

Correlation between the Electron Gas Bulk Modulus and c_{12} - c_{44} of Monovalent Metals

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When the shear elastic constants of the monovalent metals are assumed to be due to central forces, the deviation from the Cauchy relations of elasticity can be attributed to the bulk modulus of the electron gas. This modulus may be calculated from the total gas energy using the exchange and correlation contributions due to Gell-Mann and Brueckner (GB) and to Fletcher and Larson (FL). The bulk modulus of Cu based on the FL energies is found to agree quantitatively with the experimental c_{12} - c_{44} and to have also the correct volume dependence from 0 to 300°K. The bulk modulus of the Na gas at 300°K based on the exchange and correlation energies of GB agrees within 6% with c_{12} - c_{44} observed. Comparisons are also made for Ag but no agreement is found. These correlations seem inconsistent in that the same formula should work for both Cu and Na if there are central forces, and the GB result should work for neither because it is supposed to be invalid in the range of real metallic densities. The correlations provide no final criteria for the determination of the proper exchange and correlation energies of the electron gas.

IN a quantum-mechanical calculation of the elastic constants of monovalent metals, Fuchs¹ found that the ion-ion electrostatic and exchange interactions give essentially central forces between ions and a consequent central-force description of the shear elastic constants c_{44} and c_{11} - c_{12} . The extensional elastic constants c_{11} , c_{12} , and bulk modulus $(c_{11}+2c_{12})/3$ were found to involve the same central forces as the shear constants plus a volume-dependent part due to the kinetic and potential energies of the conduction electrons. Thus, instead of the Cauchy relations $c_{12}=c_{44}$ of central-force cubic lattices, one should have $c_{12}-c_{44}=B_e$ as discussed by deLaunay,² where B_e is the bulk modulus of the electron gas. However, the concept, $c_{12}-c_{44}=B_e$ is valid only for an essentially spherical Fermi surface and will not hold for multivalent cases where, say, the first Brillouin zone is filled such as in the case of Al. In this latter case, shearing distortions would shear the zone and cause the shear elastic constants to depend also on those electrons in the filled zone.³ In Ag, Au, and Cu, the known area of contact of the neck of the nearly spherical Fermi surface⁴ with the hexagonal zone face is so small that it should not affect appreciably the over-all volume dependence of the whole electron gas. Thus, for these metals, $c_{12}-c_{44}=B_e$ should still hold approximately, provided now that exchange interactions between valence and closed shell electrons can be neglected.

From the theoretical expressions given below for the exchange and correlation energies of the electron gas and the Fermi energy, we are able to calculate B_e and to make comparisons with the experimental c_{12} (isothermal)- c_{44} of Na, Cu, and Ag. These comparisons are, of course, uncertain to the same extent as the theoretical expressions themselves, the main uncertainty for real

metal densities ($2 \lesssim r_s \lesssim 8$), according to many-body theory results, being in the expression for the correlation energy. We find, however, in the comparison for Cu, that it is a modification⁵ of the usual exchange energy that is primarily responsible for the quantitative correlation observed.

To compute B_e , we take $\partial^2/\partial V^2$ of the average electron gas energy $N\bar{\epsilon}$, where $\bar{\epsilon}=\epsilon_F+\epsilon_x+\epsilon_c$. Here, $\epsilon_F=3\text{ Ry}/5\alpha^2 r_s^2$ is the usual average Fermi energy; ϵ_x and ϵ_c are the average exchange and correlation energies per electron. N is the number of electrons in the sea, V the volume, $\text{Ry}=me^4/2\hbar^2$, $4\pi r_0^3/3=V/N$, $r_0/a_0=r_s$, a_0 =Bohr radius, and $\alpha=(4/9\pi)^{1/3}$.

