consistently omitting first derivatives of *all* energy contributions. It is commonly presumed[25] that the second derivative E_0'' is small because the actual equilibrium r is larger than the value of r for the minimum of E_0. Equilibrium r then occurs in the neighborhood of the inflection point of E_0, as is shown by the available calculations for copper[26] and silver[27] and by the analytical approximation given above. The contribution of E_0'' to the bulk modulus and its hydrostatic strain derivative is probably small therefore. The third derivative E_0''' contributes to the hydrostatic strain derivative only; it is felt that it is also likely to be small in view of the fact that E_0''' is zero at a value of r just beyond the inflection point of E_0, according to the analytical approximation, and hence also near the equilibrium value of r. Quantitative estimates of the possible values of $\Omega B_0=r^2E_0''/9$ and $\Omega dB_0/d\ln r=(r^3E_0'''-3r^2E_0'')/9$ can be made by using the analytical approximation, equating br^{-1} to the Coulomb energy of the structure[22] and invoking the physical condition that $r(\text{equilibrium})>r(E_0'=0)$; these support the statements that have been made, the possible fractional error in the hydrostatic strain derivative being negligible while those in the bulk modulus may be significant but are not serious to the conclusions of this paper.

The long-range bulk modulus which has been used here is then the Fermi term only, and furthermore for this term we have used an effective mass, m^*/m, of unity for all three metals. This value of the effective mass agrees with the theoretical values of Kambe[28] which characterize the electrons at the bottom of the valence band for copper, silver, and gold. It also agrees with electronic specific heat effective masses[29] for silver and gold, but not for copper in which this $m^*/m=1.47$. We feel, however, that a "bulk modulus effective mass," which characterizes the change with volume of the average Fermi energy, is more likely to be equal to the theoretical value than to an effective mass describing the density of states at the Fermi level only.[29] We have therefore used unity for copper also.

As mentioned above, the long-range contributions to the shear stiffnesses which have been used are the Coulomb stiffnesses of Fuchs, and these have been taken at their full value. Since these terms have been taken at reduced values in other papers[2,3] in which elastic constants have been decomposed into contributions, we state our reasons. In the first place, the Fuchs values have long been known to account for the shear stiffnesses of bcc Na and K,[21] and recently this has been found[30] to be true in Li also. In the alkali metals the long-range term is the major if not the only one and the agreement argues for the validity of the Fuchs calculation. There is no direct evidence for such a long-range stiffness in copper, silver, and gold but extensive studies of the elastic constants of copper[31] and silver alloys[17] in our laboratories provide good indirect evidence. The alloy results require that sizable long-range and short-range terms must both be present, and that C/C' (long range) must be about the Fuchs ratio. These two reasons lead us to regard the Fuchs values as very reasonable estimates of the long-range shear stiffness.

In some previous decompositions of elastic stiffnesses into contributions a van der Waals term has been introduced explicitly.[26] We have omitted such a term as we feel it adds nothing to the analysis which has been carried through and is a numerically uncertain contribution at best. If a contribution to the total energy of the physical nature of the van der Waals interaction is present, it is absorbed, in our treatment, in the short-range repulsive interaction $W=A\exp(-pr/r_0)$ which we have deduced empirically. Formally the van der Waals interaction is radial and of short range and cannot be separated empirically from the repulsive term.

The uncertainties in the analysis presented in the previous section thus reside almost entirely in the theoretical long-range terms. We emphasize again that these terms are small and even large individual errors would leave the conclusions unchanged. The cumulative effect of these uncertainties added to the experimental error, particularly in B and dB/dP, could be considerable, however, so that the individual numerical values of the closure failures which have been quoted and assigned to noncentral short-range interaction should be treated with caution. Nevertheless the relative values of the closure failures appear to be reasonable for the two shear constants and for the three metals.

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