

relatively high melting point. For elements of low melting point, such as the molecular crystals, applicability of the Murnaghan equation of state has not been verified; hence the conclusions are not necessarily valid for elements of this class, for which the Simon equation was originally devised.

The fundamental fusion criterion on this theory is Eq. (7) corresponding to the Lindemann law, from which the Simon equation follows through choice of the Murnaghan equation (or one of similar analytic form) as the equation of state of the solid. However, a treatment analogous to that given here, based on a Birch equation¹⁹ (also derived from the theory of finite strain) or other justifiable equation of state, will not necessarily yield the analytic form of Eq. (31), but should be capable of representing the experimental facts as well, if Eq. (7) is accepted. Further, the evaluation (21) of the Simon exponent implies some dependence on the pressure range covered by the fusion

curve, and the evaluation of the Simon coefficient shows a dependence on the arbitrary position of the origin of the fusion curve. These considerations suggest that the Simon equation has more the character of an interpolation formula than a basic fusion equation, at least for the elements of higher melting temperature.

The fact that the Simon equation can be derived so directly from the generalized Lindemann law of I, for low pressure, justifies to some extent the step of extrapolating the law, for high pressure, to obtain the fusion curve on the basis of the Thomas-Fermi equation of state.²⁰

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¹⁹ F. Birch, *Phys. Rev.* **71**, 809 (1947).

²⁰ J. J. Gilvarry, preceding paper [*Phys. Rev.* **102**, 317 (1956)].

Grüneisen Parameter for a Solid under Finite Strain*

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An evaluation of the Grüneisen parameter (or constant) from the equation of state of a solid has been obtained by Druyvesteyn and Meyering on the basis of the theory of finite strain. The result differs (by $-\frac{1}{2}$) from the corresponding evaluation on the Debye theory, as given by Lorentz and by Slater. The value of Druyvesteyn and Meyering is derived here without use of the formal theory of finite strain, and shown to correspond physically to a model of independent pairs of nearest neighbor atoms, rather than to the Debye model of coupled atomic vibrations. This fact resolves a paradox raised by Dugdale and MacDonald in connection with an ideal harmonic solid, and ascribed by them to neglect of finite strain. The presence of a state of finite hydrostatic pressure, upon which elastic waves or pressure changes of infinitesimal amplitude are impressed, is taken into account explicitly by means of Murnaghan's theory of finite strain, to obtain the Grüneisen parameter, as evaluated from the equation of state, on the Debye model and for a Druyvesteyn-Meyering solid. The results are identical in the two cases with the corresponding values obtained without use of the formal theory of finite strain. Hence, no basis exists for the modification at finite pressure in the Grüneisen parameter from the Debye theory, as proposed by Dugdale and MacDonald. A comparison of average values over a relatively large number of elements, of Grüneisen constants as evaluated from Grüneisen's law and from the equation of state on the Debye model, shows excellent agreement at normal and at melting temperature.

I. INTRODUCTION

FROM results of Lorentz¹ and Slater,^{2,3} the Grüneisen parameter (or constant) γ_D of an isotropic solid can be evaluated from its equation of state as

$$\gamma_D = -\frac{2}{3} - \frac{1}{2}(\partial P/\partial V)^{-1}(V\partial^2 P/\partial V^2), \quad (1)$$

where P is the pressure corresponding to the volume V . As indicated by the subscript D , this result is based

on the Debye theory; it presupposes that the Poisson ratio of the solid is constant. In a number of papers⁴⁻⁶ concerned with the fusion curve and the behavior of solids under pressure, the author has assumed that the evaluation (1) of the Grüneisen parameter is valid at high pressure, for the Debye theory.

The question can be raised whether the theory of

⁴ J. J. Gilvarry, this issue [*Phys. Rev.* **102**, 308 (1956)], referred to hereafter as I.

⁵ J. J. Gilvarry, this issue [*Phys. Rev.* **102**, 317 (1956)], referred to hereafter as II.

⁶ J. J. Gilvarry, preceding paper [*Phys. Rev.* **102**, 325 (1956)], referred to hereafter as III.

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¹ H. A. Lorentz, *Proc. Roy. Acad. Amsterdam* **19**, 1324 (1916).

² J. C. Slater, *Phys. Rev.* **57**, 744 (1940).

³ J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 238, 394, 451.