$(d\ln\gamma^*/dP)$ in (18)}, we obtain

$$d\ln N(0)/dP = d\ln\gamma^*/dP = -8.31\times10^{-6} \text{ per atm.} \quad (23)$$

This result is very different from that expected from the free-electron model, according to which $N(0)\propto n^{\frac{1}{3}}$, where n is the number of electrons per unit volume. However, in general,

$$d\ln n/dP = -d\ln v/dP = \kappa, \quad (24)$$

where v is the molar volume and κ is the compressibility, and so the free electron model predicts

$$[d\ln N(0)/dP]_{\text{fr. el.}} = \tfrac{1}{3}(d\ln n/dP) = \kappa/3 \simeq +5.6\times10^{-7} \text{ per atm,} \quad (25)$$

a result 15 times smaller than the measured value and of the wrong sign. The implication is clear that the free-electron model is not very satisfactory for dealing with the pressure effect in the case of Pb.

Consider now a density of states curve having the shape near the Fermi energy as suggested by Gold.[29] On the basis of Steele's measured values of the absolute thermoelectric power of Pb,[30] Gold obtains

$$\frac{1}{N(E_F)}\left(\frac{\partial N(E)}{\partial E}\right)_{E_F} = -0.90 \text{ per ev,} \quad (26)$$

where $N(E_F)$ is the density of states for both spins, i.e., $N(E_F)=2N(0)$. The Fermi energy, E_F, is defined by the equation

$$\int_0^{E_F} N(E)dE = n. \quad (27)$$

Differentiating (27) with respect to pressure

$$\frac{dn}{dP} = n\kappa = \int_0^{E_F} \frac{\partial N(E)}{\partial P} dE + N(E_F)\frac{dE_F}{dP} \quad (28)$$

and, solving for (dE_F/dP), we obtain

$$\left(\frac{dE_F}{dP}\right) = \frac{n\kappa}{N(E_F)} - \frac{1}{N(E_F)}\int_0^{E_F} \frac{\partial N(E)}{\partial P} dE. \quad (29)$$

[29] A. V. Gold, Phil. Mag. 49, 73 (1960).
[30] M. C. Steele, Phys. Rev. 81, 262 (1951).

A detailed calculation is required to evaluate $[\partial N(E)/\partial P]$, but, as a rough approximation, we shall take it to be zero. We thus obtain from (20)

$$\frac{dE_F}{dP} \simeq \frac{n\kappa}{N(E_F)} = 5.15\times10^{-5} \text{ ev/atm,} \quad (30)$$

where we have used the values, $N(E_F)=1.30$ per ev per atom from the value of γ given by Decker[12] and $n=4$ per atom.

A general expression for the pressure variation in the density of states at the Fermi surface is

$$\frac{dN(E_F)}{dP} = \left(\frac{\partial N(E)}{\partial P}\right)_{E_F} + \left(\frac{\partial N(E)}{\partial E}\right)_{E_F}\frac{dE_F}{dP}. \quad (31)$$

According to the present approximation $[\partial N(E)/\partial P] = 0$, and so we finally obtain

$$\frac{d\ln N(E_F)}{dP} \simeq \frac{1}{N(E_F)}\left(\frac{\partial N(E)}{\partial E}\right)_{E_F}\frac{dE_F}{dP} = -4.6\times10^{-6} \text{ per atm} \quad (32)$$

upon inserting the values from (26) and (30).

The approximate result in (32) compares reasonably well with the experimental value of -8.31×10^{-6} per atm. Moreover it can be seen from (29) and (31) that the effect of including the neglected $[\partial N(E)/\partial P]$ term would make $[dN(E_F)/dP]$ more negative. Since pressure decreases the interactomic distance and therefore broadens the energy bands, it is to be expected that $[\partial N(E)/\partial P]$ is negative. It is thus possible that an improved calculation will result in still better agreement with our experimental result.

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