It is noteworthy that the same expression (3.10) defines the ϵ_{ij} whether $i = j$ or $i \neq j$, as contrasted to the case for the e_{ij} (2.3). The relations between the new ϵ_{ij} and the original e_{ij} are obviously $\epsilon_{ii} = e_{ii}$ and $\epsilon_{ij} = \frac{1}{2}e_{ij}$ for $i \neq j$.

To express Hooke's law in tensor notation it is necessary to treat the elastic moduli as the components of a tensor of fourth order,

$$T_{ij} = c_{ijkl}\epsilon_{kl}. \tag{3.13}$$

The transformation law for such a tensor is for the case of simple rotation

$$\bar{c}_{ijkl} = c_{rstv}\alpha_{ir}\alpha_{js}\alpha_{kt}\alpha_{lv}. \tag{3.14}$$

This expression which represents quite an involved relation provides much the simplest method for determining the components of the c's in a new coordinate system. Comparing Eqs. (3.1) and (3.13) with the aid of (3.10) shows that

$$c_{ijkl} = c_{uv} \tag{3.15}$$

where the double indices i, j, and k, l have been contracted to u and v respectively in accordance with the convention previously introduced. Although it might appear *a priori* that the tensor c would possess 81 independent components, Eq. (3.15) shows that the number cannot be more than 21. This reduction is a consequence of the fact that the tensor is symmetrical with respect to the interchange of i and j, k and l, and ij and kl.

By solving (3.13) for the ϵ_{ij} in terms of the T_{kl} one finds in the inverse matrix tensor formulation for the elastic compliances,

$$\epsilon_{ij} = s_{ijkl}T_{kl}. \tag{3.16}$$

The ensuing relationship between the tensor compliances and the traditional s_{uv} is more complicated than the analogous (3.15). Again from (3.10) one can show

$$s_{ijkl} = s_{uv}, \text{ if } u \text{ and } v \text{ are both 3 or less}$$
$$s_{ijkl} = \frac{1}{2}s_{uv}, \text{ if either (but not both) } u \text{ or } v \text{ is greater than 3}$$
and $\quad s_{ijkl} = \frac{1}{4}s_{uv}, \text{ if both } u \text{ and } v \text{ are greater than 3.} \tag{3.17}$

In the equations of motion for an elastic medium, the forces on an element of volume, are given by the divergence of the stress field,

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial T_{ij}}{\partial x_j} = \frac{\partial}{\partial x_j} \left\{ c_{ijkl} \frac{1}{2} \left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) \right\} \tag{3.18}$$

where ρ is the mass density. For the particular case of an elastic plane wave one can take $u_k = A_k \exp i(\omega t - \mathbf{k} \cdot \mathbf{x})$ where the A_k are the amplitude of the vibration components, ω is the angular frequency and $\mathbf{k}$ is the wave-number vector corresponding to the wavelength $\lambda = 2\pi/|\mathbf{k}|$. The resulting equations of motion, which are called the Christoffel equations, follow:

$$\rho \omega^2 A_i = c_{imjn} A_j k_m k_n. \tag{3.19}$$

In this form the equations constitute the basis for the "long wave" method that Born used to develop the elastic constants from a lattice theory (see Section 4). For applications to actual situations in which elastic constants are determined from plane wave propagation (see Section 8) it is usually preferable to transform to a coordinate system in which the direction of propagation is one of the axes, say x_1. In this situation all terms in (3.19) which involve differentiation with respect to coordinates other than that along the propagation direction then drop out. The result is

$$\rho v^2 A_i = c'_{iljl} A_j \tag{3.20}$$

where c_{ij}' are the elastic constants in the transformed coordinate system and v is the velocity of propagation. The values for v are obtained from the secular determinant of (3.20) which must vanish in order that the A_i have non-zero values.

c. The Definition and Meaning of the Elastic Constants

Before proceeding further we should examine critically the concept of the elastic constants. This concept was introduced on an empirical basis in the formulation of Hooke's law (3.1). A more fundamental significance to the elastic constants, however, is implied by their appearance as the second derivatives of w, the elastic energy density, with respect to the strains (3.3). Putting aside the somewhat simplified groundwork of familiar concepts used so far, we are faced with questions concerning the existence and nature of w itself. It should first be pointed out that the stored elastic energy is properly only a part of the complete thermodynamic potential ϕ of the crystal. In general ϕ depends on many other variables, such as the electric polarization, the magnetization, and the temperature and contains cross-product terms involving piezoelectric,