



FIG. 2. Closure failures  $\Delta$  expressed as fractions of the corresponding total experimental quantity. (a) Elastic shear constants; (b) hydrostatic strain derivatives of shear constants.

corrections which have been subtracted from experimental values. Since it is felt that this homologous series of metals must conform to a common model of their elastic stiffnesses and strain derivatives, we include copper in our conclusion, which is that the closure failures reflect a large, real contribution to the shear constants which is not included in the conventional theory outlined above.

We suggest furthermore that the closure failures must be assigned to many-body, noncentral, short-range interaction between metal ion cores. The absence of such an interaction is a major assumption in the conventional theory and the interaction seems to be the only way in which to account for these large discrepancies between theory and experiment for the shear constants. The ratios  $-\Delta(\Omega dC/d\ln r)/\Delta(\Omega C)$  and  $-\Delta(\Omega dC'/d\ln r)/\Delta(\Omega C')$  are indicative of the range of the interaction; the large values of these ratios occurring in the present results indicates that the noncentral terms are of short range indeed. It will be noted that the values of the ratios are in most cases larger than the value of  $\rho$  which characterizes the range of the radial part of the interaction. Further, the smoothness of the variation of the closure term from copper to gold for each constant and each strain derivative corresponds with the increasing amount of ion-core overlap and hence of the importance of the noncentral interaction in this sequence. There appears to be no theory available for the noncentral part of the many-body interaction between ion cores which has been suggested here and no *a priori* reason for or against the negative sign of the stiffness contribution which is found.

#### DISCUSSION

In this section we point out and discuss further the detailed assumptions involved in the analysis which was presented in the last section.

The experimental elastic constant values which have been used for the interpretation are those for the temperature of 0°K. These values are amply known, and their use enables us to avoid the difficult theoretical

question of the temperature dependence of the elastic constants, and in addition we avoid the minor point of the adiabatic-isothermal correction to the bulk modulus. On the other hand, the experimental values of the hydrostatic strain derivatives which have been used are of necessity those for room temperature. The analysis is somewhat inconsistent in this respect therefore, but we do not feel that the point is important since we expect a smaller temperature correction for the hydrostatic strain derivatives than for the elastic constants, which itself is less than 10%. The most direct justification for this expectation may be obtained from the results of Bridgman on the pressure dependence of the bulk modulus. Bridgman's experiments have been carried out at two temperatures, 30°C and 75°C and it is the coefficient  $b$ , in our notation, which is relevant. Inspection of Bridgman's tabulation<sup>4</sup> for some forty metals shows that there is practically no change of  $b$  in this temperature range for most metals. Furthermore, for those metals for which there is a significant change, the sign is as often positive as negative. We feel it quite probable that the hydrostatic strain derivatives of the shear constants will also show only a small temperature dependence.

We have used also the hydrostatic strain derivative of the *adiabatic* bulk modulus in our interpretation. A direct but approximate evaluation of the pressure derivative of  $B_s - B_T$  can be made from thermodynamics and available experimental data for Cu; the result is that the pressure derivatives of  $B_s$  and  $B_T$  differ by less than 2%. We have preferred to avoid the uncertainty involved in this correction by using the modulus which is directly determined in the pulse-echo method.

It has already been emphasized that the contributions of the long-range terms in the energy to the elastic stiffnesses and their hydrostatic strain derivatives are small. In the interpretation they may almost be regarded as corrections but some further discussion is worthwhile. In the conventional theory, as it has been used in the last section, one term in the energy of the crystal is commonly omitted in part. This term is the energy of the lowest electronic state of the valence electrons, which will be denoted by  $E_0$ . Physically  $E_0$  can be represented by the expression<sup>24</sup>  $ar^{-3} - br^{-1}$  in which the terms represent respectively the kinetic and potential energy associated with the state. In the conventional theory for the *shear* constants,  $E_0$  appears to a good approximation as the Coulomb stiffnesses  $\Omega C_{lr}$  and  $\Omega C'_{lr}$  as used here.

The lowest state energy contribution to the bulk modulus and its hydrostatic strain derivative has been ignored entirely, however, and in justification of this step the magnitudes of the derivatives  $E_0''$  and  $E_0'''$  must be considered. The first derivative of  $E_0$  is large but does not enter in this analysis at all because the equation of equilibrium has been invoked implicitly by

<sup>24</sup>N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 80.