

NONLINEAR ELASTICITY OF DIATOMIC CRYSTALS

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Abstract—We here explore symmetry considerations which seem to us relevant for simpler mechanical theories of ideal diatomic crystals, using elasticity theory for illustrative purposes. These considerations differ from those commonly employed in continuum mechanics, though the two approaches seem not to be incompatible. In more microscopic views of crystals, similar ideas are encountered in discussions of slip or twinning.

1. INTRODUCTION

IN DEALING with nonlinear elasticity of crystalline solids, the practice has been to emulate what is done in the theory of infinitesimal deformations, requiring the strain energy to be invariant under one or another of the crystallographic groups. The conceptual basis for this seems to me less than crystal clear. As we see it, the conventional treatment is only appropriate for deformations which are small though not necessarily so small as to be considered infinitesimal. As is discussed below, there is some reason to think that additional symmetries are relevant for a theory of finite deformations. Previously, we [1] discussed this for monatomic lattices. These are too degenerate to illustrate typical problems which arise in polyatomic lattices. Diatomic lattices seem representative, so, for simplicity, we restrict our attention to these.

According to our views, such materials are not solids, as the latter are defined by Noll [2]. That is, their isotropy group is not contained in the orthogonal group. Neither are they fluids, in his sense. Said differently, their symmetry virtually forces them to exhibit phenomena which would commonly be considered to be inelastic. Broadly speaking, inelastic phenomena are commonplace in real crystals and there is a dearth of mathematical theory to describe them. We feel that the ideas here presented should be of some help in remedying this situation, though we do not claim to have in hand a theory adequate to describe their behavior.

We begin by reviewing ideas inherent in the classical molecular theory of elasticity for crystals†, then formulate a continuum analogue of this theory. With some reservations, it can be forced into the mold of nonlinear elasticity theory. Here, our goal is to clarify how the implied symmetry is to be accounted for, not to extract predictions from such theories.

2. LATTICES

By a monatomic lattice, we mean a set of points, with position vectors \mathbf{p}_N ($N = 1, 2, \dots$), relative to some common origin, which are representable in the form

$$\mathbf{p}_N = n_N^\alpha \mathbf{a}_\alpha. \quad (1)$$

† Stakgold [3] gives a more comprehensive survey.

Here and below, Greek indices take on values 1, 2, 3, repeated indices indicating the usual summation. In (1) the three lattice vectors \mathbf{a}_α are assumed to be linearly independent and the n 's range over all rational integers. Such points may be thought of as the locations of identical mass points, so that one is in no way distinguished from any other. The lattice does not uniquely determine the lattice vectors, doing so only to within transformations of the form

$$\bar{\mathbf{a}}_\alpha = m_\alpha^\beta \mathbf{a}_\beta, \quad (2)$$

where the m 's are any rational integers such that

$$\det m_\alpha^\beta = \pm 1. \quad (3)$$

Such m 's form a group \mathcal{S} , group multiplication being the obvious matrix multiplication. It or, more accurately, a group conjugate to it can be considered as the isotropy group for such crystals, at least in the context of elasticity theory. Briefly, this describes the thesis which we [1] previously expounded.

It is not unusual for crystals made up of a single kind of atoms to arrange themselves in more complicated periodic structures. In the classical scheme, various possibilities are included by regarding these structures as somewhat degenerate polyatomic lattices.

A diatomic lattice consists of two monatomic lattices, one differing from the other by a uniform translation. Atoms in one may differ from those in the other. We here regard them as distinguishable. If they are not, equation (5) should be modified to reflect the indistinguishability of \mathbf{p} and $-\mathbf{p}$.

If \mathbf{p}_N and $\hat{\mathbf{p}}_N$ represent the two sets of position vectors, suitably labelled, one, say \mathbf{p}_N , is representable in the form (1), the other being represented by

$$\hat{\mathbf{p}}_N = \mathbf{p}_N + \mathbf{p}, \quad (4)$$

the constant vector \mathbf{p} denoting some translation which would bring the two into coincidence. It is easily seen that the two lattices determine \mathbf{p} only to within transformations of the form

$$\bar{\mathbf{p}} = \mathbf{p} + n^\alpha \mathbf{a}_\alpha, \quad (5)$$

where the n 's are rational integers. Of course, there is the possibility of referring the two lattices to different lattice vectors, related by transformations of the type (2), but we do not require this flexibility.

