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QUASI-HARMONIC FINITE STRAIN EQUATIONS OF STATE OF SOLIDS*

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Abstract—Thomsen's 'fourth-order anharmonic' theory, which explicitly evaluates thermal effects in finite strain equations of elasticity according to the fourth-order approximation in lattice dynamics, is reconsidered for the special case of isotropic stresses and strains. It is shown that the approximations made in the finite strain theory are independent from those made in the lattice dynamics theory, with the result that strain dependence may be described in terms of any frame-indifferent strain tensor, not just the 'Lagrangian' strain tensor, η , and that the finite strain expansions may be taken to any order, not just the fourth. This result is valid for general stresses and strains. Illustrative pressure-volume equations are derived in terms of three strain measures, including η and the frame-indifferent analogue, E , of the 'Eulerian' strain tensor, ϵ . The reference state is here left arbitrary, rather than identifying it with the 'rest' state. This results in greater convenience in applying the equations. Not being restricted to fourth order, the present equations do not depend for their application on knowing the second pressure derivatives of the bulk modulus. Expressions are obtained for isentropes and Hugoniot in terms of the same parameters as enter the original equations, which have the form of isotherms. Ultrasonic, thermal expansion and calorimetric data for MgO are used to evaluate the parameters of third-order equations of state of MgO. The equations of state are tested and refined with Hugoniot data. The third-order ' E ' Hugoniot is much closer to the data than the third-order ' η ' Hugoniot. Inclusion of fourth-order terms allows both ' E ' and ' η ' Hugoniots to fit the data within their scatter. The separation of Hugoniots corresponding to different initial densities is predicted within the accuracy of the data by the thermal part of this theory.

1. INTRODUCTION

IN AN important pair of papers, Thomsen [1,2] has given a theory extending lattice dynamics into the domain of finite strain. Such a theory allows thermal effects to be explicitly accounted for at large stresses and in terms of a small number of parameters. However, Thomsen claims that such a theory can be written only in terms of a particular 'Lagrangian' strain tensor, η , with the following reasoning. The 'fourth-order' theory of lattice dynamics of Leibfried and Ludwig[3] is based on a Taylor expansion of the lattice potential energy, ϕ , in terms of atomic displacements which is truncated after the fourth-order terms. Finite strain equations of elasticity are based on a truncated expansion of the Helmholtz free energy, A , in terms of a strain

measure (of which there are an infinity of possibilities). Since both microscopic thermal motions and a macroscopic homogeneous strain involve displacements of atoms, it follows, Thomsen argued, that in a theory which purports to describe both thermal and large strain effects, the lattice dynamics and finite strain parts of the theory should both be based on expansions to the same order in terms of the same displacement measure, so that the same approximation is involved in each part of the theory. Thomsen[1,2] conclude that η was the appropriate measure.

This argument ignores the fact, that, macroscopically, strain and temperature are independent state variables. Microscopically, the *mean relative* displacements of atoms due to a macroscopic straining of the lattice can be varied independently of the *instantaneous relative* displacements due to thermal vibrations. Thus for the isothermal description of

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properties through large strains, thermal effects need not be considered at all, macroscopically, while the isobaric description of properties to high temperatures, for instance, requires only small strains to be accounted for. The independence of strain and temperature means that the usual arbitrariness in the definition of finite strain measures [1, 4] applies (within the restrictions imposed by the 'frame-indifference' requirement [4-6]). Thus 'finite strain' equations may be written as Taylor expansions in terms of any frame-indifferent strain parameter, and truncated at any order. The role of the lattice dynamics theory is to give (approximately) the explicit temperature dependence of such equations.

In this paper, expressions for the Helmholtz free energy and the pressure resulting from the fourth-order anharmonic theory of lattice dynamics [3] are expanded in terms of three different strain parameters to obtain 'finite strain' equations with explicit temperature dependence. Since only the 'quasi-harmonic' contributions to anharmonic thermal effects enter these equations [1, 3], they are referred to here as 'quasi-harmonic equations of state.' Brief illustrative applications are given.

So that the essential points at issue will not be obscured, the treatment in this paper will be limited to the case of isotropic stresses and strains. It will thus be applicable to either isotropic materials or materials of cubic symmetry under hydrostatic stress. The strain parameters considered here, as examples of the infinity of possible strain measures, are the 'Lagrangian' strain tensor, η , the frame-indifferent analogue, \mathbf{E} , of the 'Eulerian' strain tensor, ϵ [2, 6], and the displacement gradient, \mathbf{e} , defined by Thomsen [1] (see below).

An incidental point made here is fourth-order finite strain expansions in terms of η do not, in fact, involve the same approximation as that in the fourth-order lattice dynamics theory, as claimed by Thomsen [1], since η does not depend linearly on atomic displacements. The appropriate strain measure would be \mathbf{e} .

A further difference from Thomsen's approach is that the reference state is here left arbitrary, rather than identifying it with the 'rest' state as Thomsen [1] did. The parameters of the equations are then related to measured quantities, such as the bulk modulus and its pressure and temperature derivatives, in the reference state. An inconvenient aspect of Thomsen's [1] equations is thereby avoided. Thomsen's procedure requires the solution of six simultaneous non-linear algebraic equations (his equations (40)) in order to determine the rest-state parameters from room temperature data. In the present procedure, the reference state can be identified with that of the data, and the parameters evaluated with simple independent equations.

Since expressions are obtained here for the Helmholtz free energy and the pressure as functions of both specific volume and temperature it is possible to derive expressions for any other (P, V, T) locus from these. No new parameters or approximations need be introduced in this procedure. Expressions will be derived here for isentropes and Hugoniot.

Available ultrasonic, thermal expansion and calorimetric data for MgO are sufficient to evaluate the equation of state parameters of MgO. The equations of state thus determined are sufficient to predict Hugoniot of MgO. Shock-wave data can then be used to test and refine these equations of state. Comparisons will be given of the thermal and finite strain parts of the equations of state resulting from the use of different strain measures, and of the present equations with those of Thomsen [1].

2. FREE ENERGY AND THE MIE-GRÜNEISEN EQUATION

Leibfried and Ludwig [3] and Ludwig [7] have reviewed the 'fourth-order' theory of anharmonic lattice dynamics, i.e. the case where the lattice potential energy, ϕ , is expanded to fourth-order in atomic displacements. Let the initial and final position co-