ON THE MIE–GRÜNEISEN AND HILDEBRAND APPROXIMATIONS TO THE EQUATION OF STATE OF CUBIC SOLIDS*

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Abstract—An analysis is made of the conditions under which the equation of state of a cubic solid under hydrostatic pressure takes the form given by either the Mie–Grüneisen or the Hildebrand approximation. The condition of validity of the vibrational or thermal formulation of the Mie–Grüneisen approximation is reduced to the existence of a purely volume-dependent characteristic temperature for the vibrational or thermal free energy of the solid. The analysis consists then in a search for temperature ranges where these restrictions on the functional form of the free energy, and the restrictions on the form of the internal energy imposed by the Hildebrand approximation, are satisfied for a non-metal in the quasi-harmonic approximation. The main results are as follows: (1) At temperatures somewhat above the Debye characteristic temperature for the (quasi-harmonic) high-temperature heat capacity at constant volume, it is appropriate to take as equation of state the vibrational Hildebrand equation: (2) at somewhat lower temperatures, this Hildebrand equation is generally more inaccurate than the corresponding Mie–Grüneisen equation; and (3) in the low-temperature T^3 region of the heat capacity, the equation of state reduces to the thermal Mie–Grüneisen equation. The explicit forms of the vibrational and thermal Mie–Grüneisen equations of state, and of their volume derivatives at constant temperature, are reported together with the corresponding Hildebrand equations. Some corollary results are obtained, within the quasi-harmonic approximation, on the temperature variation at constant volume of the Grüneisen parameters relating the explicit volume and temperature dependence of the vibrational and thermal free energy and of the entropy of a cubic solid, and (in an Appendix) on the temperature variation of the Debye temperatures appropriate to the various thermodynamic functions of any non-metal. The available experimental and theoretical evidence on the anharmonic contributions to the thermodynamic functions of solids is briefly discussed, and points to the conclusion that their weight is quite small in the region of temperature of interest for our analysis.

1. INTRODUCTION

THE FORMULATION of the equation of a state of a cubic solid under hydrostatic pressure which is commonly adopted to determine the volume dependence of the lattice energy of the solid from empirical data is based either on the Hildebrand approximation[2] or on the Mie–Grüneisen approximation.[3] In recent years, it has been tacitly assumed that the Mie–Grüneisen equation of state, which takes approximate account of the explicit volume dependence of the (vibrational or thermal) free energy of the solid, is a better formulation to

use than the Hildebrand equation of state, which neglects the explicit volume dependence of the (vibrational or thermal) internal energy of the solid. In effect, HUANG[4] took the Mie–Grüneisen equation of state as equation of reference in analyzing the validity of the Hildebrand equation. The same attitude is implicit also in some calculations of BORN and HUANG[5], who have adopted the vibrational Mie–Grüneisen equation of state, and an approximation to its volume derivative at constant temperature, to recalculate the parameters entering the Born expression for the lattice energy of the alkali halides from empirical data at room temperature and atmospheric pressure. More recently RICE *et al.*[6] have derived the *P–V* isotherm

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