It is common to impose geometrical restrictions to limit possible choices of \mathbf{a}_α and \mathbf{p} , for example demanding that \mathbf{p} have the shortest possible length. Roughly, the reason we don't is that we envisage lattice distortions which need not preserve such relations.

In the classical molecular theory of elasticity, such models of crystals are supplemented by special assumptions concerning deformations of the lattice, central force laws for the atoms and definitions of strain energy or stress in terms of microscopic quantities. Concerning deformation of diatomic lattices, the idea is as follows: we start with a lattice referred to lattice vectors \mathbf{A}_α , relative translation \mathbf{P} , in static equilibrium. The lattice vectors undergo a linear transformation

$$\mathbf{A}_\alpha \rightarrow \mathbf{a}_\alpha = \mathbf{F}\mathbf{A}_\alpha, \quad \det \mathbf{F} > 0, \quad (6)$$

\mathbf{F} being identified with a macroscopic deformation gradient. It is envisaged that \mathbf{P} will

change into another constant vector \mathbf{p} , though not necessarily that resulting from the same linear transformation. That is, in general,

$$\mathbf{P} \rightarrow \mathbf{p} \neq \mathbf{F}\mathbf{P}. \quad (7)$$

For given \mathbf{F} , the notion is that \mathbf{p} will take on some value permitting each atom to be subject to zero resultant force. Thus \mathbf{p} is related to \mathbf{F} in a complicated way, depending on the forms of the atomic force laws. The hope is to obtain \mathbf{p} as a smooth, single valued function of \mathbf{F} , reducing to \mathbf{P} when $\mathbf{F} = 1$. Cases normally considered involve small departures from a state which is, in a suitable sense, stable. When one or another of the implied properties of $\mathbf{p}(\mathbf{F})$ fails, it is almost a matter of definition that some instability will occur. With more general polyatomic crystals, the situation is much the same, except that \mathbf{p} is replaced by a set of vectors. Of course, there is no analogous problem for the monatomic lattice. Elasticity theory does not provide a good vehicle for discussing this type of question. Said differently, there might be some merit in converting from atomic to continuum theory before facing this question. Without doing the molecular calculations, it is fairly easy to see what type of continuum theory should result. The conventional apparatus is designed to produce theories of materials whose response is determined once it is known for homogeneous deformation and constant "polarization". Our views on symmetry are geared to similar theories, so one might well have reservations about applying them to theories less local in character.

We now attempt to make these ideas more coherent and more specific.

3. CONTINUUM THEORY

As suggested above, we consider materials whose "state" is determined by four vector fields, suggestively labelled as

$$\mathbf{p}, \quad \mathbf{a}_\alpha. \quad (8)$$

We introduce a scalar function W , representing stored energy per unit mass

$$W = W(\mathbf{p}, \mathbf{a}_\alpha). \quad (9)$$

It is assumed to be objective

$$W(\mathbf{R}\mathbf{p}, \mathbf{R}\mathbf{a}_\alpha) = W(\mathbf{p}, \mathbf{a}_\alpha), \quad (10)$$

for every rigid rotation

$$\mathbf{R}^{-1} = \mathbf{R}^T, \quad \det \mathbf{R} = 1. \quad (11)$$

Here, classical molecular theory would imply that (10) also holds for improper orthogonal transformations, i.e.

$$\det \mathbf{R} = -1. \quad (12)$$

Changes in \mathbf{a}_α are constrained by the requirement that they be derivable from fixed \mathbf{A}_α and a smooth deformation

$$\mathbf{X} \rightarrow \mathbf{x}(\mathbf{X}) \quad (13)$$

as material vectors. That is

$$\mathbf{a}_x = \mathbf{F}\mathbf{A}_x \tag{14}$$

where \mathbf{F} denotes the usual deformation gradient

$$\mathbf{F} = \nabla \mathbf{x}, \quad \det \mathbf{F} > 0. \tag{15}$$

Throughout, material coordinates \mathbf{X} are taken as independent variables, the usual practice in elasticity. We can now write

$$\hat{W} = \hat{W}(\mathbf{p}, \mathbf{F}) = W(\mathbf{p}, \mathbf{F}\mathbf{A}_x). \tag{16}$$