In the calculation of Gell-Mann and Brueckner⁶ (GB) by field theory methods, the correlation energy is given by

$$(1/\text{Ry})\epsilon_c = C + A \ln r_s + D r_s \ln r_s + E r_s + \dots, \quad (1)$$

where $C=-0.096$, $A=+0.06218$, the D and E being undetermined. DuBois⁷ evaluates D to be 0.0049 and finds ϵ_c valid only for $r_s<0.8$ and, therefore, supposedly not applicable to real metals. In the GB theory, the exchange energy is assumed to be $3\text{ Ry}/2\pi\alpha r_s$, the same as that calculated originally by Wigner and Seitz.⁸

Fletcher and Larson⁵ (FL) find ϵ_x and ϵ_c on the basis of a Bohm-Pines collective description and their calculation involves a characteristic screening length $\lambda_c \sim k_c^{-1}$ and an adjustable constant $\gamma=k_c/k_0$, where k_0 is the wave vector corresponding to the Fermi distribution top. Nozières and Pines⁹ (NP) find $\gamma=0.353$, 0.4, or 0.471 depending on details of physical assumptions as to the screening. These values of γ are used by FL but any γ in this range should be valid in FL theory. A main FL result is a modification of the usual exchange

¹ K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935); **A153**, 622 (1935); **A157**, 444 (1936).

² J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

³ R. S. Leigh, Phil. Mag. **42**, 876 (1951).

⁴ D. Shoenberg in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, New York, 1960), p. 81; R. W. Morse, *ibid.*, p. 214.

⁵ J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

⁶ M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

⁷ D. F. DuBois, Ann. Phys. (New York) **7**, 174 (1959); **8**, 24 (1959).

⁸ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).

⁹ P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

energy to

$$\epsilon_x = -\frac{3 \text{ Ry}}{2\pi\alpha} \left[\frac{1}{r_s} - \frac{4\gamma}{3r_s^{1/2}} + \frac{\gamma^2}{2} - \frac{\gamma^4 r_s}{48} \right]. \quad (2)$$

The ϵ_e of FL is a quite complicated formula given by their Eqs. (7a) and (11). However, we find for $\gamma r_s^{1/2} < 2$ that the FL formula⁵ for correlation energy converges rapidly to the much simpler form,

$$(1/\text{Ry})\epsilon_c = C(\gamma) + A \ln r_s$$

$$-\frac{\gamma^2 r_s}{8\pi^2} + \frac{\gamma^4 r_s^2}{480\pi^2} + \frac{\gamma^6 r_s^3}{26880\pi^2} + \dots, \quad (3)$$

where $A = 2(1 - \ln 2)/\pi^2 = 0.06218$ (the same as the A in GB theory), and $C = -0.1808, -0.1653, -0.1450$, for $\gamma = 0.353, 0.4, 0.471$, respectively.

Using this ϵ_x and ϵ_e of FL, we compute the bulk modulus immediately [noting $r_s = (\text{const})V^{1/3}$] in the form $B_e = B_F + B_x + B_c$, where

$$B_F = (2N \text{ Ry}/3V\alpha^2 r_s^2), \quad (4)$$

$$B_x(\text{FL}) = -\frac{N \text{ Ry}}{2\pi\alpha V} \left[\frac{4}{3r_s} - \frac{7\gamma}{9r_s^{1/2}} + \frac{\gamma^4 r_s}{72} \right], \quad (5)$$

$$B_c(\text{FL}) = -\frac{N \text{ Ry}}{V} \left[\frac{A}{3} - \frac{\gamma^2 r_s}{36\pi^2} + \frac{\gamma^4 r_s^2}{2160\pi^2} \right]. \quad (6)$$

If we put $\gamma = 0$ in the above formula for $B_x(\text{FL})$, we obtain that based on the GB theory and denote it $B_x(\text{GB})$. The corresponding B_c computed from the ϵ_e of GB is

$$B_c(\text{GB}) = -(N \text{ Ry}/V) \left[\frac{1}{3}A + (0.00109)r_s \ln r_s \right], \quad (7)$$

where we neglect higher terms in r_s because their coefficients such as the E above in Eq. (1) have not been evaluated.

