

where  $\eta_0$  and  $\alpha_0$  correspond to temperature  $T$  and pressure zero, and  $K_0$  is the bulk modulus at temperature  $T_0$  and at zero pressure.

Accordingly, Eqs. (27) and (32) yield for Eq. (1) the generalization

$$P = \frac{K_0}{n-m} \exp\left[-\int_{T_0}^T \eta_0 \alpha_0 dT\right] \times \left[\left(\frac{V_0}{V} \exp \int_{T_0}^T \alpha_0 dT\right)^n - \left(\frac{V_0}{V} \exp \int_{T_0}^T \alpha_0 dT\right)^m\right], \quad (33)$$

which exhibits the temperature dependence explicitly and reduces to Eq. (1) when the exponentials appearing are set equal to unity. This equation yields

$$(\partial P / \partial T)_V = K \alpha_0 - P \eta_0 \alpha_0 = K \alpha(T) \quad (34)$$

directly, which shows that  $\alpha_0(T)$  must be taken as strictly independent of pressure; the pressure dependence of the thermal expansion demanded by Eq. (25) is taken into account by the exponential in  $P$  which involves  $\eta_0 \alpha_0$ . One concludes from Eq. (26) that the generalization (33) yields correctly the temperature dependence of the pressure through terms of first order in  $P/K$  as a parameter of smallness, but, from Eq. (31), that the temperature dependence of the bulk modulus is given correctly only to zero order in this parameter. Note that the role of the exponential involving  $\eta_0 \alpha_0$  in Eq. (33) is to ensure that Eq. (17) be fulfilled at nonvanishing pressure; if this exponential be set equal to unity while the exponential involving only  $\alpha_0$  be retained, Eq. (17) is met only to zero order in the parameter  $P/K$ . Finally, the physical interpretations of the parameters  $\mathcal{U}$  and  $\mathcal{K}$  can be noted. From Eq. (27) and the definition of  $\alpha_0$ , it follows that  $\mathcal{U}(T)$  is simply the volume of the solid at temperature  $T$  and at zero pressure. Equations (20) and (21) yield

$$\eta \alpha = -K^{-1}(\partial K / \partial T)_P, \quad (35)$$

and hence  $\mathcal{K}(T)$  of Eq. (32) is the bulk modulus of the solid at temperature  $T$  and at zero pressure.

To this point, it has been assumed tacitly that states of the solid at zero pressure are observable at arbitrary temperature, since the coefficient  $\alpha_0$  of volume expansion must be determined experimentally. This condition is not met for a solid with a normal fusion curve, when the temperature exceeds the normal melting temperature. In this case, Birch's relation (25) must be replaced by

$$\alpha = \alpha_m \{1 - \eta_m [(P/K) - (P_m/K_m)]\}, \quad (36)$$

where  $P_m(T)$  is the pressure,  $K_m(T)$  is the bulk modulus, and  $\alpha_m(T)$  and  $\eta_m(T)$  represent values of  $\alpha$  and  $\eta$ , respectively, all of which are measured for the

solid on the fusion curve at a given temperature  $T$  (and thus can be regarded as functions only of temperature). With this value of  $\alpha$ , Eqs. (24) and (28) yield

$$\mathcal{U} = V_{m,0} \exp \int_{T_{m,0}}^T \left(1 + \eta_m \frac{P_m}{K_m}\right) \alpha_m dT, \quad (37a)$$

$$\mathcal{K} = K_{m,0} \exp \left[-\int_{T_{m,0}}^T \left(1 + \eta_m \frac{P_m}{K_m}\right) \eta_m \alpha_m dT\right], \quad (37b)$$

respectively, where  $V_{m,0}$  and  $K_{m,0}$  are the values of  $V$  and  $K$ , respectively, for the solid at the temperature  $T_{m,0}$  for fusion under zero pressure; the paths of integration are along the fusion curve. The corresponding generalized equation of state is to be applied only for  $P(T) \geq P_m(T)$ . These forms for  $\mathcal{U}$  and  $\mathcal{K}$  can be reduced to those of Eqs. (27) and (32) by writing

$$\alpha = \alpha_m (1 + \eta_m P_m / K_m), \quad \eta_0 = \eta_m, \quad (38)$$

from Eq. (36), so that  $\alpha_0(T)$  is the hypothetical value of  $\alpha$  possessed by the solid if metastable below its fusion temperature at  $P=0$ . Substituting into Eqs. (37) the values of  $\alpha_m$  and  $\eta_m$  implied by Eqs. (38), one can write

$$\mathcal{U} = V_{m,0} \exp \int_{T_{m,0}}^T \alpha_0 dT, \quad (39a)$$

$$\mathcal{K} = K_{m,0} \exp \left[-\int_{T_{m,0}}^T \eta_0 \alpha_0 dT\right], \quad (39b)$$

where the paths of integration correspond to zero pressure. Hence,  $\mathcal{U}$  and  $\mathcal{K}$  retain their physical interpretations as the volume and bulk modulus, respectively, of the solid at zero pressure for temperature  $T$ .

In the preceding, the parameters  $\mathcal{U}$  and  $\mathcal{K}$  have been written in exponential form for mathematical convenience. Only rarely does the accuracy with which  $\alpha_0$  and  $\eta_0$  are experimentally known justify retention of terms beyond the first in the expansion of the exponential. To first order,  $P(T)$  of Eq. (33) can be written as the sum of a temperature-dependent correction and the pressure  $P(T_0)$  corresponding to the isothermal equation as

$$P = P(T_0) + \frac{K_0}{n-m} [n y^n - m y^m - \eta_0 (y^n - y^m)] \times \int_{T_0}^T \alpha_0 dT, \quad (40)$$

where  $y = V_0/V$  ( $\eta_0$  has been taken as a constant). At nonvanishing pressure, the first two terms in the brackets in this equation are dominant over the terms in parentheses with  $\eta_0$  as coefficient, since the latter terms cancel for  $V = V_0$ . The relative smallness of the terms involving  $\eta_0$  is advantageous, since this parameter is difficult to determine experimentally and