

expressions of  $(\partial\gamma/\partial V)_T$  and  $(\partial\gamma/\partial T)_V$ ,

$$\left(\frac{\partial\gamma}{\partial V}\right)_T = \frac{\gamma}{V} - \frac{\gamma}{C_V} \left(\frac{\partial C_V}{\partial V}\right)_T + \frac{1}{C_V K^2} \left[ \left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P}\right)_T \right] \quad (15)$$

$$\left(\frac{\partial\gamma}{\partial T}\right)_V = \frac{V}{TC_V} \left(\frac{\partial C_V}{\partial V}\right)_T - \frac{\gamma}{C_V} \left(\frac{\partial C_V}{\partial T}\right)_V \quad (16)$$

which follow from equation (3), the first one by transforming  $[\partial(\beta/K)/\partial V]_T$  into pressure derivatives at constant temperature, noting then that  $(\partial\beta/\partial P)_T = -(\partial K/\partial T)_P$ . In the vibrational formulation of the Mie-Grüneisen approximation, the resulting equations have the form

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K} \frac{W_{\text{vib}}}{TC_V} \quad (17)$$

$$-\frac{1}{K} + V \frac{d^2 W_L}{dV^2} = \frac{V\beta^2}{C_V^2 K^2} W_{\text{vib}} \left[ \frac{TC_V}{W_{\text{vib}}} - 1 - \frac{T}{C_V} \left(\frac{\partial C_V}{\partial T}\right)_V \right] + \frac{W_{\text{vib}}}{TC_V} \frac{T}{K^2} \left[ \left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P}\right)_T \right]; \quad (18)$$

while in the thermal formulation they read

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K} \frac{W_{\text{th}}}{TC_V} \quad (19)$$

$$-\frac{1}{K} + V \frac{d^2 W_C}{dV^2} = \frac{V\beta^2}{C_V^2 K^2} W_{\text{th}} \left[ \frac{TC_V}{W_{\text{th}}} - 1 - \frac{T}{C_V} \left(\frac{\partial C_V}{\partial T}\right)_V \right] + \frac{W_{\text{th}}}{TC_V} \frac{T}{K^2} \left[ \left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P}\right)_T \right]. \quad (20)$$

In the corresponding formulations of the Hildebrand approximation, they are instead:

$$P + \frac{dW_L}{dV} = \frac{T\beta}{K} \quad (21)$$

$$-\frac{1}{K} + V \frac{d^2 W_L}{dV^2} = \frac{T}{K^2} \left[ \left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P}\right)_T \right] \quad (22)$$

and

$$P + \frac{dW_C}{dV} = \frac{T\beta}{K} \quad (23)$$

$$-\frac{1}{K} + V \frac{d^2 W_C}{dV^2} = \frac{T}{K^2} \left[ \left(\frac{\partial K}{\partial T}\right)_P + \frac{\beta}{K} \left(\frac{\partial K}{\partial P}\right)_T \right]. \quad (24)$$

HUANG<sup>(4)</sup> assumed equations (17) and (19) as valid at all temperatures and attempted to investigate the validity of the Hildebrand approximation for a non-metal by searching for temperature ranges where equations (21) and (23) coincide with equations (17) and (19), respectively, computing the ratios  $W_{\text{vib}}/TC_V$  and  $W_{\text{th}}/TC_V$  by means of the Debye model. Clearly this procedure does not establish the relative merits of the Hildebrand and Mie-Grüneisen approximations. Thus HUANG's result that the ratio  $W_{\text{vib}}/TC_V$  approaches unity at temperatures somewhat above the Debye characteristic temperature, while the ratio  $W_{\text{th}}/TC_V$  approaches unity only at much higher temperatures, represents only a numerical verification for the Debye model of the general result to this effect which is apparent from the Thirring expansions for the vibrational and thermal energies. BORN and HUANG<sup>(5)</sup>, on the other hand, have used equation (17) for the alkali halides at room temperature, adopting, however, an approximate expression for its volume derivative at constant temperature derived by neglecting the volume dependence of  $\gamma$ .

## 5. DISCUSSION OF THE RESULTS

A few definite statements on the validity of the Mie-Grüneisen and Hildebrand approximations to the equation of state of cubic solids under hydrostatic pressure are possible within the quasi-harmonic approximation. The thermal Mie-Grüneisen equation of state is correct for a non-metal in the  $T^3$  region of the heat capacity, and the validity of the Debye model for the thermal thermodynamic functions in this region, which