Table I shows the relative contributions to the total electron gas bulk modulus B_e of the Fermi, exchange, and correlation energies. The $B_e(\text{FL})$ of Na at 300°K is much too large, while the B_e based on GB theory is

TABLE I. Contributions to B_e on the basis of theories of FL and GB. Units of B_e and $c_{12}-c_{44}$ are 10^{11} dyn-cm⁻².

	Na (300°K)	Cu (0°K)	Ag (0°K)
r_s	3.99	2.656	3.00
B_F	0.857	6.529	3.56
$B_x(\text{FL})$	-0.335	-1.875	-1.14
$B_x(\text{GB})$	-0.085	-0.370	-0.25
$B_e(\text{FL})$	0.437	4.284	2.17
$B_e(\text{GB})$	-0.566	-2.876	-1.77
$B_c(\text{FL})$	-0.121	-0.442	-0.46
$B_c(\text{GB})$	0.170	3.211	1.33
$c_{12}-c_{44}$	0.160 ^a	4.317 ^b	4.62 ^c

^a W. B. Daniels, Phys. Rev. 119, 1246 (1960).

^b See reference 10.

^c J. R. Neighbours and G. A. Alers, Phys. Rev. 111, 707 (1958).

TABLE II. $B_e(\text{FL})$ and observed $c_{12}-c_{44}$ of Cu vs T . (Units are 10^{11} dyn-cm⁻²).

T (°K)	$\gamma=0.353$	$\gamma=0.371$	$\gamma=0.4$	$c_{12}-c_{44}$
0	4.243	4.284	4.375	4.317
50	4.242	4.292	4.373	4.312
100	4.234	4.284	4.365	4.283
150	4.219	4.269	4.350	4.259
200	4.203	4.253	4.333	4.239
250	4.185	4.235	4.315	4.224
300	4.166	4.216	4.296	4.213

about right, being only 6% higher than the experimental $c_{12}-c_{44}$. In the case of Ag, even the contribution due to the Fermi energy is too small, while the exchange and correlation contributions of both FL and GB theories lower B_e even more. One possible conclusion here is that in the case of Ag, due to the relatively large ion core, there are noncentral force contributions to the elastic constants and these combine with the electron gas to break the Cauchy relations of elasticity.

In the case of Cu, the bulk modulus based on the FL theory (with $\gamma=0.371$) is only 0.7% below the experimental¹⁰ $c_{12}-c_{44}$, while that based on the GB theory is 25% too small. It is of interest to see if the theoretical $B_e(\text{FL})$ has the right volume dependence (through the temperature dependence of the volume) and the results in Table II give B_e for $\gamma=0.353, 0.371$, and 0.4 in the temperature range from 0°K to room temperature. The case $\gamma=0.471$ used by NP and FL is not considered here.

To summarize, we have found in the case of Cu a rather remarkable quantitative agreement between the electron gas bulk modulus based on the theories of FL and NP and the experimental $c_{12}-c_{44}$. The parameter giving the best fit of the experimental data is 0.371, which falls between the two values 0.353 and 0.4 obtained by NP from considerations of the characteristic screening length. The change of B_e between 0 and 300°K is also in the right direction, being -1.6%, but it is less than the -2.4% change of the observed $c_{12}-c_{44}$. However, the same FL formulas for B_e fail to predict $c_{12}-c_{44}$ properly for Na and Ag and so the correlation observed for Cu must be considered fortuitous at present.