To obtain equations of equilibrium, one possibility is to assume a principle of virtual work such as applies to nonlinear elastostatics,

$$\delta \int \rho \hat{W} dV = \oint \mathbf{t} \cdot \delta \mathbf{x} dS + \int \mathbf{f} \cdot \delta \mathbf{x} dV, \tag{17}$$

the integration extending over a fixed reference configuration, with mass density ρ . Here \mathbf{t} and \mathbf{f} have the usual interpretations as surface and body forces. Though we won't, we could generalize this to include a generalized body force doing work in changing \mathbf{p} , possibly of some relevance in cases when electromagnetic fields are imposed. The only novelty in (17) involves the occurrence of \mathbf{p} , which is to be varied independently. We then get the equilibrium equations

$$\frac{\partial \hat{W}}{\partial \mathbf{p}} = 0, \tag{18}$$

$$\nabla \cdot \mathbf{T} + \mathbf{f} = 0, \tag{19}$$

$$\mathbf{T} = \rho \frac{\partial \hat{W}}{\partial \mathbf{F}}, \tag{20}$$

plus natural boundary conditions of traction type, which we do not require. Here, (18) is analogous to the equilibrium equation arising in molecular theory, to be solved for \mathbf{p} in terms of \mathbf{F} . Formally, suppose (18) is satisfied by a certain smooth function

$$\mathbf{p} = \mathbf{p}(\mathbf{F}). \tag{21}$$

With (10), there is no loss in generality in assuming it is objective

$$\mathbf{p}(\mathbf{R}\mathbf{F}) = \mathbf{R}\mathbf{p}(\mathbf{F}). \tag{22}$$

With this, we can write

$$\bar{W} = \bar{W}(\mathbf{F}) = \hat{W}[\mathbf{p}(\mathbf{F}), \mathbf{F}] \tag{23}$$

with

$$\bar{W}(\mathbf{R}\mathbf{F}) = \bar{W}(\mathbf{F}). \tag{24}$$

Then, because (18) holds,

$$\frac{\partial \bar{W}}{\partial \mathbf{F}} = \frac{\partial \hat{W}}{\partial \mathbf{F}}. \tag{25}$$

We then arrive at elasticity theory. Of course, there is the possibility of nonuniqueness of solutions of (18) for \mathbf{p} which could lead to different determinations of \bar{W} , etc.

We should now face the question of what invariance requirements should be imposed on W , other than (10), to account for material symmetries, presuming we are concerned with the diatomic crystals described before. Presumably, these should derive from the group obtained by combining (2), (5) and (10). To sum up, we should single out some subgroup, if not the entire group of transformations represented by

$$\bar{\mathbf{a}}_\alpha = \mathbf{R}m_\alpha^\beta \mathbf{a}_\beta, \tag{26}$$

$$\bar{\mathbf{p}} = \mathbf{R}(\mathbf{p} + n^\alpha \mathbf{a}_\alpha), \tag{27}$$

where the m 's and n 's are rational integers and

$$\det m_\alpha^\beta = \pm 1, \quad \mathbf{R}^{-1} = \mathbf{R}^T, \quad \det \mathbf{R} = \pm 1. \tag{28}$$

In writing (10), we have already assumed one subgroup applies, that with $m_\beta^\alpha = \delta_\beta^\alpha$, $n^\alpha = 0$ and $\det \mathbf{R} = 1$. Some, but not all of the extended group of transformations can be accomplished by continuously varying \mathbf{p} and \mathbf{a}_α , keeping the \mathbf{a}_α linearly independent. Those that can are characterized by the condition

$$\det \mathbf{R} \det m_\alpha^\beta = 1. \tag{29}$$

If \mathbf{R} be restricted as in (11), (29) would then give

$$\det m_\alpha^\beta = 1. \tag{30}$$

For theories of such continuous variations, such as we consider, such restrictions do not seem entirely unnatural and there might well be differences of opinion as to which choice to make. Similarly, in the theory of crystallographic groups, there is occasional difference of opinion as to whether to take these to be subgroups of the orthogonal or the proper orthogonal group. If there is any other sensible reason to restrict the group, it escapes me. The remaining discussion applies to the full group or to restrictions deriving from (11) and (30). By itself, (29) is a bit awkward, for the possible subsets of m 's and \mathbf{R} 's do not neatly divide into two separate groups. This induces some concern, for the group is much larger than that which has been used, with success, in the theory of infinitesimal deformations. However, the two are not as different as might first appear. In general, as represented by (26) and (27), the difference between $\bar{\mathbf{a}}_\alpha$, $\bar{\mathbf{p}}$ and \mathbf{a}_α , \mathbf{p} is not infinitesimal. Because of the discrete nature of the group, a nonzero difference is not easily converted to an infinitesimal difference. However, in special cases, the two sets of vectors need not differ at all. That is, for special choices of the vectors and certain transformations,

$$\mathbf{a}_\alpha = \mathbf{R}m_\alpha^\beta \mathbf{a}_\beta, \tag{31}$$

$$\mathbf{p} = \mathbf{R}(\mathbf{p} + n^\alpha \mathbf{a}_\alpha). \tag{32}$$

For fixed \mathbf{a}_α and \mathbf{p} , such transformations clearly form a subgroup. From (31),

$$m_\alpha^\beta \mathbf{a}_\beta = \mathbf{R}^T \mathbf{a}_\alpha, \tag{33}$$

whence follows that the subgroup of m 's form a group conjugate to a subgroup of the orthogonal group, the one which we would identify as the crystallographic group appropriate for this structure and configuration. With this hint, and what is discussed below, the reader might judge for himself whether our proposal is inconsistent with experience.

Reconsidering finite deformations, we use (13) to write

$$\mathbf{R}m_x^\beta \mathbf{a}_\beta = \mathbf{R}m_x^\beta \mathbf{F} \mathbf{A}_\beta = \mathbf{R} \mathbf{F} m_x^\beta \mathbf{A}_\beta = \mathbf{R} \mathbf{F} \mathbf{M} \mathbf{A}_x, \quad (34)$$

where \mathbf{M} is the linear transformation such that

$$\mathbf{M} \mathbf{A}_x = m_x^\beta \mathbf{A}_\beta. \quad (35)$$

The slightly ambiguous subgroup \mathcal{S}_1 represented by the m 's can thus be thought of as applying to the reference lattice vectors. As the m 's range over \mathcal{S}_1 , the \mathbf{M} 's range over a group \mathcal{S}_2 conjugate to it. Said differently, they are but different representations of the same abstract group. Of course the form of the \mathbf{M} 's will be different for different choices of the reference configuration, as reflected in differences in the \mathbf{A}_x .

Because of the invariance assumed, the solution of (18) indicated in (21) cannot be unique. For example, we can always add to \mathbf{p} integral multiples of lattice vectors. However, again because of the assumed invariance of \bar{W} , such different values of \mathbf{p} , required by symmetry, yield the same value of \bar{W} . Of course there remains the possibility of nonuniqueness of a less trivial character, possibly leading to a multi-valued \bar{W} . To correlate with elasticity theory, we must somehow gloss over this problem. The assumed invariance then translates to \bar{W} in the form

$$\bar{W}(\mathbf{R} \mathbf{F} \mathbf{M}) = \bar{W}(\mathbf{F}), \quad \mathbf{M} \in \mathcal{S}_2. \quad (36)$$

That is, \mathcal{S}_2 is at least contained in the isotropy group. It is easily seen that it is not a compact group, hence cannot be a subgroup of the orthogonal group. This isotropy group is no different from that which we [1] previously proposed for monatomic crystals. Similar arguments suggest it should apply also to polyatomic crystals. It is only in an abstract sense that they exhibit this common symmetry, since the form of the matrices depends on the form of the vectors \mathbf{A}_x and, of course, the form of \bar{W} is expected to be different for different crystals. The situation is somewhat similar to that occurring in isotropic materials, which appear to be anisotropic when referred to most stressed configurations. The group \mathcal{S}_2 has a finite set of generators, which can be obtained by applying a suitable similarity transformation to the generators of \mathcal{S}_1 described in [1], where some consequences of this symmetry are discussed in a simple situation. With the rather likely possibility that \bar{W} is multi-valued, (36) would still hold, in the sense that the set of values of \bar{W} would be transformed into itself by the indicated transformations. Of course, we are then somewhat outside the realm of elasticity theory. The system (18)–(20) seems preferable for studying such possibilities.

Here, we have done little more than attempt to motivate and explain our proposed treatment of symmetry, leaving considerable room for work to be done in exploring its implications. I am firmly convinced that, by exploring these, we will gain a better understanding of the behavior of crystalline solids.

Acknowledgment—This work was supported by a grant from the National Science Foundation.

REFERENCES

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(Received 30 October 1969)

Абстракт—Используя для иллюстрации теории упругости, исследуются соображения симметрии, которые могут оказаться уместными для простых механических теорий идеальных диатомных кристаллов. Эти соображения разнятся от тех, которыми пользуются в механике сплошной среды, несмотря на то, что эти два подхода не выдаются быть несовместимыми. При более микроскопической точке зрения, подобные идеи встречаются в обсуждениях скольжения или двойкового срастания кристаллов.