In the case of Cu, it turns out that that part of the bulk modulus computed from the modified exchange energy of FL is the part primarily responsible for the observed agreement between $c_{12}-c_{44}$ and B_e . A significant contribution to this agreement arises mainly from the term $7\gamma r_s^{-1/2}/9$ appearing in the brackets of Eq. (5). However, since many-body theoretical results for the electron gas are still undergoing modifications and improvements, it is not certain that the FL results for ϵ_x and ϵ_e are reliable for r_s near 2.6, that of Cu. If we overlook the fact that the approximate concept, $c_{12}-c_{44}=B_e$, which arises out of Fuchs' work,¹ may be too simple and too poor an approximation, but at the same time sup-

¹⁰ W. C. Overton, Jr. and J. Gaffney, Phys. Rev. 98, 969 (1955).

pose that $B_e(\text{FL})$ is indeed the incorrect bulk modulus, we must look naturally to noncentral forces as being partially responsible for the deviation from the Cauchy relations. Such a noncentral character could arise from the nonsphericity of the $3d$ charge distribution. It is known that the cubic field in metals removes the fivefold degeneracy and destroys the sphericity of the $3d$ band electrons and that the d -band charge distribution requires a cubic harmonic description.¹¹ The cubic anisotropy of this distribution gives rise to noncentral interatomic forces, but the main question is whether these forces are "significant" in magnitude. It is probable that this question cannot be answered with certainty at present because structure calculations are not yet sufficiently quantitative. On the other hand, there is evidence that, while noncentral forces might be present, they are probably "insignificant" in magnitude to cause experimentally measurable effects. Using a simple two-neighbor central force lattice model, with force constants based on accurate elastic constants of Cu, a precision machine calculation of the vibration spectrum of Cu has been carried out¹² and the detailed structure of this spectrum has been enhanced by an analytic treatment of the critical points in the phonon k space of the model. The resulting specific heat is a very accurate representation of the specific heat of the model and, this, in turn, is found to be in very close agreement with the experimental specific heat of Cu, being within 0.5% from 80 to 300°K.¹² This agreement is too quantitative to discard by reference to the familiar concept that specific heat is insensitive to the details of the spectrum, but, in order to be sure, this very point was checked by a second calculation¹² involving a varied

spectrum. Nevertheless, this excellent agreement of a simple lattice vibrational model with central forces might also be fortuitous because the agreement is not so good when the same model is used for other metals. Therefore, we must consider that the two viewpoints, "predominantly-central" forces and "central-plus-significant-noncentral" forces cannot be adequately resolved at the present time. Accordingly, we regard the quantitative bulk modulus correlation observed above for copper as being an interesting but inconclusive result and, of course, fortuitous, as we have indicated above.

In the case of Na, the assumption of predominantly central ion-ion forces is favorable on physical grounds,^{1,8} while at the same time the representation of the conduction electrons as a free gas, with proper accounting of the ground state, also leads to good agreement with experiment. Thus, the use of the electron gas bulk modulus to explain the deviation from the Cauchy relations should be a good approximation, provided that the correct exchange and correlation energies can be found. It is, therefore, somewhat surprising that the B_e based on the ϵ_x and ϵ_c of GB should differ from $c_{12}-c_{44}$ of Na with $r_s=4$ by only 6%, especially since Dubois⁷ finds that the GB theory should not be valid for $r_s>0.8$.

The relative contributions of B_x and B_e to the over-all gas bulk modulus B_e based on the different theories for ϵ_x and ϵ_c are worth noting. The constant term C in ϵ_c , the magnitude of which is one of the main points of difference between the various theories for ϵ_c , disappears upon differentiation to obtain the bulk modulus. Thus, this C term is only important in calculations which involve the energy, such as cohesive energy calculations, and only terms containing r_s contribute to the bulk modulus. The same $A \ln r_s$ term appears in both FL and GB theories and contributes the predominant amount to B_e . The remaining terms in r_s , $r_s \ln r_s$, r_s^2 , etc., though having different coefficients in the different theories, only cause the bulk modulus contributions B_e to differ by about 25% and the total bulk moduli B_e to differ by a much smaller amount.

¹¹ R. S. Leigh, Proc. Phys. Soc. (London) **A71**, 33 (1958); Joseph Callaway, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

¹² W. C. Overton, Jr., *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 677; further details of these calculations to be published.